Development of efficient adsorbent materials for removal of toxic substances from water

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DEVELOPMENT OF EFFICIENT ADSORBENT MATERIALS FOR REMOVAL OF TOXIC SUBSTANCES FROM WATER

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ABSTRACT

Water contamination by chemicals such as metal ions and dyes is a serious environmental issue globally. One of the most promising solutions to solve such a problem is the use of adsorption technology. In recent years, the development of efficient and environmentally benign adsorbents using precursors of biopolymer, biomasses, and industrial wastes, etc, has attracted particular research attentions, due to the concerns of economics, environment, and sustainability. In this thesis work, efficient adsorbents as promising alternatives for commercial activated carbons were developed and their adsorption properties were investigated for applications in water treatment. In particular, a series of projects were carried out and important findings are summarized as follows.

In the first project, high quality mesoporous activated carbon with surface area of $\sim 1,100 \text{ m}^2/\text{g}$ was derived from waste tyres via the developed steam activation and acid washing protocol. Due to its specific mesoporous structure texture with volume fraction of mesopore (2 - 50 nm) $> 70 \%$, it presents excellent sorption capacities towards basic dye, higher than that of commercial activated carbons. The optimization of synthesis parameters, batch sorption equilibrium, kinetics and mechanisms have been studied and discussed. In the second project, zeolite templated activated carbons (ZTC) with tailored pore size distribution were prepared by the chemical vapor deposition (CVD) method using zeolite NaY as the template and benzene as the carbon precursor. It was found that the CVD temperature of 650°C results in carbons with the highest surface area of $1,511 \text{ m}^2/\text{g}$, and a good structural periodicity. The Ag(I) adsorption performance of the ZTC was studied. Besides porous carbon materials, nonporous colloidal carbon nanospheres (CNS) with rich surface functional groups were prepared from glucose solution for adsorption of

pollutants from aqueous solutions. The surface of the nonporous CNS after being activated by NaOH was enriched with -OH and -COO^- functional groups. Despite the low surface area ($< 15 \text{ m}^2/\text{g}$), the activated CNS exhibited excellent adsorption performance toward basic dyes and Ag(I) . The adsorption rate is fast, all MB with concentration of 94 ppm, and all Ag(I) with concentrations lower than 2 ppm, can be completely adsorbed in less than 6 minutes. This can be attributed to the minimum mass transfer resistance of the nonporous structure and the rich surface functional groups. Ag(I) ions were all deposited and reduced as Ag^0 nanoparticles on the external surface of CNS. The pollutants spent CNS can be easily and efficiently regenerated for recycling runs. For example, the dye spent CNS adsorbents have been regenerated using the sulphate radical based oxidation method and recycled for many adsorption runs with retained capacity. The adsorbed silver can be easily and fast recovered by dilute acid solutions and the CNS can be reactivated with a NaOH solution. The NaOH activated CNS reported here could represent a new type of low-cost and efficient adsorbent nanomaterials for pollutants removal of from wastewater. Lastly, biosorbent of molecular imprinted chitosan (CS) hydrogel beads were prepared to enhance the Ag(I) sorption selectivity and to solve the shortage of decreased adsorption capacity after chemical crosslinking of chitosan beads. The imprinted beads with optimal imprinting ratio show a higher adsorption affinity to Ag(I) under $\text{Ag(I)}/\text{Cu(II)}$ competitive adsorption conditions, the Ag(I) adsorption rate is faster and Cu(II) adsorption rate is much slower as compared with that of non-imprinted beads. The adsorbed Ag(I) can be easily desorbed from the biosorbent using diluted HNO_3 solution. The materials and methods developed in this thesis work are believed to provide promising solutions for efficient removal of metal ions and organic dyes from wastewater.

LIST OF ABBREVIATIONS

AC	Activated carbon
CAC	Commercial activated carbon
CNS	Carbon nanosphere
EGDE	Ethylene glycol diglycidyl ether
CS	Chitosan
CRCS	Crosslinked chitosan
GLA	Glutaraldehyde
ECH	Epichlorohydrin
EDTA	Ethylenediamine tetraacetic acid
PET	Polyethyleneterephthalate
PVC	Polyvinyl chloride
TC	Template carbon
OMC	Ordered microporous/mesoporous carbon
ZTC	Zeolite templated carbon
CVD	Chemical vapor deposition
HMF	5-hydroxymethyl-2-furaldehyde
CD	Cyclodextrin
SDS	Sodium dodecylsulfate
SEM	Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
PSA	Pore and surface analyzer
PSD	Pore size distribution

FTIR	Fourier transform infrared spectroscopy
ATR	Attenuated total reflectance
MCT	Mercury cadmium tellurium
XRD	X-ray Diffractometer
ICP	Inductively Coupled Plasma
TEM	Transmission electron microscopy

NOMENCLATURE

K_F	Freundlich constant ((mg/g)(L/mg) ^{1/n})
K_L	Langmuir affinity parameter (L/mg)
q_m	Langmuir maximum sorption capacity (mg/g)
C_0	Initial concentration (mg/L)
C_e	Equilibrium concentration (mg/L)
C_t	Concentration at time t (mg/L)
q_e	Adsorption capacity at equilibrium (mg/g)
q_t	Adsorption capacity at time t (mg/g)
k_1	Rate constant of the first order adsorption (1/h and 1/min)
k_2	Rate constant of the second order adsorption (g/(mg h) and g/(mg min))
t	Time (h and min)
k_d	Intraparticle diffusion rate constant (mg/g h ^{1/2})
N_t	Volumetric sorption capacity (Kg/ m ³)
ρ	Sorbent volumetric mass (Kg/ m ³)
K	Sorption kinetic constant (m ³ (1/Kg)(1/h))
V	Volume (ml)
S_{BET}	BET surface area (m ² /g)
S_{micro}	Micropore volume (m ² /g)
V_{meso}	Mesoporous volume (cm ³ /g)
T	Temperature (K)

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CHAPTER 1 INTRODUCTION AND OBJECTIVES

1.1 Introduction

Water contamination by pollutants such as metal ions and dyes, etc, has been a serious environmental issue with the rapid development of industries such as mining operations, metal plating facilities, paper industries, batteries, dying, textiles and others. Most metal ions in wastewater are toxic to human beings, including precious metal ions (e.g. silver and gold ions) which are of particular economic interests due to their high value and scarcity. Most dyes are toxic and even carcinogenic to aquatic life and are harmful to aquatic systems [1]. Though dyes in wastewater is hazardous, wastewater containing dyes is difficult to treat [2].

The removal of these water pollutants from various water resources has gained great scientific and practical interests. Various physical, chemical and biological methods that have been reported for cleaning contaminated wastewater include chemical precipitation, ion exchange, membrane filtration, and electrochemical treatment technologies, etc. All these methods have their associated problems. They are either cheap but does not work at low concentrations, or are effective but expensive, or produce large amounts of byproducts and sludge which are expensive to dispose [3-4]. As compared to these methods, adsorption technology has been an attractive and promising option due to the advantages of relative low cost, flexibility and simplicity in design and operation [5-6].

Activated carbon (AC) has been the most widely used adsorbents in wastewater

treatment applications throughout the world [7]. However commercial AC usually has several disadvantages such as: relative high cost compared to other adsorbents in case of expensive starting materials, high energy cost due to high temperature synthesis process, and complex reagents used to improve sorption performance, high cost and difficulty in regeneration, and non-selectivity [8-9]. Conversion of industrial or agriculture wastes to effective AC as a potentially low-cost alternative to commercial AC has attracted great research interest [10]. Since the industrial or agricultural wastes have little economic value and often impose a disposal problem, the conversion of waste materials to activated carbons with similar or better characteristics and sorption performance is attractive from the point view of decreasing cost and environmental protection. Another challenge for AC development is to synthesize high performance AC with controlled and uniform physical structure, since it has been demonstrated that the porous characteristic of AC strongly influences the adsorption performance of various adsorbates [11]. Synthesis of micro/mesoporous ordered AC derived from various templates such as zeolite and silica have attracted many research interests because of their potential industrial applications in areas such as: gas storage, adsorption separation, electrodes, supercapacitor, and catalyst supports [12-14], even though templated AC also has such a disadvantage of high cost.

Recently, the development of efficient, relatively low cost, and low temperature produced carbonaceous adsorbents as a viable alternatives to activated carbons has also attracted considerable research attention. Colloidal carbon nanosphere (CNS) as a novel carbonaceous material has attracted much research interests and attentions for their potential applications in fields, such as drug delivery, photonic band-gap

crystals, and adsorbents [15-17]. Conventional activated carbon or porous carbon spheres commonly possess hydrophobic or relatively chemically inert surfaces, and are prone to aggregation because of the polymerization/carbonization treatment at high temperatures of 800 - 1000 °C. Therefore, a harsh chemical treatment is unavoidable for further surface modification to achieve good dispersion in water and enhanced adsorption performance. Compared to AC, the synthesis of CNS is absolutely “green” and simple since it is achieved via a hydrothermal reaction of cheap and nontoxic bio-chemicals (glucose, cyclodextrin, etc.) at mild temperatures (140 °C - 180 °C). The surface of the CNS contains rich hydrophilic functional groups such as –OH and –C=O [18-19]. The advantage of this synthesis approach is that toxic reagents such as organic solvents, initiators, nor surfactants (which are commonly used for synthesis of porous carbon nanosphere at high temperature) are not utilized.

Besides carbonaceous materials, biosorbents have also attracted increasing research attentions recently. Biosorption is a promising adsorption technology using biosorbents, specifically living or dead microorganisms as adsorbents to adsorb pollutants from aqueous solutions. As compared with conventional adsorbents (e.g. activated carbons), the advantages of biosorption are: low operating costs, environmentally benign, efficient at low pollutant concentrations, and easy regeneration [20-21]. The mechanism of biosorption is generally based on interactions such as electrostatic interactions, ion exchange and chelating or complexation between metal ions and the surface groups on the adsorbent surfaces [22]. The binding process is usually reversible, which allows easy desorption and regeneration of the adsorbents. Chitosan, the N-deacetylated derivative of chitin under alkaline

conditions, is one of the best representative biopolymers. Chitosan is the most abundant biopolymer after cellulose. Because of its low cost, biodegradability, biocompatibility, non-toxicity, and good sorption capacities, chitosan and its derivatives have been developed for many versatile applications [23-32].

1.2 Objectives

This thesis work was aimed to develop efficient and relatively low cost adsorbents including activated carbon with particular porous structure, non-porous carbonaceous nanosphere adsorbent with rich surface functional groups and bio-sorbent, for metal ion (Ag(I)) and dye containing wastewater treatment applications.

1.3 Outline of thesis work

Most commercial AC suffer from disadvantages such as high cost due to expensive starting materials, non-selectivity, difficulty in regeneration and high energy cost during the production. In this thesis work, we first developed an efficient mesoporous activated carbon from a low-cost waste material, waste tyre, for removing bulky dye molecules from aqueous solution. We also synthesized another activated carbon with a particular and regular pore structure. Zeolite templated AC (ZTC) with tailored narrow micropore size distribution and pore structural regularity was prepared, and the Ag(I) adsorption property of the ZTC was studied. It was found such high surface area ($1511 \text{ m}^2/\text{g}$) and tailored and narrow pore size microporous AC did not show excellent adsorption capacity to Ag(I).

In the second section, we focus on nonporous material-colloidal carbon nanospheres with rich surface functional groups. Colloidal carbon microspheres have been utilized

as template to synthesize hollow metal and metal oxides shell structures [33-35]. However, there have been only a few studies on application of CNS as a carrier for removal of water pollutants. The rich surface functional group distribution surface property and simple, “green” synthesis method make CNS promising adsorbent in wastewater treatment. The density of such functional groups of COO^- and OH was increased by a mild treatment in acids or bases to improve the adsorption properties of this adsorbent. The regeneration of pollutants loaded CNS was also expected and proven to be easy and fast for respected uses of this adsorbent in our study. To the best of our knowledge, there is no literature reporting the post treatment of carbon spheres by acids and bases for enhancing adsorption performance and the easy recycling property after adsorption. The adsorption characteristics, mechanism and regeneration of the activated CNS towards pollutants were investigated.

In the third part, biosorbent of chitosan hydrogel beads was synthesized and studied for Ag(I) adsorption. Hydrogel beads of chitosan have been efficient adsorbents for metal ion removal from liquid phase. Since the hydrogel type can reduce the crystallinity of chitosan thus enhance the metal ion uptake capacity. However, the sorption selectivity is low for specific metal ions, which is unbeneficial for selective uptake and recovery of metal ions especially noble metals (Ag(I)) from water. There have been only a few studies for enhancing the adsorption selectivity of chitosan for metal ion using molecular imprinting method.

The outline of the thesis is summarized as follows,

Chapter 1 outlines the background and objective of this study.

Chapter 2 introduces current research on metal ion and toxic dye containing

wastewater treatment utilizing various adsorbents, including activated carbons from various raw materials, carbonaceous spheres, and chitosan-based biosorbents. The adsorption theoretical background of the study will also be presented.

Chapter 3 presents 1 materials and experimental methods, including various adsorbents preparation, characterization, and adsorption measurement.

Chapter 4 reports the preparation and characterization of a high quality mesoporous TAC and the adsorption performance of the TAC for a basic dye Malachite Green removal from aqueous solution.

Chapter 5 describes the preparation of zeolite templated microporous carbon with regular porous structural and centered pore size distribution via a chemical vapor deposition (CVD) method, the effect of synthesis conditions on the structural development of the ZTC, and the Ag(I) adsorption performance of the ZTC in aqueous solution.

Chapter 6 introduces the preparation, alkaline activation and characterization of well-dispersed carbonaceous nanosphere, including the basic dyes adsorption performance, modeling of adsorption isotherm and kinetics, effect of adsorption operation parameters, and the regeneration and recycling of the adsorbent using sulphate radical based oxidation method in aqueous solution.

Chapter 7 presents Ag(I) adsorption properties and mechanism of alkaline treated carbon nanospheres in batch studies, and the recovery of Ag(I) from adsorbent and fixed-bed adsorption of Ag(I) in continuous operational mode for potential large-scale applications.

Chapter 8 introduces the adsorption property and selectivity of Ag(I) in aqueous solution by prepared Ag(I) imprinted chitosan hydrogel beads in aqueous solution.

Chapter 9 presents conclusions of this study and future study recommendations.

CHAPTER 2 LITERATURE REVIEW

2.1 Chitosan

Chitosan is the N-deacetylated derivative of chitin under alkaline conditions. It consists of linear β -(1,4)-N-acetyl-D-glucosamine(GlcN) and N-acetyl glucosamine (GlcNAc) units. Its precursor, chitin (poly (β -(1 $\rightarrow$ 4)-N-acetyl-D-glucosamine), is the most abundant bio-polymer after cellulose. The main commercial sources of chitin are crab and shrimp shells. Fungal biomass, and insect cuticle may also be sources of chitin. The immunogenicity of chitin is exceptionally low. It resembles cellulose in its low solubility in water and low chemical reactivity. The deacetylation of chitin to chitosan is rarely complete, so pure chitin or chitosan composed only of a simple monomer unit rarely exists. The structures of chitin and chitosan are shown in Fig. 2.1.

Fig. 2.1 The structure of chitin (predominantly contains GlcNAc) and chitosan (predominantly contains GlcN)

Because of the low cost, biodegradability, biocompatibility, non-toxicity, and good sorption capacities, chitosan and its derivatives have been developed for many

versatile applications. In biomedical field, they are employed in tissue engineering, drug delivery, wound dressing, bone substitute, suture material etc [25,28-30]. In biotechnology, chitosan have been used as enzyme immobilization matrix, cell-stimulation materials, antibacterial agents, et al. [24,26-27]. Chitosan and its derivatives have also been found important applications in the fields of food [31-32], cosmetics [23], et al. In water treatment, they are utilized as effective adsorbents for the removal of various contaminants including metal ions, dyes, et al. [36-39]. Chitosan and the derivatives demonstrate excellent performance for adsorption/desorption of transition metal ions [37].

2.2 Chitosan based materials for biosorption of metal ions

2.2.1 Effect of operation parameters

Many studies have shown that pH can affect the metal ions adsorption capacity of chitosan [40-45]. It was reported that the amino groups of chitosan are the major sorption sites for binding with the metal ions [46-52]. These sorption sites may bind with metal ions through different mechanisms at different pH value and for sorption of different metal ions. It was reported that the free electron doublet on nitrogen may interact with metal cations under neutrality or weak acidity conditions [49,52]. In acidic solutions, the amine groups are protonated facilitating the biosorbent to attract metal anions [47]. Ozer [53] reported that the optimal pH value for lead and nickel adsorption is 5.0. Vianna et al. [54] found that the uptake capacity is maximal at pH 4.5 for copper, cadmium and zinc, and decreased significantly when the pH was decreased to 3.5 or 2.5. This suggests that electrostatic interaction between the charged functional groups and the metal ions was the main biosorption mechanism.

For alkaline and alkaline earth metal ions, chitosan was reported to show low sorption capacity [37].

It was reported that these factors that may affect the adsorption performance of chitosan, deacetylation degree, crystallinity, and molecular weight. The fraction of deacetylation is a major parameter in influencing the uptake of metal ions [55-57] because it affects the fraction of free amino groups [58-61]. In 1979, Kurita et al. [62] reported that crystallinity and deacetylation ratio can affect the adsorption capacity of chitosan. The degree of deacetylation determines the amount of free amine groups for interactions with other compounds. The free amine groups on chitosan that can be protonated under acidic conditions are critical for the solubility of chitosan in dilute acid solutions and the sorption affinity to metal ions, dyes, and other contaminants [63]. Many methods have been developed for defining the degree of deacetylation, including infrared spectrometry, ¹H-NMR spectroscopy, ¹³C solid-state NMR, various titration schemes, and near-infrared (NIR) spectroscopy [64-68]. Moreover, the residual crystallinity of chitosan may also control the accessibility to these free amine sites. It was also reported that improved sorption capacity of metal ion on chitosan by decrystallization [69-70]. It was demonstrated that hydrogel beads of chitosan or freeze drying can reduce its crystallinity, and as a result, the metal ion uptake capacity was enhanced [71].

The preparation of chitosan and its derivatives in the forms of flakes, beads, films, and fibers is an established topic. In the area of membranes, several studies on the formation of chitosan membranes have been reported [72-73]. The uptake ability of chitosan membrane for metal ions has been studied [74-76]. Chitosan fibers were first

produced by von Weimarn [77]. Since then there have been limited reports on the production of chitosan fibers, and their use in the removal of metal ions [78-79]. There have been extensive researches on removal of metal ions on flake or powder forms of chitosan, and it is demonstrated that decreasing the particle size can increase the adsorption capacity to metal ions, but this phenomenon is not valid for modified chitosan with enhanced polymer porous structure [80-84]. However, the great pressure drop and column blocking caused by the low porosity of flakes in fixed bed system limited its application. Therefore, chitosan beads have been prepared and crosslinked to give them a better mechanical strength and acidic resistance [85-86].

Only a limited number of studies have been found on the adsorption of metal ions in multi-component solutions on chitosan. Roberts [87] reports that sorption selectivity depends strongly on experimental conditions, and suggests a need for more study of sorption of metal ions in multi-component solutions. The selective sorption of metal ions can be increased by modification of the polymer, for example, the template formation methods [88-90].

2.2.2 Chitosan derivatives

2.2.2.1 Crosslinked chitosan

Though chitosan has good adsorption capacity of metal ions, it dissolves in acidic solution ($\text{pH} < 4$), and has low mechanical strength. Therefore cross-linking is commonly used to increase its stabilities. The adsorption capacity generally decreases because some of the active group ($-\text{NH}_2$) for metal ion chelating were attached with

cross-linking agent [91]. It was reported that cross-linking reaction in homogeneous conditions leads to enhanced adsorption capacity as compared to heterogeneous crosslinking. The homogeneous condition is that the cross-linking agent, glutaraldehyde, was added into the chitosan/acetic acid solutions to promote the crosslinking reaction in a homogeneous liquid phase, and the final crosslinked products were precipitated. Unlike the heterogeneous condition, the crosslinking agent reacts with solid state chitosan in aqueous solutions. It was reported that uptake capacity of chitosan for copper increased from 74 % to 96 % (as compared with raw chitosan flake) when it was cross-linked by glutaraldehyde in homogeneous conditions [92]. It was reported that the enhanced adsorption capacity of homogeneous crosslinked chitosan was mainly due to the decreased crystallinity of chitosan upon the dissolving step of chitosan in acetic acid, though some amino groups are occupied by crosslinker [92]. Hsien et al. reported that uptake capacity of Cd^{2+} on a cross-linked chitosan by glutaraldehyde decreased exponentially with the increase of extent of cross-linking under heterogeneous cross-linking conditions [93]. Besides glutaraldehyde, many other cross-linking agents have been used such as epichlorohydrin [94-95], EGDE (ethylene glycol diglycidyl ether) [96-97]. Fig. 2.2 [98] shows the scheme for chemical structure of various crosslinked chitosan.

Fig. 2.2 The chemical structures of some cross-linked chitosan (cross-linking agents a: glutaraldehyde, b: epichlorohydrin, c: ethylene glycol diglycidyl ether)

Recently, a method of amine-shielded cross-linking of chitosan hydrogel beads was investigated for enhancing metal adsorption performance [96]. It was reported that the amine group on chitosan was firstly shielded by reacting formaldehyde with chitosan hydrogel beads, then EGDE crosslinking was performed, finally, the shielded amine group by formaldehyde on chitosan was washed off by a HCL treatment. It was observed that chitosan beads crosslinked with this method showed a higher adsorption capacity for copper ions than the beads directly crosslinked with EGDE.

2.2.2.2 Chitosan modification

A large range of chitosan derivatives have been developed by grafting functional groups on chitosan for efficient uptake of metal ions. N-carboxymethyl chitosan-glycine glucan [99-101], containing weak carboxylic acids for metal ion exchange, and dithiocarbamate chitosan [102-103] containing a thiol group could be attractive for the sorption of heavy metal ions. Grafting of crown ether on chitosan using a Schiff's base reaction has also been reported [104-106].

In the case of chitosan gel beads, the drawback of poor volumetric density of sorption sites due to the high water content can be compensated by grafting new amine groups. For example, poly (ethylene imine) has been grafted on chitosan via different linker-spacer agent, such as glutaraldehyde [107], hexamethylene diisocyanate [108-109], and epichlorohydrin [110-112]. Synthesis of phosphorous derivatives of chitosan has also been reported [113-115], this derivative adsorbent presents limited application for metal ion sorption because of the solubility in water and their affinity for alkaline metals.

Chelating chitosan based resins by grafting of sulfur compounds on chitosan have been synthesized in many studies [116-117]. Sulfur derivatives of chitosan with chloride functional groups and sulfur groups can be also used [118]. These sulfur derivatives of chitosan have been applied for adsorption of mercury and precious metals.

2.2.3 Summary of sorption capacities of chitosan-based adsorbents towards metal ions

The maximum adsorption capacities of different metal ions on chitosan based adsorbents were summarized in the following tables. The tables provide basic information for evaluating the possibility of using chitosan for metal ion uptake in a batch adsorber.

Table 2.1 Summary table for the sorption capacities (q_m , mmol/g) of metal cations on chitosan-based materials

Metal	Sorbent	Form	pH	q_m mmol/g	Refere- nce	Desorption solution
Cu(II)	Carboxymethyl-CS	Flakes	5.0	2.5	[119]	--
	Raw CS	beads	4.5	1.0	[120]	--
	GLA-CRCS	beads	4.5	0.3-0.49	[120]	--
	Alginate-CS	beads	4.5	1.06	[120]	--
	GLA-CRCS	beads	1	3.8-5.0	[91]	--
	GLA, ECH, EGDE-CRCS	beads	6	0.7-1.3	[121]	EDTA
	TPP-CRCS	beads	5	3.2	[122]	--
	Thiourea-magnetic CS	microsphere	5	1.04	[123]	EDTA
	Cellulose-CS	hydrogel	6	--	[124]	--
		beads				
	Raw CS	gel beads	6	--	[125]	--
	CS coated ceramic alumina	powder	4	1.3	[126]	NaOH
	Raw CS	Flakes	5.4-6	1.8-2.2	[127]	--
	Raw CS	Flakes	4.2	0.6	[128]	--
	Raw CS	Flakes	5-6	1.5	[129]	--
	Raw CS	Flakes	5.7	1.2	[130]	--
	Raw CS	Flakes	3.5-4.5	1.2	[131]	--
	Raw CS	Flakes	5	1.5-2.5	[132]	
	Histidine-CS	membrane	4-6	2.0-3.0	[133]	--
	Cellulose acetate/CS	membrane	5	0.8	[134]	EDTA
	CRCS	membrane	5-6	3.2	[135]	--

Cd(II)	Xanthate-CS	Flakes	8	3.2	[136]	H ₂ SO ₄
	Raw CS	Beads	8	2.1	[80]	--
	GLA-CRCS	Beads	6.5	1.3	[93]	--
	Raw-CS	Flakes/Beads	7	0.6-1.3	[137]	--
	Raw/CRCS	Flakes/Beads	6.5	4.0	[86]	--
Pb(II)	Raw CS	Gel beads	6.5	--	[138]	--
	Ethylene imine-CS	Gel beads	--	2.03	[116]	--
	Thiourea-CS	Gel beads	--	2.4-2.9	[116]	--
	TiO ₂ -CS	film	3-4	0.2	[139]	--
	Raw CS	Flakes	5.0	0.7	[140]	--
	Xanthated CS	Flakes	4	1.6	[141]	HCL, EDTA
	Raw CS	Flakes	5	0.2	[142]	--
	Poly(acrylic acid)	Flakes	4	1.4	[143]	1M HNO ₃
	Carboxymethyl CS	Resin	5.9	1.9	[144]	--
Ni(II)	Ni-imprinted	Flakes	6-7	0.7	[145]	--
	Complexane-CS	Flakes	2	2.0	[146]	--
Hg(II)	Aminated-CS	Beads	7	2.3	[147]	EDTA
	GLA-CRCS	Membrane	6	4.4	[148]	1M NaCL
	Raw-CS	Membrane	6	2.1	[148]	1M NaCL
	Raw-CS	Particle	6	5.6	[149]	--
	Thiourea-magnetic CS	Resin	5	2.8	[150]	Potassium iodide
	Ethylenediamine-CS	resin	5	2.0	[151]	H ₂ SO ₄ /HCL
	Thiol-CS	Gel beads	7	8	[152]	--
Cr(III)	Raw CS	Flakes	5	0.5	[153]	--
	N-benzyl sulfonate CS	Flakes	--	--	--	--
Ag(I)	Molecular-imprinted CS	Flakes	7	1.84	[154]	Na ₂ S ₂ O ₃
	Raw CS	Flakes	6	0.39	[48]	--
	Thiourea-magnetic CS	Resin	6.9	2.1	[155]	Thiourea
	Crown-ether CS	Flakes	--	--	[156]	H ₂ SO ₄
	Ethylenediamine-CS	Flake resin	5	1.37	[157]	HNO ₃

	Histidine moiety-CS	Flake resin	--	--	[158]	HNO ₃
Abbreviations: CS, chitosan; CRCS, crosslinked chitosan. GLA, glutaraldehyde; ECH, epichlorohydrin; EGDE, ethylene glycol diglycidyl ether; EDTA, ethylenediamine tetraacetic acid.						
Table 2.2 Summary table for the sorption capacities (, mmol/g) of some metal anions on chitosan-based materials						
Metal	Sorbent	Form	pH	q_m mmol/g	Reference	Desorption solution
Mo(VI)	Raw CS	Flakes	3	7-8	[83]	--
	Raw CS	Beads	3	7-8	[71]	--
	GLA-CRCS	Flakes	3	1-5	[83]	--
	GLA-CRCS	Beads	3	7-8	[71]	--
V(V)	Raw CS	Flakes	3	7-8	[159]	--
	Raw CS	Beads	3	7-8	[71]	--
	GLA-CRCS	Flakes	3	2-5	[71]	--
	GLA-CRCS	Beads	3	7-8	[71]	--
Pd(II)	GLA-CRCS	Flakes	2	1.5	[107]	--
Chloropalladate	Thiourea-CS	Flakes	2	1.5	[47]	--
	PEI/Thiourea CS	Beads	2	2-4	[116]	--
Pt(IV)	GLA-CRCS	Flakes	2	1.5	[160]	--
Chloroplatinate	Thiourea-CS	Flakes	2	2	[47]	--
	PEI/Thiourea CS	Beads	2	2-3	[116]	--
Au(III)	Thiourea-Magnetic CS	Resin	0.5	3.6	[155]	Thiourea, H ₂ SO ₄
Cr(VI)	Raw CS	Flakes	2	0.6	[161]	--
	Raw CS	Flakes	4	0.5	[162]	--
	Raw CS	Membrane	6	--	[94]	NaCL
	GLA-CRCS	Membrane	6	--	[94]	NaCL
	ECH-CRCS	Membrane	6	--	[94]	NaCL

ne						
As(V)	Modified	Beads	2-3		[51,163-164]	--
	CS-coated	Powder	4	1.3	[165]	NaOH
	Ceramic alumina					
	Molybdate-CS	Beads	5	--	[166]	H ₂ SO ₄

Abbreviations: CS, chitosan; CRCS, crosslinked chitosan. GLA, glutaraldehyde; ECH, epichlorohydrin.

2.3 Activated carbon materials for wastewater treatment

2.3.1 Waste material based AC

Activated carbon has been the most widely used adsorbents for wastewater treatment, due to its unique characteristics such as developed porous structure, high surface area et al. AC has been utilized not only as adsorbents, but also as catalysts and catalyst supports for separation in gaseous/liquid phases and the purification of chemicals [167]. Due to the high production cost of AC, the preparation of low cost AC from waste materials has been intensively studied recently.

AC porous texture often consists of a wide range pores includes micropore (< 2 nm), mesopores (2 – 50 nm), and macropores (> 50 nm) [168]. In order to obtain highly developed AC porous structure with high adsorption performance from these waste materials, physical or chemical activation is often applied with AC production from waste materials. Physical activation is normally followed carbonization by activation with steam or CO₂ at temperatures ranging from 700 to 1100 °C to open and develop the porous network of AC [7]. Carbonization is a pyrolysis process conducted in a thermal degradation process in which the material is heated in an oxygen-free

atmosphere to remove the non-carbon elements [169]. Chemical activation is an AC preparation method using different chemical activating agents to develop AC porous structure; the mixture of the activation agent and the carbon is often heated at a maximum of around 750 °C. Different activation agents have been utilized including zinc chloride (ZnCl_2) [170], Phosphoric acid (H_3PO_4) [171-172], Potassium hydroxide (KOH) [173], Potassium carbonate (K_2CO_3) [174-175], and sodium hydroxide (NaOH) [176]. It was reported that raw materials and activation parameters have a strong effect on the physical characteristics of AC. Such parameters are normally investigated to optimize the AC preparation procedure for a certain raw material, including carbonization time, carbonization/activation temperature and activation agent flow rate in physical activation and impregnation duration and impregnation ratio for chemical activation [177-178]. It was found that to obtain a specific AC, the optimal preparation parameters also strongly depend on the type of raw materials [10].

Agricultural wastes are rich and inexpensive source of AC. These waste materials have little economic value and often have disposal environmental problems due to their abundance. Thus conversion of agricultural or forest waste into AC would add economic value and decrease AC production cost. Different AC has been derived from a wide range of agricultural wastes including rice husk [179-180], coffee husk [181], walnut shell [182-183], corn cob [177], olive cake [184], coirpith [185], pecan shell [186], sugar cane bagasse [187], olive seed [188], etc. It was reported that with a optimal preparation procedure, agricultural wastes derived AC can compete with commercial AC, even show a better sorption performance [183,189]. Woody waste is another rich source for AC preparation due to the abundance of industrial wastes and

also some forest residues. Woody waste derived AC have been applied to remove organic contaminants, metal ions, and acid dyes from aqueous phase [190-192].

With the rapid development of industries, there is an accumulation of industrial waste materials, most of which are difficult to degrade in nature and hard to be recycled to other useful materials. Such industrial wastes including plastic wastes, such as polyethyleneterephthalate (PET) [193] and polyvinyl chloride (PVC) [194], oil combustion residues [195], waste tyres [196], and sewage sludges [194], has been used as raw materials for AC application and studied for pollutants removal from aqueous phase. Some relevant studies on preparation and application of AC from waste materials are shown in Table 2.3.

Table 2.3 List of preparation and adsorption performance of AC from waste materials

Contaminants	Raw material	AC surface area (m ² /g)	pH	T (°C)	q _m (mg/g)	Reference
Malachite Green	Rice husk	--	5-6	Room T	77	[176]
Malachite Green	Rice husk	180	7	30	10	[180]
Astrazon yellow 1GL	Apricot stone	560	10	30	221	[197]
Remazol Brilliant Orange 3R	Coffee husk	745	4	30	66.7	[181]
Acid Blue 25	Waste tea	820	7	30	203	[198]
Malachite Green	Groundnut shell	1200	--	30	222	[199]
Acid Blue 113	Waste tyre	562	5	25	9	[200]

Reactive dye,	Sawdust	900	10.7	25	368-510	[201]
Remazol dye						
Methylene Blue	Rattan sawdust	1083	Natural	30	294	[202]
Methylene Blue	Durian shell	991	Natural	30	289	[203]
Methylene Blue	Waste newspaper	1260-1740	--	--	390	[204]
Methylene Blue	Sewage sludge	390	5	25	194	[205]
Methylene Blue	Waste tyre	1014	--	--	455	[196]
Methylene Blue	Waste tyre	602	Natural	30	227	[206]
Rhodamine B	Waste tyre	720	Natural	25	277	[207]
Hg (II)	Bagasse pith	530	6	30	172-188	[208]
Ni (II)	Almond husk	--	5	20	31-37	[209]
Pb (II)	Palm shell	957	5	27	95.2	[210]
Pb (II)	Peanut husk	114	6-7	20	485	[211]
Ni (II)	Peanut husk	16	6-7	20	485	[211]
Zn (II)	Peanut husk	13	6-7	20	485	[211]
Pb (II)	Sugarcane	536	6	30	200	[212]
Hg (II)	bagasse pith	536	6	30	188	[212]
Cd (II)	Sugarcane	536	6	30	153	[212]
Co (II)	bagasse pith	536	6	30	129	[212]
Zn (II)	Sugarcane	902	6	25	60	[213]
Cu (II)	bagasse pith	--	5	25	29	[214]
Pb (II)	Sugarcane	--	5	25	108	[214]

2.3.2 Templated AC

Recently, template synthesis of ordered porous carbons with tailored pore structures and high specific surface area has gained great research interest, for application as adsorbents, catalyst supports, sensors and electrode [215-218]. The controllable pore

size distribution makes templated AC promising porous materials for removal of pollutants from water stream or energy storage. These template-synthesized porous carbons (designated as TC) are potential promising adsorbents and provide a good opportunity for fundamental study of adsorption [219-221]. The most attractive advantage of this method is that the pore size of a carbon material can be easily controlled through selecting the appropriate template, precursors, and pyrolytic method [222-223].

The synthesis of ordered templated carbon generally involves three steps: impregnation of the porous template with carbon precursor to form the composite, followed by carbonization (or pyrolysis) in an inert media (e.g. N₂), and finally liberation of carbonized carbon from the composite by acid washing (HF is popularly used) [220]. Ordered templated carbon contains highly ordered (microporous or mesoporous) replicas which resemble the structural characteristics of the template and is termed as the ordered microporous/mesoporous carbon or OMC. There have been some reviews on synthesis of template carbon [224-226]. Since Knox et al. prepared carbons with template method using porous glass as template in 1986, various template carbon has been synthesized using a wide range of rigid inorganic porous materials. Up to now, synthesis of high quality ordered mesoporous carbon (OMC) from rigid templates, such as zeolites or silicas has been well established. Zeolites are aluminosilicate crystals with ordered structure and uniform sub-nanometer pores. The wall thickness of a number of zeolites are around 1nm, thus making them excellent candidates for templates synthesis of quality ACs. Many research efforts have been devoted to develop zeolite templated carbon (ZTC) using various types of zeolites (NaY, NH₄Y, HY, β , ZSM-5, L, et al.), and with various impregnation methods

(incorporation-carbonization, chemical vapor deposition (CVD), or the combination of the two) [227-229].

Since mesoporous M41S silica materials were synthesized by Knox et al. in 1992 [230], many mesoporous silica materials with uniform pore structure and high surface area have been prepared using various organic agents, surfactants and copolymers. A range of mesoporous silica materials with structural periodicity have been successfully used as templates to synthesize ordered mesoporous carbon materials. Ordered mesoporous carbon samples have been synthesized using MCM-48 silica (with hexagonal 1D channel structure) [231-232], and silica HMS [233] as template. Various ordered mesoporous carbon [234-239] and hexagonally nanotube type mesoporous carbon [240-242] have been synthesized using hexagonally ordered mesoporous silica SBA-15 as a template. Also ordered cubic mesoporous carbon has been synthesized using SBA-16 as template with cubic Im3m structure [243-244].

Because of the specific textural properties such as high surface area, tunable pore size distribution and large pore size, OMC has been studied as adsorbents for removal of pollutants from aqueous phase and showed high adsorption performance. For example, MOCs prepared by using SBA-15 as template and sucrose as carbon precursor was studied for adsorption of a basic dye Methylene Blue with determined adsorption capacity of 196 mg/g [14], removal of a sulphur methyl mercaptan [237], and a reactive dye (Ramazol Red 3BS) with determined adsorption capacity of 500-580 mg/g [245]. MOC prepared by using SBA-15 as template and furfuryl alcohol as carbon precursor presents surface area of 1491 m²/g to 1770 m²/g, and was investigated for removal of a basic dye Malachite Green [246], and reactive dye reactive blue 19 and acid red 57 [11]. The adsorption capacity was high and was

determined as 354 mg/g towards Malachite Green, 733 mg/g and 1131 mg/g for reactive blue 19 and acid red 57 respectively. Zeolite X templated OMC has also been synthesized and studied for adsorption of Methylene Blue with adsorption capacity of 436 mg/g [247].

2.4 Colloidal carbon nanospheres and applications

Colloidal spheres with fixed diameter are of great interest for applications involving biodiagnostics, drug delivery, and photonic band-gap crystals [15-17]. The conventional porous carbon sphere surface obtained via carbonization at higher temperatures of 800 - 1000 °C is often inert, therefore harsh surface modification is required [248]. The main concern regarding carbonized porous carbon sphere is the strong tendency toward aggregation, which makes it difficult to prepare well-dispersed carbon spheres [249]. Recently, a 'green' synthetic approach has been developed for syntheses of colloidal carbon microspheres via monosaccharide (such as glucose and fructose) hydrothermal treatment at 160 °C to 180 °C in a closed system. The surface of colloidal sphere is rich in functional groups, hydrophilic with functionalities of -OH and -C=O.

There have been a few reports regarding synthesis of colloidal carbon spheres. Typically, colloidal carbon nanosphere can be derived from hydrothermal treatment of aqueous monosaccharide solutions such as fructose and glucose. Aqueous glucose solution was transformed to colloidal carbon nanospheres with size ranging from 150 nm to 1500 nm by hydrothermal reaction at mild conditions of 160 °C to 180 °C in a closed teflon-sealed autoclave [16]. The parameters of reaction time, reaction temperature, and concentration of glucose have an effect on the diameters of the

carbon spheres, and the dominant parameter is reaction time. It was reported that the diameter of carbon sphere grew from 200 nm to 1500 nm as the reaction time increased from 2 to 10 hrs. The obtained CNS is rich in carboxyl group and hydroxyl groups on the sphere framework. The CNS was reported to have the ability to incorporate nanoparticles in the sphere cores by using metal nanoparticles as nuclei mixed with glucose aqueous solutions for hydrothermal reaction or by in situ hydrothermal reduction of noble metal ions with glucose solution [16]. Silver and palladium nanoparticles have been attached onto the CNS surface by a room temperature surface reduction method or by reflux method. Aqueous monosaccharide solution of fructose and glucose were also studied of the dehydration dynamics in a closed system to form colloidal carbon spheres [250]. It was reported that carbon spheres prepared from fructose exhibits a raspberry-like morphology, while carbon spheres prepared from glucose exhibit smooth surfaces. It was noted that glucose may dehydrate more likely through an intermolecular condensation reaction, as proven by that almost no formation of HMF (5-hydroxymethyl-2-furaldehyde (HMF)) was detected during the initial hydrothermal treatment at $< 180^{\circ}\text{C}$. However, fructose initially forms HMF through an intramolecular dehydration process followed by subsequent water loss to form carbon, the levulnic acid (4-oxopentanoic acid) formed by dehydration of HMF speeds up dehydration of the remaining fructose. α -, β -, and γ -cyclodextrin (CD) solutions have been utilized for syntheses of colloidal carbon spheres with size in range of 70-150 nm under hydrothermal conditions at 160°C in closed systems [18]. It was shown CD slowly hydrolyzes to glucose and form HMF followed by carbonization into colloidal carbon spheres.

By hydrothermal synthesis of the monosaccharide solutions in the presence of specific

agents, the property of derived CNS such as morphology, surface chemistry, etc can be modified for specific applications. For example, by hydrothermal treatment of an anionic surfactant sodium dodecylsulfate (SDS) and glucose solution at 180 °C, hollow carbonaceous sphere can be derived for potential application in biochemistry, pharmaceuticals, et al. [19]. CNS with enhanced yield and sphere size of 1-4 μm was synthesized by hydrothermal reaction of xylose and fructose together with phenolic compounds such as phenol, resorcinol, and phloroglucinol. [251]. A silver nanoparticles dispersed CNS was prepared by a one-step ultrasonic electrodeposition method by electrolysis of slurry consisting of sucrose derived colloidal carbon sphere in the presence of silver perchlorate electrolyte [252]. A Fe_3O_4 magnetic carbonaceous nanoparticles were obtained via hydrothermal reaction of glucose in the presence of ferrous gluconate aqueous solutions to form Fe(II) dispersed nanosphere, followed by further thermal treatment.

Such carbonaceous nanospheres have been studied for applications such as contaminant removal from aqueous solution [253-254], catalyst support [255-256], fabrication of electrochemical immunoassay [257-259], and as templates to fabricate hollow metal and metal oxides shell structure [34-35,260], et al. It was reported that carboxylate-rich carbonaceous micro-material was synthesized by hydrothermal carbonization of glucose and acrylic acid. The adsorption performance of the carboxylate rich material to pb(II) and Cd(II) was investigated, the adsorption capacity was 351.4 mg pb(II)/g and 88.8 mg Cd(II)/g [253]. A honeycomb-like Ni nanoparticles/carbonaceous composite nanomaterials was prepared via hydrothermal treatment of glucose solutions with Ni nanoparticles. The composite material presents uptake capacity of 21.4 mg pb(II)/g, 14.3 mg Cd(II)/g and 6.4 mg Cu(II)/g from

aqueous solution [254]. An imidazole functionalized carbon sphere was prepared by hydrothermal treatment of glucose in the presence of organic monomers (e.g. vinyl imidazole). After further functionalization, the materials were utilized as catalysts for organocatalysis [255]. A hollow carbon sphere was fabricated by hydrothermal carbonization of mixture of glucose, template polystyrene sphere, and surfactant P123, finally, the template and P123 were removed by intermittent microwave heating. Pt nanoparticles were loaded on the hollow nanosphere as a catalyst to improve kinetics of methanol oxidation [256]. The application of a gold nanoparticles coated microwave-hydrothermal CNS for fabrication of an electrochemical immunoassay was also reported [258-259].

2.5 Theories for adsorption in liquid phase

2.5.1 Adsorption isotherm model

Adsorption can be classified as physical adsorption (the universal van der Waals interactions) or chemical adsorption. Contrary to physisorption, chemisorptions occur only as a monolayer. Physisorption is typically a reversible processes. In some adsorption process, both physisorption and chemisorptions play a role.

To understand the adsorption mechanism from theoretical analysis, adsorption isotherm equations are developed to describe experimental adsorption equilibrium data. The equation parameters often provide some insight into the sorption mechanism. Obtaining the ‘best fit’ isotherm model becomes more and more important.

The Freundlich adsorption isotherm was proposed and popularized the usage by Freundlich [261]. The Freundlich isotherm was based on assumption of an

exponentially decaying sorption site distribution. This empirical model can be used to describe sorption on heterogeneous surfaces and multilayer sorption. The equation is expressed as following:

$$q_e = K_F C_e^{1/n} \quad (2.1)$$

Where C_e (mg/l) is monolayer equilibrium concentration of the dye solution, q_e (mg/g) is equilibrium adsorption capacity, and K_F ((mg/g)(L/mg)^{1/n}) is the Freundlich constant and $1/n$ is the heterogeneity factor.

Langmuir [262] derived an isotherm equation based on the assumption of energetically equivalent number of adsorption sites on the adsorbent surface, and at each of which one molecule of a perfect gas may be adsorbed. The Langmuir equation was applied to chemisorptions and with some restrictions to physical adsorption. The Langmuir model is probably the most widely applied adsorption isotherm equation. It may be represented as follows:

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (2.2)$$

Where q_m (mg/g) is the sorption capacity, K_L (L/mg) is the affinity parameter.

The dimensionless constant, R_L is defined by the following equation to determine the adsorption process is favorable or unfavorable for the Langmuir model,

$$R_L = 1 / (1 + K_L C_0) \quad (2.3)$$

Where, C_0 (mg/L) is the initial concentration of the dye solution, and K_L is the Langmuir isotherm constants. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The parameter q_m is useful parameters for comparing adsorbent capacities.

In 1975, Jossens and coworkers [263] derived an isotherm equation which incorporates features of both the Langmuir and Freundlich equations, based on a three-parameters isotherm proposed by Redlich and Peterson[264]. It can be described as follows:

$$q_e = K_R C_e / (1 + a_R C_e^{b_R}) \quad (2.4)$$

Where, K_R , a_R and b_R are all the Redlich–Peterson constants, with $0 < b_R < 1$. It is also useful to note that, when b_R equals to 0, the Redlich–Peterson equation becomes Henrys’ law equation, and it results in Langmuir equation when b_R is unity. Because of its dual features, the Redlich-Peterson isotherm has been very well applied to some systems. This applies particularly to adsorbents that are heterogeneous and can function by more than one mechanism.

2.5.2 Kinetics of adsorption in liquid phase

Kinetic models have been used to describe experimental data to investigate potential adsorption rate controlling mechanism.

The Pseudo-first order equation of Lagergren [265] is generally expressed as follows:

$$dq_t / dt = k_1 (q_e - q_t) \quad (2.5)$$

Integrating this for the boundary conditions of $t = 0, q_t = 0$; $t = t, q_t = q_t$, gives

$$q_t = q_e (1 - e^{-k_1 t}) \quad (2.6)$$

Where q_e (mg/g) and q_t (mg/g) are equilibrium adsorption capacity and adsorption capacity at time t , respectively, k_1 is the rate constant of adsorption (1/h).

However, equation (2.5) is transformed into its linear form,

$$\log(q_e - q_t) = \log(q_e) - (k_1 / 2.303)t \quad (2.7)$$

If the plot of $\log(q_e - q_t)$ versus time t presents a linearship with the intercept of $\log(q_e)$, then this model fits the experiment data well.

Several researchers used the pseudo-first-order equation of Lagergren for uptake kinetic of metal ions, however, the fitting result is often moderate or poor [162,266-268].

For the rate constant for second order sorption [269],

$$dq_t / dt = k_2(q_e - q_t)^2 \quad (2.8)$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, and then is rearranged, gives

$$t / q_t = 1 / (k_2 q_e^2) + t / q_e \quad (2.9)$$

Where k_2 (g/(mg h)) with t (h); and (g/(mg min)) with t (min), is the rate constant of the second order reaction. Eq. (2.9) suggests that the plots of t/q_t versus t is a straight line. The values of q_e and k_2 can be derived from the intercept and the slope of the plot, respectively.

The pseudo-second-order kinetic model has been the most widely tested model for the sorption of pollutants from wastewater since it was proposed [270]. All the literature fits using this method for chitosan-metal ion systems provide a high degree of correlation between the model results and the experimental data over the whole range of the uptake capacity.

The intraparticle diffusion model is expressed as [271]:

$$q_t = k_d t^{1/2} + C \quad (2.10)$$

Where C is the intercept, and k_d ($\text{mg/g h}^{1/2}$), the intraparticle diffusion rate constant and can be derived from the slope of the line of q_t versus $t^{1/2}$. If only intraparticle diffusion is the rate limiting, then the plot of q_t versus $t^{1/2}$ will be linear and passes through the origin. Otherwise, other adsorption mechanism may also be involved.

CHAPTER 3 EXPERIMENTAL METHOD

3.1 Materials

Chitosan flakes with DD % of 90 % and Mw $\sim$ 180,000 were obtained from Bio21 Co. Ltd., Thailand. Methylene blue (MB) ($C_{16}H_{18}N_3SCL.3H_2O$, molecular weight 373.9, high purity), Methyl violet 2B (MV2B) ($C_{24}H_{27}ClN_3$, molecular weight 393.9, dye content 75 %), were supplied by Alfa Aesar. Malachite green oxalate (MG) ($C_{52}H_{54}N_4O_{12}$, CI = 42,000, molecular weight 927.02, dye content > 80%) was supplied by Kanto Chemical Co. Inc. The molecular structures of the dyes are shown in Fig. 3.1. $AgNO_3$ (99+ %, Sigma-Aldrich), Ag standard solution for ICP (1000 mg/L, Fluka), Epichlorohydrin (> 98%, Fluka), Oxone ($2KHSO_5.KHSO_4.K_2SO_4$, 4.7 % active oxygen, Alfa Aesar), Alpha-D(+)-glucose (99+ %, anhydrous, Acros Organics) $Co(NO_3)_2.6H_2O$ (98%, GCE), zeolite NaY (CBV100, ZEOLYST INTERNATIONAL), Benzene (> 99.7 %, BDH AnalaR), HCL (37 %, OReC), HNO_3 (> 69 %, Honeywell), NaOH (98.95 %, Fisher Scientific), were of analytical grade and used as received.

Fig. 3.1 Molecular structure of (a) Methylene Blue, (b) Malachite Green Oxalate and (c) Methyl Violet 2B.

3.2 Adsorbent synthesis

3.2.1 Experimental preparation of tyre AC

(1) Pyrolysis

Waste tyres were cut into small cubes with size of $\sim 5 \times 5 \times 5$ mm, they were dried in an oven and then pyrolyzed in a horizontal quartz tube located in a tube furnace (CARBOLITE CTF12/65/650) under nitrogen, the nitrogen flow rate was 200 ml/min. The temperature was ramped from an ambient temperature to 700 °C at a rate of 5 °C /min, soaked for 1 hr, and cooled to room temperature in air.

(2) Acid treatment (demineralization)

The chars of about 2.5 g were treated with 200 ml 1M HCl acid at room temperature for one day. The system was subjected to constant stirring to ensure good mixing between the liquid acid and the char samples.

(3) Steam activation

Fig. 3.2 shows the schematic diagram of the activation process. Liquid water was pumped continuously into an evaporator (with a temperature of 300 °C), where it was

vaporized, mixed with the carrier gas (N_2), and then brought into contact with the char samples. The water supply rate was varied from 0.5 to 1.0 ml/min (equivalent to a steam flow rate of 620 ml/min to 1440 ml/min at 300 °C, respectively). The activation temperature was set at 900 °C (from literature values and trial runs) and the reaction time was varied from 1 to 4 h.

Fig. 3.2 Schematic diagram of the activation process: (1) N_2 gas cylinder; (2) gas flowmeter; (3) evaporator (with heater); (4) tube furnace; (5) quartz tube reactor; (6) temperature controller; (7) peristaltic pump; (8) water tank; (9) gas outlet.

3.2.2 Templated carbon synthesis

The experimental setup of templated carbon is the same as that in Fig. 3.2. The difference is that the part (8) is not water tank but a sealed container filled with carbon source-benzene. Sodium zeolite Y (NaY) was dried overnight at 200 °C in a vacuum oven before loaded in a quartz boat and placed into a flow-through tube furnace. The furnace was heated to the targeted temperatures (600 - 950 °C) at a ramp rate of 5 °C /min under a nitrogen flow rate of 15 cm^3 /min. When the target temperature was reached, liquid benzene was injected into the evaporator at the rate of 0.11 ml/min via

a syringe pump. The CVD processes were maintained for ~3 hrs before the benzene stream was cut off. The system was then left to cool down under a nitrogen flow at ambient conditions. The resulted zeolite-carbon composite was washed with 46 % HF solution for 24 hrs to remove the template. Finally, the obtained ZTC was washed with excessive deionized water and dried in an oven for 24 hrs.

Seven carbon samples, namely: BTC 600, BTC 650, BTC 700, BTC 750, BTC 850, BTC 900, and BTC 950 were prepared, which correspond to the CVD temperatures of 600, 650, 700, 750, 850, 900 and 950 °C, respectively, with the benzene feed rate of 0.11 ml/min. In addition, another carbon sample was prepared with a doubled benzene feed rate of 0.22 ml/min at the CVD temperature of 650 °C, which was named as BTC 650-2.

3.2.3 Synthesis and activation of carbon nanosphere (CNS)

The fabrication method of the native CNS was based on that reported in the literature [16]. Briefly, 40 ml of an aqueous solution of 0.5 M glucose was added into a Teflon-lined autoclave which was then subjected to heating at 160 °C for 12 hrs. The as-prepared CNS were washed with deionized water and ethanol for three times each via centrifugation, then dried in an oven at 60 °C for 12 hrs.

To activate the CNS surface for adsorption of silver ion and basic dye, the as-prepared CNS were soaked in the aqueous solutions of sodium hydroxide. Briefly, 0.12 g of dry powder was dispersed in 100 ml of NaOH aqueous solution of a certain concentration. The mixture was stirred at 300 rpm for 1 hr at room temperature. The product was

collected by filtration and washed with a copious amount of deionized water (about 1 L) to remove the residual NaOH until the pH of the filtrate reached near neutral. The activated CNS samples were dried in an oven at 90 °C for 12 hrs. The effect of NaOH concentration was studied. The CNS samples activated with 0.01 M, 0.05 M, 0.1 M, 0.5 M and 1.0 M of NaOH solutions were denoted as CNS/OH0.01, CNS/OH0.05, CNS/OH0.1, CNS/OH0.5 and CNS/OH1.0, respectively. The native sample without activation was named as CNS.

3.2.4 Experimental preparation of chitosan hydrogel beads and Ag imprinted chitosan hydrogel beads

The experimental set up for preparation of chitosan gel beads was shown in Fig. 3.3 and Fig. 3.4 shows the flow chart for preparation Ag-imprinted chitosan gel beads. Ag(I) imprinted certain mass of AgNO₃ was dissolved in 1 % acetic acid, then 2 g chitosan powder was added and stirred overnight to form dissolved Ag(I) containing chitosan solution. The ratio of mass of AgNO₃ to that of chitosan powder ranged from 3 to 100 mg/g. The chitosan aqueous solution was stirred over night and filtered by pumping through a syringe needle (27G) drop-wisely into 1 M sodium hydroxide solution under stirring to form spherical gels beads (with the diameter ~2 mm). The hydrogel beads were removed by filtration and rinsed with tap water until neutral. The as prepared Ag(I) imprinted chitosan beads by phase inversion method was subject to ECH crosslinking with optimal crosslinking degree. Briefly, 20 ml of Ag(I) imprinted chitosan gel beads were dispersed in 30 ml of 1 M NaOH solution and 1ml of ECH was added as crosslinker, reacted at 50 °C for 5 hrs. After crosslinking, the imprinted Ag in the beads was washed off with enough 2 M HNO₃ solution until no Ag(I) leaching out was tested. Finally, the beads were regenerated with 0.2 M NaOH for 8

hrs and washed with DI water to around pH 6 in DI water. The original crosslinked chitosan beads without Ag(I) imprinting was prepared in the same way, but no AgNO_3 was added.

Fig. 3.3 The illustration of the fabrication of CS hydrogel beads
1: CS solution, 2: peristaltic pump, 3: syringe needle, 4: tank containing NaOH, 5: freezing dryer.

Fig. 3.4 Flow chart of the preparation of the Ag(I) imprinted biosorbent

3.3 Characterization methods

Scanning electron microscope (SEM) and field emission scanning electron microscope (FESEM) were used to characterize the morphological characteristics of adsorbent. The samples were firstly coated with platinum under a vacuum for 60

seconds using an auto fine coater (JEOL JFC-1600). The micrographs of sample were collected using SEM (JEOL JSM-6390LA) and FESEM (JEOL JSM-6500F), respectively.

N₂ adsorption: The pore structure of adsorbent was characterized with nitrogen isotherm at 77 K, which was measured with a commercial pore and surface analyzer (PSA, Quantachrome Inc, Autosorb-6B). The specific BET surface areas (S_{BET}) were determined with N₂ isotherm at 77K in the pressure range (P/P_0) of 0.05-0.2. The pore size distributions (PSD) of the carbon samples were derived from the N₂ isotherm via the nonlocal density functional theory (NLDFT). Prior to nitrogen adsorption isotherm measurements, the samples were degassed overnight under vacuum by Autosorb degasser (PSA, Quantachrome Inc.) to remove contaminants, such as water, CO₂, hydrocarbons, etc. Normally, the degassing temperature is at 200 °C and the vacuum is below 1.0×10^{-4} torr.

Fourier transform infrared spectroscopy (FTIR): The Fourier transform infrared (FTIR) spectra of carbonaceous adsorbent were directly recorded in attenuated total reflectance (ATR) mode by a FTIR spectrometer (NICOLET 5700, Thermo) with a mercury cadmium tellurium (MCT) detector. The FTIR spectra of CS-carrageenan PEC were recorded using KBr pellet in a Perkin Elemer Spectrum One FTIR. The samples were finely ground together with KBr. All the FTIR spectra were recorded in the range of 4000-500 cm⁻¹. The number of scan was set at 64 and the spectra resolution was 4 cm⁻¹.

X-ray Diffractometer (XRD): An advanced X-ray Diffractometer (XRD, Bruker D8)

with $\text{CuK}\alpha$ radiation was used to characterize the crystal phase of carbonaceous adsorbents.

Raman: Raman spectra was obtained via a Renishaw Ramanscope in the back scattering configuration using 633 nm (1.96 eV) laser wavelength to study the crystallographic disorder of activated carbons.

Zeta potential: Zeta potential of the CNS sample in deionized water was determined using a zeta meter (BIC PALS Zeta Potential Analyser) by dispersing 12.5 mg of the samples in 25 ml of deionized water.

Inductively Coupled Plasma (ICP): Teledyne Instruments Leeman Labs Inc. - Prodigy High Dispersion ICP-AES (Perkin Elmer ICP Optima 2000 DV) was used to determine metal ion concentration. The ICP instrument is calibrated prior to analysis of the actual samples. Calibration is done using standard solutions of the metals that is to be tested at a fixed incremental concentration. In our study, silver ions standard solutions are prepared at different concentrations for calibration. After calibration of the ICP mass spectrometer, a straight line graph will be generated for determining actual concentration of silver ions in the samples. The samples must be filtered using 0.45 μm pore size filter before being tested in the ICP mass spectrometer. This will improve accuracy and maintain the workability of the instrument.

3.4 Adsorption experimental

3.4.1 Adsorption capacities and isotherm

The adsorption capacities of adsorbent were studied in a batch mode. As-prepared

adsorbate (Ag(I) or basic dye) aqueous solutions (25 ml) diluted from 1000 ppm stock solution at various concentrations were dispensed into conical flasks, which contained certain accurately weighed adsorbent samples. The mixtures were shaken at 200 rpm at room temperature to complete adsorption. The solutions were then withdrawn and filtered through PTFE syringe filters (pore size: 0.45 μm). For Ag(I) adsorption experiment, the clear Ag(I) solution filtrates obtained were diluted in 2 % HNO_3 for determination of Ag(I) concentration by ICP-AES. For basic dye adsorption, the concentrations of the dye filtrate aqueous solution were analyzed using UV/Vis spectroscopy (Shimadzu 2450). The detailed adsorption parameters including adsorbent dosage, adsorption duration will be described in following chapters. To investigate the effect of pH value on adsorption performance, the pH value of the adsorbate aqueous solution was adjusted by adding 0.1 M NaOH and HCL. The amount of the adsorbate adsorbed onto adsorbent was calculated according to the following equation:

$$q_e = (C_0 - C_e)V / m \quad (3.1)$$

Where, q_e (mg/g) is the adsorption capacity at equilibrium, C_0 and C_e (mg/L) are the initial and equilibrium concentrations of adsorbate in solutions respectively. V is the volume of the aqueous solution and m is the dosage of the adsorbent in the solution.

3.4.2 Adsorption kinetics

The adsorption kinetics of adsorbate with adsorbent was carried out at various initial adsorbate concentrations. Briefly, certain mass of adsorbent sample was dispersed in certain volume of adsorbate aqueous solution and the mixture was stirred at 200 rpm at room temperature. At different time intervals, 2 ml (dye) and 5 ml (metal ion) of the

aqueous solution was withdrawn, filtered to get clean aqueous solution and prepared for further concentration measurement. The amount of adsorbate adsorbed at time t , q_t (mg/g), was calculated by

$$q_e = (C_0 - C_t)V / m \quad (3.2)$$

Where C_t (mg/l) is the concentration of adsorbate aqueous solution at time interval of t (h), q_t is the adsorption capacity at time interval of t , V (ml) is the volume of aqueous solution, and m (mg) is the weight of adsorbent. The detailed adsorbent dosage and volume of aqueous solution was presented in Figures of adsorption kinetics in main chapters.

For powder adsorbents (activated carbons (TAC, ZTC) and CNS), in calculation of $q_e = (C_0 - C_t)V / m$, the ratio of V / m is considered constant in original solution as well as sample extracted. For these adsorbents were extracted together with the adsorbate aqueous solution under magnetic stirring, it is supposed that the adsorbents distribute almost uniformly in solution due to the magnetic stirring when solution was extracted. In sample extraction, the volume of sample extracted is predetermined; however, the mass of adsorbent extracted simultaneously could not be measured. Therefore, this is only a tentative method for the calculation of q_e . However, it is still commonly used in kinetics experiments in the literatures because of easy understanding and feasibility. For chitosan beads, in calculation of $q_e = (C_0 - C_t)V / m$, the parameter m is used as a constant because that chitosan beads (with diameter of 2-3 mm) were not extracted together with the adsorbate aqueous solution, and solution volume (V) is used as the decreased volume with 5 ml of sample extraction.

CHAPTER 4 PREPARATION OF A TYRE DERIVED ACTIVATED CARBON AND THE APPLICATION FOR A BASIC DYE REMOVAL

4.1 Introduction

This chapter is reproduced with permission from [Song X.H., R. Xu, A. Lai, H. L. Lo, F. L. Neo, K. Wang, Preparation and characterization of mesoporous activated carbons from waste tyre, Asia-Pacific Journal of Chemical Engineering, 2011, DOI: 10.1002/apj.544] Copyright 2011, John Wiley and Sons. Activated carbons prepared from waste materials for wastewater treatment are preferable from the point of view of reducing cost and environmental protection. Waste tyres are disposed in large amount annually around the world, which pose environmental and health issues. Many efforts were reported to recycle waste tyres into additives, pavement materials, or energy, etc. Among those options, it is very attractive to convert the tyres into tyre-derived activated carbons (TAC). The production of TAC generally involves a pyrolysis process followed by an activation process. Steam and CO₂ are commonly used as activation agents. Nevertheless, it has been reported that tyre chars present higher reactivity with steam than with CO₂ [272-275]. The feasibility of preparation of mesoporous activated carbons from waste tyre with steam activation and application as adsorbent for the toxic dye, MG from aqueous solutions was approached.

In this project, high quality mesoporous TAC for dye containing wastewater treatment was synthesized. The effect of production parameters on the property of the TAC was

investigated, and the effect of acid wash treatment on final TAC quality was studied. The structure and surface property of the TACs was also characterized and examined. The potential application of TAC in removal of toxic basic dye from wastewater was further explored. The detailed sorption performance and mechanism of the synthesized mesoporous TAC for basic dye Malachite Green in aqueous solution was studied in this study. The sorption capacity of a commercial BPL activated carbon (CAC) for the dye was also compared with that of TAC.

4.2 Experimental

The TAC synthesis method was shown in section 3.2.1. The effect of synthetic conditions including effect of acid washing treatment, and steam activation duration on the TAC textural properties was studied and the surface texture of the tyre carbon was characterized by N₂ adsorption, SEM and Raman analysis method. The adsorption performance of as-prepared TAC to Malachite Green Oxalate was studied. The experimental methods of adsorption are listed in section 3.4.

4.3 TAC synthesis without acid treatment

Herein, the TAC samples were labeled by their preparation conditions. For example: H₂O_1h_0.5 corresponds to steam activation for 1 hr with the water feed rate of 0.5ml/min, while H₂O_1h_HCl suggests the acid treatment of 1 hr.

Firstly, tyre chars were subject to direct steam activation. The water feeding rate is 0.5 ml/ min while the activation time varied from 1 to 4 hrs. The nitrogen isotherms of the TAC samples were shown in Fig. 4.1A while their textural properties were listed in Table 4.1. From Table 4.1, the highest surface area ($S_{\text{BET}} = 542.2 \text{ m}^2/\text{g}$) was obtained

at 2 hrs. A further increase in activation time to 4 hrs will result in a decreased surface area ($S_{\text{BET}} = 461.3 \text{ m}^2/\text{g}$). It was also found that increasing water feed rate to 1 ml/min would not significantly improve the surface area of the TACs (less than 20 %). Judging from their surface areas and pore sizes in Table 4.1, we can conclude that the pores in these TAC samples are largely microporous with underdeveloped porous structure, even at high burn-off ratio ($\sim 84 \%$).

Fig. 4.1 N₂ sorption isotherms on TACs (A) steam rate of 0.5 ml/min without acid treatment; (B) steam rate of 1.0 ml/min with acid treatment.

4.4 TAC synthesis with acid treatment

Secondly, the tyre chars were subject to acid treatment (acid wash) prior to the activation process of 1, 2, 3, and 4 hrs, respectively. The activation temperature was kept at 900 °C and the water feeding rate was fixed at 1.0 ml/min. Table 1 lists the textural properties of the TACs, while Fig. 4.1B shows their nitrogen isotherms. It was observed that acid treatment considerably increased the surface area of the derived TAC.

The optimum steam activation time is 3 hrs. Insufficient activation time could lead to incomplete pore development. When activation time increased from 1 hr to 3 hrs, BET surface area and pore volume progressively increased to 1193 m²/g and 1.5 cm³/g, which could be attributed to the burning off carbon bone or some built micro/mesopore walls by steam to generate pore structures. However, it was noted that a further increase in activation time to 4 hrs will result in a high burn-off ratio only, but a decrease in both surface area and pore volume. It was proposed that further longer activation duration could lead to burning off more mesopore walls and the collapse of formed mesopore structure.

Fig. 4.2 shows the pore size distributions of the TACs derived from N₂ adsorption isotherms. It was observed that, with the sample of H₂O_3h_HCl, a major mesopore pore peak appeared at 3.8 nm and a minor micropore peak was identified at 1.1 nm. The mesopore volume is ~ 80 % of the total pore volume, suggesting that the TAC was predominantly mesoporous. Carbons with such structure are advantageous for adsorbing bulky molecules such as dyes, PAHs and biomolecules.

Fig. 4.2 Pore size distributions of the TACs with acid treatment

The effect of acid treatment can be clearly seen in Table 4.1, which compares the surface area of the TACs samples with and without acid treatment. It has been postulated that acid treatment is effective in removing inert mineral matter (ZnO) in tyre chars [276-277], leading to more opened channels for the activation agent (steam) to diffuse into the char and enhance the activation reactions.

Table 4.1 Characteristics of TACs through steam activation without/with acid wash

TAC	H ₂ O Activation		Flow rate		Degree	S _{BET}	Total
Sample					burn-off		pore
	Temp	Duration	N ₂	H ₂ O	(%)	(m ² /g)	Volume
	(°C)	(hr)	(cm ³ /min)	(ml/min)			(cm ³ /g)
H ₂ O_1h_0.5	900	1	100	0.5	27	258.0	0.23
H ₂ O_2h_0.5	900	2	100	0.5	50	542.2	0.51

H ₂ O_4h_0.5	900	4	100	0.5	84.9	461.3	0.44
H ₂ O_1h_HCl	900	1	100	1.0	32.3	301.90	0.28
H ₂ O_2h_HCl	900	2	100	1.0	58.7	404.23	0.61
H ₂ O_3h_HCl	900	3	100	1.0	84.4	1193.00	1.51
H ₂ O_4h_HCl	900	4	100	1.0	86.5	819.30	0.81

4.5 TAC Structural characterization

The FESEM image of TAC samples (H₂O_3h_HCl) was shown in Fig. 4.3. It is seen that the sample is comprised of many amorphous graphite domains with large interparticle voids, confirming a heterogeneous structure and a high porosity.

Fig. 4.3 FESEM image of TAC sample (H₂O_3h_HCl)

The Raman spectroscopy of tyre carbon is shown in Fig. 4.4. It has been known that the D-band (~1320 cm⁻¹) indicates the broken symmetry of disordered graphic lattice while the G-band (~1580 cm⁻¹) corresponds to the Raman-allowed E2g mode of graphite. We could see that the intensity of band G and D are weak for TACs with less

than 2 hrs' activation ($\text{H}_2\text{O_1h_HCl}$ and $\text{H}_2\text{O_2h_HCl}$). When activation time is increased to 3 and 4 hrs, the intensity of both bands increase significantly, indicating the structural development in TACs is accompanied by the formation of graphite carbons with disordered morphologies.

Fig. 4.4 Raman spectra of TACs with prior HCL treatment (a = $\text{H}_2\text{O_1h_HCl}$; b = $\text{H}_2\text{O_2h_HCl}$; c = $\text{H}_2\text{O_3h_HCl}$; d = $\text{H}_2\text{O_4h_HCl}$)

FTIR spectra of the TAC ($\text{H}_2\text{O_3h_HCl}$) identified a number of peaks at the following bands: 1581 cm^{-1} ($\text{C}=\text{C}$ -C aromatic stretching band vibration), 1248 cm^{-1} (C-O-C stretching vibration in ether), 588 cm^{-1} (C-S stretching vibration). The FTIR spectra indicates the carbonaceous bone of TAC, and no rich hydrophilic functional groups were dispersed on the surface of TAC.

Fig. 4.5 shows the pore size distributions of the TAC ($\text{H}_2\text{O_3h_HCl}$) (inserted figure) and that of the BPL commercial activated carbon (CAC) derived from N_2 adsorption

isotherms. It is evident that TAC comprises a large portion of mesopores with the sizes ranging from 2.0 nm to 6.0 nm, while CAC contains primarily micropores with the peak at ~ 1.1 nm.

Fig. 4.5 N₂ adsorption isotherms at 77 K, inserted: the pore size distributions of ACs

Table 4.2 shows the results of elemental analysis of TAC (H₂O_3h_HCl) and CAC, which reveals that the sample consists mainly of carbon (> 80%) and about 1.3 % of sulphur, which is the inherent character of tyre rubbers.

Table 4.2 The structural characteristics of TAC and CAC

ACs	Surface area (m ² /g)		Pore volume (cm ³ /g)		Elemental analysis (%)			
	S _{BET} ^a	S _{micro} ^b	V _{meso} ^c	V _{total} ^d	C	H	N	S
TAC	1193	224	1.359	1.51	80.45	0.83	0.12	1.31
CAC	931	792	0.194	0.603	--	--	--	--

Note: ^a BET surface area; ^b Micropore surface area, calculated by using t-plot method.
^c Mesoporous volume, calculated by using BJH method. ^d Total pore volume, obtained at P/P₀=0.99.

4.6 Adsorption performance

4.6.1 The effect of pH on MG sorption

Fig. 4.6 shows the Malachite Green Oxalate dye removal percentage (efficiency) of TAC (H₂O_3h_HCl) against the initial pH of the solutions with the initial MG concentrations C₀= 400, 650, and 1000 mg/L, respectively. The first point (with pH ~ 3.0) represents the natural pH. We see that, as the initial pH increases, the removal efficiency improves quickly and reaches nearly 100 % when pH > 5.

Fig. 4.6 Effect of solution pH on the sorption of MG on TAC (30 °C)

MG is a polar molecule while the TAC’s surface contains complicated functional

groups. The pH value of the solution significantly affects the surface charge of TAC as well as the degree of ionization of the dye. It is well known that MG is protonated under acidic conditions and deprotonated under basic conditions. At low natural pH, the concentration of hydrogen ions is high and may occupy some sorption sites on the carbon surface and, together with the charged groups on the surface of TAC, present electrostatic repulsive force towards the cationic dye molecules. This explained the observation in Fig. 4.6 that acidic condition is unfavorable for the sorption of MG in aqueous solution.

4.6.2 Sorption kinetics

Fig. 4.7 shows concentration of the dye solution left in aqueous solution at time t (C_t) versus the sorption time t in MG sorption process with initial concentrations $C_0 = 170, 260, \text{ and } 360 \text{ mg/L}$, respectively. It is seen that the final equilibrium (with the uptake $> 99 \%$) can be reached for each solution (with same dosage) at $\sim 30 \text{ min}$, 2 hrs , and 15 hrs , respectively. The sorption kinetics were measured on TAC at 30°C with three dye concentrations ($170, 260, \text{ and } 360 \text{ ml/L}$), respectively. The corresponding kinetic data were converted and shown in the inserted figure in Fig. 4.7 as symbols while the fittings to pseudo-second-order kinetics equation ($t/q_t = 1/(k_2 q_e^2) + t/q_e$) were plotted as solid lines. It is seen that, under the experimental conditions, the sorption kinetics were well described by the pseudo-second-order kinetics equation. Table 4.3 lists details of the fitting results of the two models. It is shown that, the pseudo-second-order model gives $R^2 = 1$, for all concentrations.

Fig. 4.7 Effect of contact time on MG sorption on TAC at 30 °C, natural pH, TAC dosage= 1g/l (inserted: Sorption kinetics of MG on TAC at 30 °C and the fitting of the pseudo second order kinetic model.)

Table 4.3 The fitting results of experimental kinetics with different sorption kinetics models.

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-second-order kinetic		
		q_e	k_2	R^2
		(mg/g)	(g/(mg h))	
360	352.5	357.1	0.026	1
260	251.9	250.0	0.422	1
170	167.9	166.7	5.161	1

4.6.3 Adsorption isotherm and mechanism

Fig. 4.8 shows the sorption isotherm data (dots) of MG on the TAC at 30 °C. The capacity was found to be ~ 420 mg/g at the equilibrium concentration of 40 mg/g, which is among the best MG capacity ever reported. The isotherm data were then fitted to the Langmuir equation: $q_e = q_m K_L C_e / (1 + K_L C_e)$, where q_m is the sorption capacity and K_L is the affinity parameter]. The fitting result is shown in Fig. 4.8 as the solid line while the optimal isotherm parameters are listed in Table 4.4. The model fitting is seen good with $R^2 > 0.99$.

Fig. 4.8 Sorption isotherm of MG on ACs at 30 °C (natural pH, TAC dosage 1 g/l)

Table 4.4 The fitting results of experimental kinetics with different models

Adsorbent	Isotherms	Temperature	Constants		
	Langmuir	T (K)	q_m (mg/g)	K_L (L/mg)	R^2

TAC	303	426.1	3.06	0.9999
CAC	303	151.5	0.3	0.9900
Freundlich	T (K)	$K_F ((\text{mg/g})(\text{L/mg})^{1/n})$	$1/n$	R^2
TAC	303	335.7	0.072	0.9169
CAC	303	48.6	0.291	0.9069

The adsorption isotherm of MG was also measured on the CAC and presented in Fig. 4.8 as symbols (white circle). The sorption capacity of CAC was found only ~ 149 mg/g, much lower than that of TAC. This result confirms the importance of the mesopores in the adsorption of bulky dye molecules. The sorption mechanisms of MG in the mesoporous TAC are discussed as below:

MG is a bulky molecule with the primary group (N-methylated diaminotriphenyl-methane) of $1.21 \times 1.19 \times 0.53$ nm. Meanwhile, dye molecules may form dimmers (large molecules) in aqueous solutions [278], which further restrict their access into small pores. Micropores with the pore size around 1.1 nm (The micropore peak of CAC) can accommodate approximately only a single layer of dye molecules (along the favourable orientation). On the other hand, mesopores with the size ≥ 2 nm would present good capacity (multilayer sorption).

4.7 Summary

A highly mesoporous carbon was prepared via steam activation of waste tyres. The optimal tyre carbon possesses a surface area of ~1100 m²/g, a pore volume of ~ 1.50 m³/g, and with a burn off ratio of ~ 85 %. Acid wash was found to play an important role in the structural development of the carbon. The derived TAC presented good

potential for sorption towards the bulky dye molecules of MB. The mesoporous tyre-derived activated carbon presents excellent sorption property for the basic dye (MG) in aqueous solution. Pore size selectivity of the mesoporous TAC towards the big molecule dye plays important role for the high sorption capacity. The sorption isotherm can be fitted well with the Langmuir equation while the kinetics was described by the 2nd order rate equation. The pH of the dye solution significantly affects the dye sorption efficiency on the carbon.

CHAPTER 5 SYNTHESIS AND CHARACTERIZATION OF ACTIVATED CARBONS PREPARED FROM BENZENE CVD ON ZEOLITE Y

5.1 Introduction

This chapter is reproduced with permission from [Song. X. H., Teo. W. S., Wang, K., Synthesis and characterization of activated carbons prepared from benzene CVD on zeolite Y, Journal of porous materials, January 2011, P1-5, DOI 10.1007/s10934-011-9462-0.] Copyright 2011, Springer. Activated carbons derived from template synthesis have attracted much research interest because of their potential industrial applications in such areas as: gas storage, adsorption, electrodes, supercapacitors, and catalyst supports [12-13,279]. The templated carbon is generally prepared via the controlled pyrolysis of a carbonaceous precursor contained in the porous network of a template material, followed by acid wash to remove the template [223]. Various template materials have been studied in this application, e.g., microporous zeolites [280-284] and mesoporous silicas [237,243-244,285-287], etc. The carbon precursors involve a range of gas/liquid chemicals, including furfuryl alcohol [283,288-292], acetonitrile [221,284,293-294], propylene [227,280,295], ethylene [296-297], acetylene [290,296], vinyl acetate [228], sucrose [279] and methanol [298].

Zeolites are the most popular templates because of their ordered structure and uniform sub-nanometer pores [224-225]. The wall thickness of a number of zeolites are around 1nm, making them excellent candidates for the synthesis of quality zeolite-templated carbon (ZTC). Kyotani et al. investigated ZTCs prepared with various methods and

with different templates [282,290,299-300]. They found that, with the simple chemical vapor deposition (CVD) method, zeolite NaY has the best structural transferability to its ZTCs, compared with other templates such as zeolite β , ZSM-5 and mordenite [281].

Benzene CVD has been popularly used in modifying the porous structure of activated carbons. Kawabuchi et al. [301] tailored the structure of carbons/carbon fibers using benzene CVD method and found that the adsorption selectivity of CO_2/CH_4 of the carbons is greatly improved while the adsorption capacities of those adsorbents are largely retained. Su et al. [302] prepared ZTCs by a two step method, i.e., impregnating furfuryl alcohol into HY zeolite followed by benzene CVD at 900 °C and a further thermal treatment at 900 °C. They found that benzene CVD can significantly increase the yield and the structural ordering of the derived ZTCs.

In this work, we performed benzene CVD directly on NaY template to prepare ZTCs using the single step CVD method. The ZTCs are characterized and the effect of synthesis conditions (such as CVD temperatures, benzene flow rates) on the structural development will be investigated. To authors' knowledge, such a synthesis process has not been reported in the literature. The as obtained was applied for Ag(I) adsorption from aqueous solution, the adsorption kinetics and capacity was investigated.

5.2 Experimental

The ZTC synthesis method and experimental setup were presented in section 3.2.2. The ZTCs were characterized by SEM, XRD, nitrogen adsorption, and Raman

spectroscopy, and Ag(I) adsorption performance was also studied.

5.3 SEM and XRD analysis

Fig. 5.1 shows the SEM images of zeolite Y and three other carbon samples (BTC 650, BTC 700, and BTC 900). It can be seen that the crystal morphology of the carbon samples bear some similarity to that of the zeolite template. As the CVD temperature increased from 650 °C to 900 °C, the average size of the graphite crystals becomes larger and more rigid in geometry.

Fig. 5.1 SEM images of (a) Zeolite Y, (b) BTC650, (c) BTC700, and (d) BTC900

Fig. 5.2 shows the XRD patterns of zeolite Y and the carbon samples. A broad diffraction peak at $\sim 6^\circ$ (2θ) can be seen on such samples as BTC 650, BTC 650-2, BTC 700, BTC 750, and BTC 850, which corresponds to the characteristic diffraction peak {111} of zeolite Y. This suggests that the long range structural ordering is partly

transferred from the zeolite to the carbon samples. When the temperature is further increased above 850 °C, this diffraction peak diminished while a broad diffraction peak at 26° (2 θ) appeared, such as on the samples of BCT 850 and BCT 900, which corresponds to the {002} diffraction of graphitic carbon [283]. These observations indicate that, as the CVD temperature increases, the derived carbon samples gradually lose the structural characteristics of the template zeolite and become more similar to carbon graphite. Therefore, lower CVD temperature at ~ 650 °C favors the formation of ordered structure of the carbon samples, which is in consistent with previous results obtained from propylene CVD [284].

The structural replication of the ZTCs depends on the sufficient carbon deposition/infiltration in the micropores and channels of the zeolites, whereby the carbon structure development is constrained by the spatial channel/pores limitation of the zeolite. In principle, smaller channels would hinder the deposition process, possibly the graphitization and the stacking processes as well. In the CVD process, carbon precursor deposits initially on the external surface and the outer regions of pores of zeolites. Lower CVD temperature will slow down the carbonization process of the precursor; therefore facilitate the infiltration of carbon precursor into the channels of the template. On the other hand, a higher CVD temperature (850 °C - 900 °C) will result in a too fast deposition/carbonization rate so that the carbon source will easily deposit on the external surface and the outer region of the pores of the zeolite crystals, which block the access to the pores/channels. This is partly explained by the observation that ordering structure was best transferred from zeolite to the carbon samples at lower CVD temperature of 650 °C to 750 °C, and no structure replication occurred at CVD temperatures of 850 °C and 900 °C.

Fig. 5.2 XRD patterns of Zeolite NaY and the carbon samples derived at different CVD temperature

5.4 Nitrogen isotherm and pore size distribution

Fig. 5.3A presents the adsorption and desorption isotherms of N₂ on the carbon samples at 77 K. All the samples show considerably adsorption capacity and steep gradient in the isotherms at the low adsorption pressure (e.g. at $P/P_0 = 0.05$), an indication of adsorption in micropores. Desorption hysteresis is observed on all carbon samples, which correspond to the existence of mesopores. Such mesoporosity is generally resulted from the incomplete filtration of the adsorbates in the microchannle of the template, the deposition of carbon onto the external surface, or the interparticle voids, et al.

The BET surface area, total pore volume and micropore volume are determined from the nitrogen adsorption isotherm, respectively, and summarized in Table 5.1. We see that BCT 650 presents the highest specific surface area ($1511 \text{ m}^2/\text{g}$) as well as the highest micropore volume of $0.355 \text{ cm}^3/\text{g}$. In comparison, other CVD temperatures, either lower or higher, will result in carbons with lower surface areas. A CVD temperature above 900°C is seen to drastically reduce the surface area to $\sim 300 \text{ m}^2/\text{g}$, possibly due to the graphitization and pore blockage. In comparison, this optimal surface area is not as high as those derived from CVD process with acetylene [290] or acetonitrile [294]. However, as benzene CVD is popularly used as the assistant treatment for structural modification, our results serve as good reference in future applications.

Next, as for a ZTC sample with CVD temperature of 650°C , and a doubled the benzene feed rate (0.22 ml/min). The lower specific surface area ($1253 \text{ m}^2/\text{g}$) and micropore volume ($0.283 \text{ cm}^3/\text{g}$) of the sample are in agreement that from Kyotani et al. [227], where a too high concentration of carbon precursor will adversely affects the properties of the sample produced. Therefore for CVD temperature of 650°C , lower optimal benzene flow rate is desired. Longer CVD times above 3 hrs did not improve the quality of the derived ZTCs.

Fig. 5.3 (A) Nitrogen sorption isotherms of (a) BTC 650, (b) BTC 650-2, (c) BTC 700, (d) BTC 750, (e) BTC 850 and (f) BTC 900, and (B) Pore size distribution (PSD) of ZTCs

Table 5.1 The Textural Properties of the ZTC samples.

Sample	CVD Temperature	Surface area	Total Pore volume	Micropore volume
	(°C)	(m ² /g)	(cm ³ /g)	(cm ³ /g)
BTC 600	600	1182	0.758	0.283
BTC 650	650	1511	0.927	0.355
BTC 650-2	650	1253	0.856	0.283
BTC 700	700	1356	0.792	0.338
BTC 750	750	1233	0.782	0.314
BTC 850	850	753	0.597	0.1
BTC 900	900	392	0.457	0.027

Fig. 5.3B shows the pore size distribution of the ZTC samples. A major micropore peak at ~ 1.1 nm is observed for BTC 650, BTC 700 and BTC 750. The pore size of BTC 650-2 sharply peaked at 1.2 nm, indicating the ordered micropore structure of the resultant carbon samples at lower CVD temperatures. This property, together with

XRD diffraction patterns, strongly support that the micropores of BTC 650 to BTC 750 represents the spacing replicated from the porous network of the zeolite template. BTC 850 and BTC 900 present broad peaks of pores from 1.0 - 2.0 nm with less micropore volume, which indicates poor structural regularity in these samples and is in agreement with the XRD results.

5.5 Raman spectroscopy

Raman spectroscopy was used to probe the level of graphitization of the carbon samples. Fig. 5.4 shows the Raman shift of BTC600 to BTC900. From the figure, two bands can be seen at 1350 cm^{-1} (D band, which is generally ascribed to amorphous carbons) and 1580 cm^{-1} (G band, which is generally ascribed to carbon-carbon stretching (E_{2g}) mode for grapheme sheets) [303]. The presence of G band indicates various levels of graphitic domains in the carbon samples and is consist with the XRD patterns. The relative intensity of band D increases for carbon samples prepared at higher CVD temperatures. The approximate ratio of the intensity of the two bands, I_D/I_G is 0.81 (BTC 650), 0.97 (BTC 850) respectively. The trend in I_D/I_G observed here implies a possible decrease in graphitic domain size in carbon samples prepared at higher CVD temperatures [304-305].

Fig. 5.4 Raman shift of ZTC samples.

5.6 Ag (I) adsorption performance

Fig. 5.5 (A) Adsorption rate of Ag(I) on ZTC 650 ((a) C₀ = 202 ppm, (b) C₀ = 1.75

ppm), and (B) adsorption capacity of Ag(I) on ZTC 650 (ZTC dosage 1 g/l)

The ZTC 650 sample was subject for Ag(I) adsorption in aqueous solution. The adsorption capacity can reach maximum at initial 5 minutes (Fig 5.5A). At initial Ag (I) concentration of 1.75 ppm, q_t increased to 1.75 mg/g with removal percentage of 100%, after adsorption of 5 minutes. At initial Ag(I) concentration of 202 ppm, q_t reached maximum of 22.5 mg/g with removal percentage of 12.4 % at adsorption time of 10 min (Fig. 5.5B). The maximum adsorption of ZTC to Ag(I) was measured as 22.5 mg/g, the adsorption capacity is lower than that of CNS/OH (144.9 mg/g) in later chapter. This may be due to the hydrophobic property of ZTC as compared with hydrophilic surface of CNS.

5.7 Summary

Templated carbons were synthesized using sodium form zeolite Y as the template and benzene as the carbon precursor. At the CVD temperature of 650 °C, the optimally derived carbon presents a specific surface area of 1511 m²/g, micropore volume of 0.355 cm³/g, and a micropore peak at 1.1 nm. This sample also possesses a structural periodicity transferred from the template zeolite. Higher CVD temperatures and increased benzene feed rate will result in carbons with lower specific surface areas, less micropore volumes, and more heterogeneous porous structure. The ZTC presents Ag(I) adsorption capacity of 22.5 mg/g in aqueous solution, much lower than that of CNS/OH, indicating chemical interaction between the surface functional groups and metal ion plays more important role in metal ion adsorption.

CHAPTER 6 SURFACE ACTIVATED CARBON NANOSPHERES FOR ADSORPTION OF BASIC DYES FROM AQUEOUS SOLUTION

6.1 Introduction

This chapter (section 6.3) is reproduced in part with permission [Song, Xianghua, Guanwan, Poernomo, Jiang Rongrong, Leong, Susanna Su Jan, Wang Kean, Xu Rong, Surface activated carbon nanospheres for fast adsorption of silver ions from aqueous solutions, *Journal of Hazardous Materials*, 194, 2011, 162-168.] Copyright 2011, Elsevier. The advantages of simple synthesis method, environmental benign and rich functional group surface properties make colloidal carbon nanosphere potential promising adsorbent for water treatment. The adsorption rate is expected to be faster than porous AC upon due to the direct contact of dye molecule with the sorption sites on CNS external surface, herein pore diffusion mechanism is not involved due to the nonporous structure of the nanosphere. The hydrophilic functional groups containing surface property of CNS makes it feasible for surface modification at mild condition to increase the function group density to increase adsorption capacity. To the best of our knowledge, there is no literature reporting the post treatment of carbon spheres by mild acids and bases treatment for enhancing dye adsorption performance. In this study, we synthesized well dispersed CNS and carried out surface activation under mild base condition for the CNS to enhance adsorption performance. The adsorption characteristics including effect of pH value, effect of ionic strength, adsorption isotherm, and adsorption kinetics were investigated. The adsorption mechanism of enhanced adsorption performance of base activated CNS was also explored. The dye

spent CNS/OH was regenerated with sulphate radical based oxidation method and was recycled for dye adsorption for six runs.

6.2 Experimental

6.2.1 Characterization and adsorption

The CNS synthesis, activation methods were presented in section 3.2.3. Herein the CNS sample activated with 0.5 M NaOH solution (CNS/OH0.5) was denoted as CNS/OH and utilized for adsorption characterization. The native sample without activation was named as CNS. The samples were characterized using FTIR, FESEM and nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$. Adsorption experimental methods are given in section 3.4. The pH value of the dye aqueous solution was adjusted by adding 0.1 M NaOH and HCL for effect of pH value study. The ionic strength of the dye aqueous solution was adjusted to 0.01 M, 0.1 M, 0.25 M and 0.5 M by NaCL.

6.2.2 CNS/OH regeneration and recycling

In adsorption procedure, 50 ml of 156 ppm MB dye aqueous solution with 25 mg of CNS/OH was added in a conical flask under stirring for 6 hrs. After adsorption, the CNS/OH was separated out via centrifugation, and then dispersed in 10 ml of 10 mM Co^{2+} aqueous solution. At the mean time, 0.1 mmol (60 mg) of oxidant, oxone was added into the Co^{2+} solution. The mixture was stirred for 20 minutes at room temperature. After that, the regenerated CNS was separated via centrifugation, reactivated with 25 ml of 0.5 M NaOH, washed three times with distilled water and finally dried in oven. Four sets of this adsorption/regeneration were conducted at the same time, for a little CNS was lost during the centrifuge washing. The regenerated CNS/OH was then applied to next adsorption/regeneration recycling run. During the

regeneration process, the separated Co^{2+} catalyst solution and the 0.5 M NaOH solution was recycling utilized in each run.

6.3 Properties of activated carbon nanosphere

Fig. 6.1A displays the FESEM image of the as-prepared CNS sample. Well dispersed nanospheres with relatively uniform diameters of around 400-500 nm were formed. Similar to the literature results [16,19,306], the hydrothermally formed CNS in this work has a nonporous structure as indicated by its low specific surface area of $12.7 \text{ m}^2/\text{g}$. The N_2 adsorption-desorption isotherm shown in Fig. 6.1B consistently indicates a Type II isotherm typically for nonporous materials [307]. The measured pore volume was as low as $0.02 \text{ cm}^3/\text{g}$ which should be mainly contributed by the inter-particle space. Activation of CNS by NaOH of all the concentrations used (0.01 - 1.0 M) did not cause any noticeable changes in the morphology, surface area and pore volume. Hence NaOH activation only modified the surface of CNS without affecting the bulk carbon core.

Fig. 6.1 (A) FESEM image of as-prepared carbon nanospheres (CNS), and (B) N_2 adsorption-desorption isotherm of CNS

The FTIR spectra of CNS, CNS/OH0.1 and CNS/OH0.5 are shown in Fig. 6.2. The main characteristic absorption peaks of CNS can be assigned accordingly as shown in Fig. 6.2A: 3100-3400 cm^{-1} to O–H stretching vibration, 1700 cm^{-1} to the stretching vibration of C=O in carboxyl group [250,253,308-310] or lactone group [311], 1615 cm^{-1} to C=C stretching, 2923 cm^{-1} to aliphatic hydrocarbon –CH, 1023 cm^{-1} and 1302 cm^{-1} to C–OH stretching and OH bending vibrations in C–OH, respectively [16,253], and 1361 cm^{-1} to symmetric stretching vibration of deprotonated carboxyl group, –COO[−] [16,312-313]. FTIR spectra of CNS/OH0.1 and CNS/OH0.5 are shown in Fig. 6.2B and 6.2C, respectively. In comparison with that of CNS, the intensity of absorption band in the range of 3100-3400 cm^{-1} was significantly increased especially for CNS/OH0.5, which indicates an enrichment of hydroxyl groups after NaOH activation. The deprotonated carboxylate groups (–COO[−]) centered at around 1360 cm^{-1} was also noticeably increased [312-313]. Correspondingly, the peak due to C=O stretching in carboxyl and lactone groups at 1700 cm^{-1} was greatly decreased. The above observations suggested that NaOH reacted with the carboxyl and lactone groups present on the surface of CNS according to the following reactions [314-316].

Zeta potential of CNS and CNS/OH0.5 dispersed in deionized water was measured to be −28.7 mV and −42.7 mV, respectively. The more negative zeta potential of NaOH activated carbon nanospheres can be consistently interpreted by the occurrence of the above two reactions which generated the negatively charged –COO[−] functional group

on the surface [317-318]. The increase in surface densities of the functional groups like -OH and -COO^- is expected to be beneficial for adsorption of Ag(I) ions from water.

Fig. 6.2 FTIR spectra of (A) CNS, (B) CNS/OH0.1, and (C) CNS/OH0.5

6.4 Adsorption isotherm

Adsorption equilibrium isotherm is used to describe the adsorbate concentrations distribution in the solid and liquid phase when adsorption reaches equilibrium. Modeling isotherm by isotherm models and to obtain the best fit equilibrium isotherm model to describe the isotherm data is important for adsorption system design and understand adsorption mechanism. The correlation of the equilibrium experimental data with isotherm equations is important for practical operation. The adsorption isotherm of dyes onto CNS/OH (CNS/OH0.5) and native CNS was shown in Fig. 6.3.

It is obvious that sorption capacity of CNS/OH is much higher than that of native CNS for all the three dyes, the measured maximum adsorption capacity of CNS/OH is 682 mg/g for MB, much higher than that of native CNS of 56 mg /g. The enhanced adsorption performance after activation can be explained by the enriched deprotonated carboxylic groups and hydroxyl groups on CNS/OH as evidenced in FTIR spectra. At MB initial concentration (C_0) of 303 ppm, MG initial concentration of 147 ppm, and MV2B initial concentration of 186 ppm, C_e upon adsorption equilibrium is all measured as almost zero, respectively, and the removal percentage was all almost 100%, indicating the high adsorption efficiency of CNS/OH for basic dyes. The adsorption capacity (q_e) of CNS/OH increases significantly with the increase of initial dye concentration (C_0), should be due to that the sorption sites on CNS/OH surface contact with more dye molecules as C_0 increases, facilitating to reach adsorption saturation of the adsorbent.

The maximum adsorption capacity of CNS/OH in aqueous solution was measured as 684 mg/g for MB at C_0 of 402 ppm, 310 mg/g for MG at C_0 of 245 ppm, and 395 mg/g for MV2B at C_0 of 240 ppm, respectively. The adsorption capacity of the CNS/OH for basic dye is among the highest adsorption performance [319], higher than most conventional AC, including commercial AC [320-321], agricultural and industrial waste derived AC [322-324], clay [325], bioadsorbent [326], and solid waste [327-328].

Fig. 6.3 Adsorption isotherm of MB dye, MGO dye and MV2B dye onto CNS/OH and native CNS. (adsorbent dosage: 12.5 mg/25 ml dye solution, C₀ of MB: 159 - 460 ppm, MV2B: 91 - 347 ppm, MG: 95 - 297 ppm, t = 24 hrs)

Herein, two common adsorption isotherm model, Langmuir and Freundlich model were applied to describe the adsorption data. Langmuir model describes a monolayer adsorption process and is usually applied to chemisorptions and with some restrictions to physical adsorption. The linear equation of Langmuir model [262] is presented as follows:

$$C_e / q_e = C_e / q_m + 1 / K_L q_m \tag{6.1}$$

Where C_e (mg/L) is equilibrium concentration of dye solution, q_e (mg/g) is equilibrium adsorption capacity, q_m (mg/g) is maximum adsorption capacity, and K_L (L/mg) is the affinity parameter. The plot of C_e / q_e versus C_e gives straight lines (Fig.

6.4A) with correlation coefficient R² of 1.000 (Table 6.1), therefore the adsorption

follows Langmuir adsorption isotherm, suggesting the adsorption of basic dyes on CNS/OH may be associated with chemical adsorption rather than physical adsorption. The dimensional constant, $R_L = 1 / (1 + K_L C_o)$ is defined to determine the adsorption isotherm is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), or irreversible ($R_L = 0$). R_L values for basic dyes adsorption onto CNS/OH were larger than 0 and less than 1, indicating the favorable adsorption (Table 6.1).

Freundlich isotherm model [261] is derived by assuming adsorption on heterogeneous surfaces as well as multilayer adsorption and is represented by following linear equation:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{6.2}$$

Where K_F ($\text{mg/g(L/mg)}^{1/n}$) is the Freundlich constant and $1/n$ is the heterogeneity factor. The Freundlich is not suitable for the adsorption of the dye on CNS/OH as the low correlation coefficient of 0.7185 to 0.8430 and the non-straight line of $\ln q_e$ versus $\ln C_e$ (Fig. 6.4B).

Fig. 6.4 The fittings of adsorption isotherm data of CNS/OH for basic dye to linearized Langmuir (A) and Freundlich adsorption models (B)

Table 6.1 The adsorption isotherm parameters of dyes adsorption on CNS/OH

Isotherms	Parameter	Dyes		
		MB	MV2B	MG
Langmuir	q_m (mg/g)	666.7	400	312.5
	K_L (L/mg)	5	4.2	10.7
	R^2	1.000	1.000	1.000
	R_L	0.0004	0.0003	0.0007
Freundlich	K_F (mg/g(1/mg) ^{1/n})	521.2	345.7	296.9
	$1/n$	0.0694	0.0326	0.0097
	R^2	0.7185	0.7644	0.8430

6.5 Effect of contact time and adsorption kinetics

Adsorption rate experiments for the dyes adsorption have been carried out, and the dye adsorption capacity versus time t was measured. As shown in Fig. 6.5, the maximum adsorption of MB onto CNS/OH can be reached at 5 minutes, and 20 minutes for MV2B and MG to complete adsorption. The slower adsorption rate to complete adsorption for MV2B and MG, as compared to MB, should be due to that natural pH values of MG ($pH_{\text{natural}} = 3.6$) and MV2B ($pH_{\text{natural}} = 4.2$) aqueous solution is lower than that of MB solution ($pH_{\text{natural}} = 4.9$), as the adsorption rate experiment is conducted at natural pH value of dye solutions unadjusted. The natural pH value of MG and MV2B aqueous are measured as 3.6 and 4.2 respectively, lower than that of MB (4.9). Since it has been reported that adsorption rate of basic dye in aqueous solution increases with increasing solution pH, because the mass transfer increased

with solution pH increasing [329]. Even though, as compared to other adsorbents, the adsorption rate of this adsorbent is fast for basic dyes in aqueous solution, and faster than activated carbons [330]. The fast adsorption rate should be due to the non-porous property of the adsorbent and the rich functional groups on the adsorbent surface for adsorption, decreasing the mass transfer duration.

To investigate the adsorption kinetic mechanism for the adsorption process, the pseudo-second-order, and pseudo-first-order kinetics model was applied to describe the experimental data. The R^2 values of 0.9981 to 0.9999 for the second-order kinetic model was all higher than that of first-order kinetic model of 0.9266 to 0.9481 (Table 6.2), indicating the adsorption kinetic of basic dyes on the adsorbent well follows pseudo-second order kinetic model. As the pseudo-second-order model is based on the assumption that chemical sorption is the rate-determining step [331], the above results obtained suggested that the basic dyes were chemically adsorbed.

Fig. 6.5 Effect of contact time on adsorption capacity (inset: pseudo-second-order kinetic model (line portion) of the experimental data) (adsorbent dosage: 50 mg/100 ml dye solution, C_0 of MB: 94 ppm, MG: 94 ppm, MV2B: 80 ppm)

Table 6.2 Second-order and first-order kinetic model fitting results of basic dyes adsorption on CNS/OH.

Dye	$q_{e,exp}$	2 nd -order kinetic model			1 st -order kinetic model		
	(mg/g)	$t/q_t = 1/(k_2 q_e^2) + t/q$			$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)t$		
		$q_{e,cal}$	k_2	R^2	q_e	k_1	R^2
		(mg/g)	(1/min)		(mg/g)	(g/mg)	
MB	187.8	188.6	0.035	0.9999	232.8	3.03	0.9266
MV2B	161.8	169.5	0.0027	0.9981	621	0.898	0.9481
MG	188.8	192.3	0.0066	0.9998	317.96	0.864	0.9256

6.6 Effect of pH value

At initial concentration of 290 ppm MB, 175 ppm MV2B and 150 ppm MG, and CNS/OH dosage of 10 mg/ 25 ml at room temperature, the dye adsorption capacity was measured at pH value ranging from 2.6 to 9.4. As shown in Fig. 6.6, there is no significant increase in the dyes removal percentage at pH value higher than 5 for MB and MGO, and higher than 4.2 for MV2B. The slightly higher adsorption capacity at pH 8 - 9.4 for MB and MV2B may be due to the dye color loss in highly base aqueous solutions [332]. The dye removal amount decreased significantly from 88 % (MB), 85 % (MV2B), and 98 % (MG) at pH 4.7 to 5.9 to 37 % (MB), 41 % (MV2B) and 55 % (MGO) as pH decreased to pH 2.6. Therefore at pH lower than 4.2 to 5, pH value of solutions has great effect on dye adsorption as it controls the electrostatic interactions between the CNS/OH surface and the dye. The adsorption of the cationic dye by CNS/OH can be attributed to the interaction between the deprotonated carboxyl and hydroxyl groups on CNS/OH and the cationic dye molecule. Therefore, decreasing the pH value of solution make the surface property of CNS/OH changed, making more protons available to protonate the COO^- . This results in decreasing dye adsorption due to decreased electrostatic interaction.

Fig. 6.6 Effect of pH value on basic dye adsorption on CNS/OH

6.7 Effect of ionic strength

Dye containing wastewater discharged from industries usually contains high salt concentrations, which may significantly affect the dye adsorption performance. Fig. 6.7 shows the effect of ionic strength of NaCL on dye uptake capacity. It was found the dye removal amount is almost identical at ionic strength of 0.01 M and 0.1 M. As ionic strength increased to 0.25 M and 0.5 M, the dye adsorption capacity of CNS/OH decreased 43 - 49 % and 56 - 69 % for MB and MV2B, and decreased 9 - 17 % for MG, as. This decrease could be attributed to the competition of salt cation Na^+ with cationic dye molecules for the adsorption sites on the adsorbent surface during adsorption process [333-334]. Another may be due to the great ionic strength decreased the dye activity, reducing its transfer to the adsorbent surface.

Fig. 6.7 Effect of ionic strength of dye adsorption capacity of CNS/OH

6.8 Basic dye loaded CNS/OH regeneration and recycling

Dye spent carbons have been regenerated utilizing thermal treatment [335], surfactant based desorption [6,336], wet chemical oxidation [337-338], electrochemical oxidation [339], and microwave irradiation [340]. Herein, Methylene Blue was used as the model dye. The MB dye (156 ppm) loaded CNS/OH was regenerated with sulphate radical based oxidation method due to the high efficiency, low cost and fast reaction kinetics of the catalytic process [341-342]. Co^{2+} in aqueous solution serves as a homogeneous catalyst coupling to the oxidant to accelerate the generation of sulfate radical for oxidizing degradation of the dye [341-342]. The regenerated CNS was recycled for dye adsorption for six runs. During the oxidation process of the MB spent CNS/OH, after dispersion of MB adsorbed CNS/OH in the Co^{2+} catalyst containing solution, the light red Co^{2+} solution changed to blue color because of some degree of

desorption of MB from the CNS/OH. The blue color mixture solution quickly faded after adding the oxidant oxone, and the finally separated solution containing Co^{2+} remained light red color, which indicates the adsorbed MB was oxidized instead of desorbed in the solution. The Methylene Blue dye removal percentage in each recycling run was shown in Fig. 6.8. The MB removal percentage is from 99.8% to 99.6%, almost unchanged in the first five recycling runs, and decreased to 98.1% and 96.2% in the fourth and fifth runs. This oxidation method is efficient for recycling usage of the basic dye spent CNS/OH.

Fig. 6.8 Methylene Blue removal percentage using regenerated CNS/OH in recycling runs (25 mg CNS/OH, 50 ml 156ppm MB solution)

6.9 Summary

The surface of the activated carbon nanospheres was enriched with functional groups

of $-\text{OH}$ and $-\text{COO}^-$ after activation which facilitates basic dye adsorption via chemical interaction between the deprotonated functional groups on CNS/OH and the cationic dye molecule. The maximum adsorption of CNS/OH was measured as 682 mg/g for MB, 310 mg/g for MG, and 395 mg/g for MV2B. The adsorption rate is fast, the maximum adsorption of MB onto CNS/OH can be reached at 5 minutes, and 20 minutes are needed for MV2B and MG to complete adsorption. As pH value of dye aqueous solution decreased from pH 4.7 - 5.9 to pH 2.6, The dye removal amount decreased from 88 % (MB), 85 % (MV2B), and 98 % (MG) to 37 % (MB), 41 % (MV2B) and 55 % (MG) respectively. And higher ionic strength of 0.25 - 0.5 M NaCl caused decreased dye adsorption capacity. The sulphate radical based oxidation method can efficiently regenerate the MB dye spent CNS/OH, and the regenerated CNS/OH was recycled seven runs for MB adsorption without obvious adsorption capacity reducing.

CHAPTER 7 SURFACE ACTIVATED CARBON NANOSPHERES FOR FAST ADSORPTION OF SILVER ION FROM AQUEOUS SOLUTION

7.1 Introduction

This chapter is reproduced with permission from [Song, Xianghua, Guanwan, Poernomo, Jiang Rongrong, Leong, Susanna Su Jan, Wang Kean, Xu Rong, Surface activated carbon nanospheres for fast adsorption of silver ions from aqueous solutions, *Journal of Hazardous Materials*, 194, 2011, 162-168.] Copyright 2011, Elsevier. Silver as one of the precious metals is in high demand since it plays important roles in many aspects of human life. For example, silver and its compounds are often used as disinfectants in wastewater treatment, food/beverages/drugs processing, and drugs, etc [343]. On the other hand, the monovalent ionic silver, Ag(I), is of particular environmental concern, due to its potential impact on human health and ecosystems. It has been reported that when ingested by humans, silver is metabolized and deposited in the subcutaneous fat. The greyish-blue color of silver gives rise to the cosmetic disorder of argyria, in which the affected person's skin is discolored [344]. It was also found that ion regulatory failure of the human body due to an inhibition of uptake of active Na^+ and Cl^- can be caused by Ag(I) exposure. The World Health Organization (WHO) and the US Environmental Protection Agency (EPA) classified soluble silver ions as hazardous substances in water systems and limited the level of silver in drinking water to be 100 ppb (100 $\mu\text{g/L}$) [158]. Therefore, with the increasing concerns on the toxicity of soluble silver ions in water and the scarcity of silver sources, it is necessary to remove and recover silver from water. In particular, it

remains a challenging task to recover silver from wastewater of low silver concentrations efficiently and economically. Adsorption has been widely used as an effective separation technology in water treatment owing to its simplicity in process design and operation [345]. The surface composition and property of the adsorbent materials can be modulated by chemical treatment using various reagents such as acids, bases, oxidants, polymers, et al. [346-349]. For activated carbon and other types of carbon materials, it has been widely reported that the adsorption capacities towards metal ions can be enhanced by chemical treatment with acids and bases [314-315,346,349-350].

Herein, the potential application of carbon spheres in removal and recovery of Ag(I) ions from water, especially from water with dilute Ag(I) ion concentrations (< 1 ppm) was explored. Colloidal carbon nanospheres (100 - 300 nm in diameter) were synthesized and activated by a simple treatment with aqueous solutions of NaOH. The effect of alkaline treatment on the surface functional groups and adsorption properties of carbon nanospheres was systematically investigated in batch studies. In addition, a fixed-bed adsorption column was used to investigate the efficiency of Ag(I) ion removal and recovery under the continuous operational mode for potential large-scale applications.

7.2 Experimental

7.2.1 Characterization and adsorption

The CNS synthesis and activation method was presented in section 3.2.3. The CNS samples activated with 0.01 M, 0.05 M, 0.1 M, 0.5 M and 1.0 M of NaOH solutions were denoted as CNS/OH0.01, CNS/OH0.05, CNS/OH0.1, CNS/OH0.5 and

CNS/OH1.0, respectively. The native sample without activation was named as CNS. The FESEM and FTIR and N₂ adsorption characterization of samples were given in section 6.3. The samples were also characterized by TEM and XRD. The adsorption method in batch mode was presented in section 3.4.

7.2.2 Recovery and reusability of Ag(I) spent carbon nanosphere

To recover the adsorbed silver and reuse the carbon nanospheres after adsorption, aqueous solutions of 0.2 M and 1.0 M HNO₃ were used to dissolve silver from the surface of carbon nanospheres. The adsorption was first conducted by adding 15 mg of CNS/OH0.5 in 25 ml of Ag(I) solution of 2 ppm. The mixture was shaken at 200 rpm at room temperature for 12 hrs. The resulting silver adsorbed carbon nanospheres were separated from the solution by centrifugation and dispersed in 25 ml of HNO₃ solution for desorption. The mixture was then shaken at 200 rpm. After a certain period of time, 10 ml of the solution was withdrawn and filtered to get clear solution for ICP-AES analysis. After recovery of silver, the carbon nanospheres were regenerated by soaking in 50 ml of 0.5 M NaOH solution for 1 hr at room temperature, followed by washing with deionized water until the pH of the filtrate reached near neutral. The adsorption capacity of the regenerated CNS/OH0.5 was obtained under the same conditions as those used for the fresh CNS/OH0.5 for comparison.

7.2.3 Continuous study of Ag(I) adsorption with CNS/OH using a fixed-bed adsorption column

The efficiency of sample CNS/OH0.5 in removing Ag(I) ions from solutions of low concentrations (0.1 ppm and 1 ppm) was studied in a fixed-bed packed column. To

avoid excessive pressure drop, CNS/OH0.5 powder was mixed well with silica beads (Acros Organics, particle size: 0.2 - 0.5 mm) at a mass ratio of 1:50 before packing the column. The inner diameter and length of the column were 1.5 cm and 20 cm, respectively. The amount of CNS/OH0.5 required to fully pack the column was around 240 mg. The continuous adsorption study was carried out at room temperature, during which the Ag(I) solution was fed into the vertically oriented column by a peristaltic pump. The flow mode was downward and the flow rate was fixed at 6 ml/min. At certain time interval, 15 ml of the effluent was collected and diluted in 2 % HNO₃ solution for ICP-AES analysis. Breakthrough and exhaustion in continuous adsorption were usually defined as the phenomenon when the concentration of the adsorbate in the effluent reached about 3 - 5 % and 90 % of that in the feed, respectively [351]. After saturation was reached, the column was eluted with an aqueous solution of 0.5 M HNO₃ for initial 15 minutes at 5 ml/min with an upward flow mode to wash off the entrained CNS particles deposited on the column bottom during adsorption flow mode to decrease the pressure in the column, followed by elution for another 2 hrs at 5 ml/min with an downward flow mode. Then column was then washed with deionized water at 5 ml/min for 3 hrs followed by regeneration with 0.01 M NaOH solution at 5 ml/min for 3 hrs. Finally, the column was washed with deionized water overnight at 2 ml/min until pH of the effluent water reached around 8.5 - 9.0. The adsorption performance of the regenerated column was evaluated under the same conditions as those of the fresh column.

7.3 Adsorption capacities

The effect of NaOH concentration for activation of CNS on their adsorption capacities is shown in Fig. 7.1. At a lower initial Ag(I) concentration (C_0) of 9 or 38 ppm, the

adsorption capacities of various CNS/OH samples were similar. At higher C_0 of 96 ppm, the adsorption capacity was in the order of $\text{CNS/OH1.0} \approx \text{CNS/OH0.5} > \text{CNS/OH0.1} \approx \text{CNS/OH0.05} > \text{CNS/OH0.01}$. It can be seen that the adsorption capacity of sample CNS at higher C_0 was much lower than those of activated carbon nanospheres even when the concentration of NaOH was as low as 0.01 M. The richer surface hydroxyl and deprotonated carboxylic groups on CNS/OH as evidenced in FTIR spectra contributed to the higher adsorption capacities.

Fig. 7.1 The effect of NaOH concentration for activation of CNS on their adsorption capacities for Ag(I) ions

The maximum adsorption capacity of CNS/OH0.5 was obtained from the adsorption isotherm with C_0 ranged from 7 ppm to 320 ppm at room temperature (Fig. 7.2). At relatively lower C_0 of 7 ppm and 40 ppm, C_e measured was almost zero, indicating its

high efficiency ($> 99.9\%$) in removal of Ag(I) ions from solutions of low concentrations. The removal percentage at C_0 of 100 ppm was still as high as 98.3 %. The maximum adsorption capacity was around 152.1 mg/g when C_0 reached 320 ppm. Although the adsorption capacity of our sample is lower than those of polymeric adsorbents, e.g., poly(aniline-co-5-sulfo-2-anisidine), with functional groups in every unit of the polymer chains [151,352-354], the NaOH activated CNS obtained in this work is much more efficient than those traditional adsorbents such as activated carbon, coke [355], brewery waste biomass [331], peat [355], et al. Linearized Langmuir and Freundlich adsorption models were used to analyze the adsorption equilibrium of Ag(I) on CNS/OH0.5. As shown in Fig. 7.2 inset, Langmuir model can well describe the adsorption of Ag(I) on CNS/OH0.5 with a correlation coefficient of 0.9990, whereas Freundlich model is not suitable as a low correlation coefficient of 0.8838 was resulted. Langmuir isotherm is based on the assumption of a monolayer adsorption on a homogeneous surface. It can be generally applied to chemisorption and with some restrictions to physical adsorption [262]. The good fitting of our equilibrium data to Langmuir isotherm may indicate the chemisorption mechanism of Ag(I) onto CNS/OH in aqueous solutions. The maximum adsorption capacity obtained from Langmuir model is 144.9 mg/g, which is very close to the maximum experimental adsorption capacity of 152.1 mg/g. In contrast, the native CNS offered a much lower maximum adsorption capacity of less than 20 mg/g under the same experimental adsorption conditions. Furthermore, the adsorption equilibrium data of native CNS can neither be fitted to Langmuir nor Freundlich model (data not shown).

Fig. 7.2 The adsorption isotherm and the corresponding Ag(I) ion removal efficiency of CNS/OH0.5; inset: fittings to linearized Langmuir and Freundlich adsorption models. (CNS/OH dosage: 25 mg /25 ml Ag(I) aqueous solution, C₀ of Ag (I): 7ppm to 320 ppm, t = 12 hrs)

7.4 Adsorption kinetics and mechanism

The adsorption of metal ions on materials surface can generally be classified to three processes: physical adsorption, ion exchange and complex/redox adsorption. Physical adsorption occurs through the weak van der Waals interaction and hence is not stable. Adsorption via ion exchange is mainly through the exchange of metal ions with the active protons in the adsorbent. The complex/redox adsorption has been often

reported when the adsorbents were polymers containing functional groups such as -NH_2 , -CN , -SH , $\text{-SO}_3\text{H}$, etc. Such groups have strong chelating ability with metal cations [352-354]. Furthermore, if the metal ions belong to the heavy metal group like Ag^+ with a high standard reduction potential, the functional groups are capable to reduce them to metals [352]. Although less well studied, -OH and -COOH groups have also been reported cable of reducing Ag(I) to metallic silver [356-357].

To investigate the mechanism of adsorption, adsorption rate was studied and kinetics models were used to describe the adsorption process. As shown in Fig. 7.3, it was remarkable that Ag(I) sorption onto the CNS/OH0.5 was very fast at a wide range of C_0 from trace 98 ppb to 202 ppm. The adsorption was completed in less than 6 minutes with 100% of removal efficiency when C_0 was lower than 2 ppm (Fig. 7.3A). With a much higher C_0 of 202 ppm, the adsorption was also completed within a short duration of 20 minutes and the corresponding removal efficiency was 74 % (Fig. 7.3B). Such fast adsorption kinetics should be attributed to the nonporous structure of the carbon nanospheres. The adsorption mainly took place on the external surface of the colloidal nanospheres with minimum mass transfer resistance. In addition, the surface of our carbon nanospheres was enriched with the functional groups for catching the Ag(I) ions efficiently from even dilute solutions. In contrast, other adsorbents with micro- or mesoporous structures like polymer, activated carbon, chitosan, etc., often take long time (typically a few hrs to days) to reach the adsorption equilibrium [331,352-355,358]. Our Ag(I) sorption kinetic data can be well fitted to the pseudo-second-order kinetics model with almost perfect correlation coefficient of 0.9999 to 1.0 (Fig. 7.3 inset), while poor fittings were generated if the pseudo-first-order model was used (results not shown). As the pseudo-second-order model is based

on the assumption that chemical sorption is the rate-determining step [331], the above results obtained consistently suggested that the Ag(I) ions were chemically adsorbed.

Fig. 7.3 The amount of Ag(I) ions adsorbed on CNS/OH0.5 at different time, (A) $C_0 = 98$ ppb, 952 ppb and 1940 ppb, and (B) $C_0 = 202$ ppm; inset: fittings to the second order kinetics model. (CNS/OH dosage: 240 mg/240 ml Ag(I) aqueous solution)

To provide further evidences for the redox adsorption mechanism, CNS/OH0.5 after adsorption of Ag(I) ions from the solution with a high C_0 of 1080 ppm (0.01M) was analyzed with XRD and TEM techniques. Experimentally, 25 mg of CNS/OH0.5 was mixed with 25 ml of 0.01M (1080 ppm) Ag(I) aqueous solution. The mixture was shaken at 200 rpm for 6 h. The solids after adsorption of Ag(I) ions were collected by centrifugation and dried in oven before characterization by XRD and TEM methods. The XRD pattern of this sample (Fig. 7.4A-a) can be indexed to face-centered cubic (FCC) metallic Ag^0 crystals (PDF no. 001-1167) as indicated by the presence of (111), (200) and (220) planes. The XRD pattern of CNS/OH0.5 before Ag(I) adsorption (Fig. 7.4A-b) only exhibits a broad and weak band at around 20° which can be assigned to

the amorphous phase of CNS [359]. The TEM image (Fig. 7.4B inset) indicated that nanoparticles of around 5 - 30 nm were deposited on the surface of carbon nanospheres. The high resolution TEM image of an individual nanoparticle (Fig. 7.4B) shows a lattice distance of 0.224 nm which is in good agreement with that of the (111) plane of FCC metallic Ag⁰. The above results provide direct evidences for the redox adsorption of Ag(I) ions to Ag⁰ nanoparticles on NaOH activated carbon nanospheres due to their rich surface functional group of -COO⁻ and -OH. The chelating ability of carboxylate groups toward toxic metal ions has been reported [360-362]. On the other hand, it has been shown that the hydroxyl group of poly (ethylene glycol) can reduce Ag(I) to Ag accompanied by oxidation of hydroxyl to aldehyde group [357]. Hence the chelation/redox mechanism in which -COO⁻ acts as a chelating group and -CH₂OH acts as a reducing agent is proposed for our process.

Fig. 7.4 (A) XRD patterns of CNS/OH0.5 (curve a) and CNS/OH0.5 after adsorption of Ag(I) ions (curve b), and (B) HRTEM image of a representative silver nanoparticle formed on CNS/OH0.5 after adsorption of Ag(I) ions; inset: TEM image of the same sample.

7.5 Recovery of silver after adsorption and regeneration of CNS/OH0.5

Aqueous solutions of HNO_3 were used to recover silver from CNS/OH0.5 after adsorption with C_0 at 1920 ppb. The eluted Ag(I) ion concentration and recovery percentage at different time duration are shown in Fig. 7.5. It can be seen that desorption (or rather dissolution) was also very fast since silver nanoparticles were only present on the external surface of carbon nanospheres. More than 96 % and 99 % of Ag(I) can be recovered in 5 minutes and 2 hrs, respectively, even when a lower HNO_3 concentration of 0.2 M was used. After desorption of Ag(I) ions in the acidic solution, the carbon nanospheres were reactivated with 0.5 M NaOH . The adsorption capacity of the regnearted CNS/OH0.5 sample was almost the same as that of the original CNS/OH0.5. Hence it was demonstrated that the functional groups for Ag(I) adsorption can be easily regenerated by treatment with NaOH again.

Fig. 7.5 The percentage recovery of Ag(I) ions from CNS/OH0.5 adsorbed with Ag(I) ions with aqueous solutions of HNO_3 at 0.2 M and 1.0 M

7.6 Removal of Ag(I) ions in a continuous mode

Owing to the fast adsorption rate, the activated carbon nanospheres could be potentially used in a continuous mode for large-scale applications. The removal of Ag(I) ions (C_0 at 1ppm) in a continuous mode with CNS/OH0.5 packed in a fix-bed column was studied. The breakthrough curves, i.e. the plot of the effluent Ag(I) concentration versus the contact time, are shown in Fig. 7.6. The column can remove almost all Ag(I) ions with the effluent Ag(I) concentrations lower than 10 ppb in the initial 35 hrs. After saturation, the column was regenerated in the same column and reused for adsorption. The regenerated column exhibited the similar adsorption performance for Ag(I) removal with the breakthrough time slightly reduced to 32 hrs. In addition, the removal of the trace amount of Ag(I) ions (C_0 at 100 ppb) with the packed column was studied. The curve in Fig. 7.6 shows that the effluent Ag(I) concentration reached breakthrough point only after 46 hrs. Thus the NaOH activated carbon nanospheres developed in this work could be potentially applied for large-scale water treatment.

Fig. 7.6 The effluent Ag(I) concentration versus the contact time in a continuous mode using a fixed-bed packed with a mixture of CNS/OH0.5 and silica beads, $C_0 = 1$ ppm (fresh and regenerated column) and 100 ppb (fresh column)

7.7 Summary

Colloidal carbon nanospheres (CNS) obtained by a “green” synthesis method can be easily activated with aqueous solutions of NaOH. The surface of the activated carbon nanospheres was enriched with functional groups of $-OH$ and $-COO^-$ which induced chelation and redox adsorption of Ag(I) ions to metallic silver nanoparticles. The maximum adsorption capacity obtained with carbon nanospheres activated with 0.5 M NaOH was 152 mg/g. With the initial Ag(I) concentration lower than 2 ppm and the adsorbent dosage of 1 g/L, all Ag(I) ions can be adsorbed within the first 6 minutes. Such fast adsorption kinetics can be attributed to the nonporous structure and rich surface functional groups of the activated carbon nanospheres. The adsorption kinetic data can be well fitted to the pseudo-second-order kinetics model. The adsorbed silver

can be easily recovered by a dilute HNO_3 solution and the carbon nanospheres after silver recovery can be reactivated by the same treatment with NaOH solution. Continuous studies employing a packed column indicated the potential applications of such adsorbents in practical applications for removal of trace amount of Ag(I) ions for drinking water production.

CHAPTER 8 ADSORPTION OF Ag(I) BY MOLECULARLY IMPRINTED CHITOSAN GEL BEADS IN AQUEOUS SOLUTION

8.1 Introduction

Chitosan and its derivatives have proven good adsorption capacity of metal ions [36-39,147,155]. There have been extensive researches on removal of metal ions on flake or powder form of chitosan [80-84]. However, the great pressure drop and column blocking caused by the low porosity of flakes in fixed bed system limited its application. Therefore, chitosan beads have been prepared and crosslinked to give them a better mechanical strength and acidic resistance as chitosan dissolves in acidic solutions ($\text{pH} < 4$) [85-86]. After crosslinking, the adsorption capacity generally decreases because some of the active groups ($-\text{NH}_2$) for metal ion chelating were bonded to the cross-linking agent [91]. To overcome the shortage of decreased adsorption capacity after chemical crosslinking of chitosan, and to enhance the sorption selectivity for Ag(I) of chitosan, molecularly imprinted chitosan hydrogel beads were prepared in this study. As far as the author knows, there are very few studies on the removal of Ag(I) by molecular imprinted chitosan based biosorbents [154,363]. The objective of the study was to study the adsorption efficiency of Ag(I) in aqueous solution by preparing Ag(I) imprinted chitosan hydrogel beads in aqueous solution. The imprinting degree was optimized, the adsorption selectivity, adsorption capacity, and adsorption/desorption rate of the biosorbent was also investigated.

8.2 Experimental adsorption of Ag(I) in batch mode

The preparation method for the Ag imprinted chitosan gel beads was shown in section 3.2.4. Un-crosslinked and nonimprinted chitosan hydrogel is named as native chitosan hydrogel beads, which is prepared with similar preparation method of Ag imprinted chitosan, without Ag imprinting and crosslinking step; crosslinked native chitosan beads without Ag imprinting is named as ECHCR or Nonim; the obtained Ag imprinted chitosan adsorbent (with ECH crosslinking) was named as Agim3 to Agim75, according to the mass ratio of AgNO_3 imprinted to chitosan. After obtaining the biosorbent, the wet gel beads were blot dried to obtain the wet mass and then freeze dried overnight to obtain the dried mass separately, and the ratio of blot dried wet mass to dried mass of both imprinted and non-imprinted hydrogel beads was determined for further calculation of adsorption capacity based on dried mass.

To find the optimal Ag(I) imprinting degree for Ag(I) adsorption and selectivity, the adsorption capacity of Ag(I) in aqueous solution with various Agim beads with imprinting ratio ranging from 0 to 100 was tested. Briefly, blot dried gel beads (from Agim3 to Agim100) according to dried mass of 15.0 mg, was dispersed in 25 ml of Ag(I) (AgNO_3) aqueous solution with concentration of 10 ppm at natural pH of 5.6. After adsorption of 12 hrs, the solution was filtered with PTFE syringe filter (0.45 μm), and was kept in 2 % HNO_3 solution for ICP measurement.

Competitive adsorption capacity of imprinted and non-imprinted beads for Ag(I) as compared with Cu (II) was studied. Blotting dried wet gel beads having a dry mass of 14.0 mg, was dispersed in 25 ml of aqueous solution containing 10 ppm from each of Ag(I) and Cu(II), at natural pH value of 5.6. After sorption duration of 12 hrs, the solution was filtrated and kept in 2% HNO_3 for further ICP determination of the Ag(I)

and Cu(II) concentration.

Ag(I) adsorption isotherm of imprinted and non-imprinted beads in aqueous solution was carried out at room temperature. Briefly, blotting dried gel beads according to dried mass of 10 mg was dispersed separately in 25 ml of Ag(I) solution with concentrations ranging from 1 ppm to 200 ppm, at natural pH of 5.6. After adsorption of 12 hrs, the solution was filtrated and prepared for ICP analysis. Competitive adsorption rate of Ag(I) and Cu(II) in Ag(I)/Cu(II) two component containing aqueous solution was studied. Briefly, blotting dried wet beads (imprinted and nonimprinted) according to dried mass of 80 mg, was dispersed in 150 ml of metal ion aqueous solution containing 10 ppm from each of Ag(II) and Cu(II). After certain time interval, 5 ml of aqueous solution was filtered and prepared for ICP analysis.

Desorption of adsorbed Ag(I) from the imprinted chitosan was studied. Briefly, after adsorption of 25 ml of 2 ppm Ag(I) for 12 hrs, the biosorbent was separated by filtration and was blotting dried, followed by dispersion in 25 ml of 0.5 M and 1 M HNO₃ separately for desorption. A series of such experiment was conducted at the same time, after certain time interval, the eluted solution was separated with filtration and kept for ICP measurement. The desorption efficiency could be calculated by the mass balance: $D = (C_d / (C_0 - C_e)) * 100$. Where D is desorption efficiency (%), C_d is the desorbed Ag(I) concentrations in desorption process, C_0 and C_e are Ag(I) initial and equilibrium concentration in adsorption process, separately.

8.3 Results and discussion

8.3.1 Adsorption capacity of Agim beads with different imprinting ratio

To find the optimal Ag(I) imprinting degree, the adsorption capacity of Ag(I) in aqueous solution with various Agim beads was tested. As shown in Fig. 8.1, the adsorption capacity was all increased for Agim3 to Agim100, as compared with Non-imprinted beads. But there is no obvious difference in Ag(I) sorption capacity between Agim3 to Agim100. Indicating in Ag(I) single ion containing aqueous solution, the Ag(I) adsorption capacity of the Agimprinted beads did not increase with the increase of Ag(I) imprinted ratio. Furthermore, adsorption selectivity of the Agim gel beads was further explored.

Fig. 8.1 Ag(I) adsorption capacity of Ag(I) imprinted chitosan gel beads and nonimprinted in single Ag(I) component aqueous solution

8.3.2 Adsorption selectivity

Adsorption capacity of imprinted and non-imprinted crosslinked chitosan (Nonim) beads for metal ions under competitive conditions from aqueous solution containing 10 ppm of Ag(I) and 10 ppm of Cu(II), was studied. As shown in Fig. 8.2 and Table 8.1, in Ag(I)/Cu(II) two components aqueous solutions, all the imprinted beads (from Agim3 to Agim100) showed higher adsorption capacity to Ag(I) than non-imprinted beads (Nonim).

Distribution and selectivity coefficients of Ag(I) with respect to Cu(II) was calculated as follows: $K_d = ((C_0 - C_e)/C_e) * (\text{Volume of the solution(ml)}/\text{mass of adsorbents (g)})$. Where K_d , C_0 and C_e represents the distribution coefficient, initial and final solution concentrations, respectively. The selectivity coefficient for the competitive binding of metal ion can be obtained by following equation: $k = K_d(\text{template metal})/K_d(\text{interferent metal})$. A comparison of the k values of the imprinted polymer with those of metal ions allows an estimation of the effect of imprinting on selectivity. It can be seen in Table 8.1 that the K_d and k for Ag(I) of Agim75 and Agim100 were higher than that of non-imprinted beads. The selectivity coefficient of Agim75 and Agim100 are 7 and 8 times greater than non-imprinted beads, respectively. Therefore, Agim75 was selected as the optimal imprinting ratio for enhanced Ag(I) competitive adsorption selectivity and capacity. The lower Ag(I) competitive adsorption capacity of Agim3 to Agim50 with lower Ag(I) imprinting mass (the Ag(I) adsorption selectivity coefficients were calculated as 0.51 to 1.10) should be attributed to that silver oxide was formed during phase inversion process in sodium hydroxide and was removed upon nitric acid washing to form more pores in beads which benefit both the

metal ions (Ag(I) and Cu(II)) adsorption. For higher the imprinting ratio to 75 and 100, more Ag(I) was left in solidified chitosan to form Ag(I) selective binding sites and molecular geometry. Therefore, Ag(I) competitive adsorption capacity of Agim75 and Agim100 was much higher than others.

Fig. 8.2 Competitive adsorption capacity of Ag(I) and Cu(II) on the Ag(I) imprinted beads and non-imprinted beads

Table 8.1 Competitive adsorption of Ag(I) and Cu(II) on the Ag(I) imprinted beads and non-imprinted beads

Adsorbent	Metal ions	q_e (mg/g)	K_d (ml/g)	k
Nonim	Ag(I)	8.66	2038	0.54
	Cu(II)	10.61	3753	
Agim 75	Ag(I)	11.39	3955	

	Cu(II)	6.24	1056	3.75
Agim 100	Ag(I)	11.43	3943	
	Cu(II)	5.80	935	4.21

8.3.3 Effect of pH value

Fig. 8.3 shows the effect of pH value on Ag(I) uptake capacity that as pH value increased from 2 to 5.6 and 6.9, the Ag(I) removal amount abruptly increased from 6.2 % to 90.6 % and for Agim75 and from 4.0 % to 64.2 % for Nonim. Adsorption capacity almost reached plateau with pH value increased from 5.6 to 7.0. Therefore, adsorption property was studied at natural pH value of 5.6.

Fig. 8.3 Effect of pH value on adsorption capacity of Agim75 for Ag (I) in aqueous solution

8.3.4 Effect of initial Ag(I) concentration and adsorption isotherm

Adsorption experiments conducted showed that the Ag (I) adsorption capacity of native, Agim75 and Nonim chitosan hydrogel beads increased with the initial Ag(I) concentrations increased, as shown in Fig. 8.4. The adsorption capacity of Agim75 increased to 118 mg/g with equilibrium Ag(I) concentrations increased to 101 mg/L. There was no increase in Ag(I) uptake capacity beyond this point. The Ag(I) uptake capacity of imprinted beads (Agim75, ECH crosslinked) was always higher than that of non-imprinted beads (Nonim, ECH crosslinked), and a little lower than that of native chitosan beads (without crosslinking and imprinting treatment). The 118 mg/g saturation uptake capacity of Agim75 (C_e of 101 mg/L) is higher than 95 mg/g uptake capacity of Nonim beads (C_e of 111 mg/L), and slightly lower than 125 mg/g (C_e of 98 mg/L) uptake capacity of native chitosan beads. This observation indicated that the effect of crosslinking on decreasing adsorption capacity was decreased upon Ag imprinting. The enhanced Ag(I) uptake capacity of Agim75 as compared with crosslinked chitosan should be attributed to chelation of Ag(I) with $-NH_2$ functional groups in chitosan, and also the selective binding sites and molecular geometry obtained from imprinting.

Fig. 8.4 Adsorption isotherm of Ag(I) with native, ECH crosslinked and Agim75 (ECH crosslinked) chitosan beads in aqueous solution (at natural pH value)

8.3.5 Effect of adsorption time on biosorption

Effect of time on biosorption of Agim75 and Nonim for Ag (I) and Cu (II) in competitive conditions was shown in Fig. 8.5A and B, respectively. The slope of the lines joining data reflects the adsorption rate. It was shown in Fig. 8.5A that Ag(I) uptake slope of Agim75 was much sharper than that Cu(II) uptake slope under competitive condition, means imprinted biosorbent presented faster adsorption rate towards template metal ion Ag (I), and slower uptake rate towards Cu (II). The uptake capacity of Agim75 for Ag(I) increased abruptly in initial 1 hr, around 80 % of Ag(I) in aqueous solution can be uptake, and the uptake plateau can be almost reached in initial 3 hrs. While uptake capacity for Cu (II) slowly reached plateau after 5 hrs. Another phenomenon is that the final Ag(I) uptake capacity was higher than Cu(II)

uptake capacity on Agim75. The faster adsorption rate and higher adsorption capacity of imprinted beads towards the template metal ion (Ag(I)) under competitive adsorption conditions, should be due to the enhanced sorption affinity towards Ag(I) after imprinting. It was observed in Fig 8.5B that for non-imprinted beads, there is no obvious difference in the adsorption rate for Ag(I) and Cu(II) under competitive

Fig. 8.5 Competitive adsorption rate of Agim75 (a) and Nonim beads (b) for metal ions of Ag(I) and Cu(II)

8.3.6 Desorption of adsorbed Ag(I) from the Agim75 chiotsan gel beads

Two concentrations of HNO₃ solution, 0.5 M and 1.0 M, were used as eluent for recovery of adsorbed Ag(I) from the adsorbent. The experimental result shows that more 99 % adsorbed Ag(I) can be recovered by 0.5 M and 1.0 M HNO₃ in the initial 5 minutes.

Fig. 8.6 Desorption efficiency of Ag(I) from imprinted chitosan

8.4 Summary

The imprinted chitosan hydrogel beads offered higher adsorption capacity for Ag(I) and better adsorption selectivity in aqueous solution, as compared with non-imprinted chitosan beads. The imprinted biosorbent also offered high uptake rate for template ion Ag(I) and slower adsorption rate for other ion (Cu(II)) in aqueous solution, due to the enhanced adsorption affinity towards template ion after imprinting. The adsorption capacity also increased as pH value increased from 2 to 7.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

Efficient and environmentally, benign adsorbent materials for wastewater treatment were successfully developed. They include high quality mesoporous AC derived from waste tyre, templated activated carbons, activated carbon nanospheres and molecularly imprinted chitosan hydrogel beads. The important findings are summarized as follows.

A highly mesoporous carbon was prepared via steam activation of waste tyres. Acid wash was found to play an important role in the structural development of the carbon. The derived TAC presented a good potential for sorption towards the bulky dye molecules of MG in aqueous solutions. It was demonstrated that pore size selectivity of the mesoporous TAC towards the big molecule dye plays an important role for enhancing the high sorption capacity.

Templated carbons were synthesized using sodium form zeolite Y as the template and benzene as the carbon precursor. In spite of the high surface area ($1151 \text{ m}^2/\text{g}$) and regular pore size distribution, the Ag(I) adsorption capacity of ZTC is much lower than that of nonporous activated carbon nanosphere, indicating surface chemical properties of adsorbent plays more important role in the metal ion Ag(I) adsorption.

Low cost and efficient adsorbent well dispersed colloidal carbon nanospheres with enriched functional groups was synthesized with simple and “green” method and activated under mild base condition. The advantages are obvious, high adsorption

capacity toward basic dyes and the metal ion Ag(I), because of the rich functional groups on the carbon nanosphere surface, fast adsorption rate because of the non-porous structure, easy of regeneration. It was found that, the functional groups of –OH and –COO[–] on the surface of the CNS were enriched after activation and facilitates basic dye by chemical interactions between the deprotonated functional groups on CNS/OH and the cationic dye. The surface of the activated carbon nanospheres induced chelation and redox adsorption of Ag(I) ions to metallic silver nanoparticles due to the enriched with functional groups of –OH and –COO[–]. The dye spent CNS/OH can be easily regenerated with sulphate radical based oxidation method and the regenerated CNS/OH can be recycled seven runs for MB adsorption without adsorption capacity changing. The adsorbed silver can be easily recovered by a dilute HNO₃ solution and the carbon nanospheres after silver recovery can be reactivated by the same treatment with NaOH solution. The adsorbents were also subject to continuous studies of Ag(I) removal employing a packed column indicating the potential applications of such adsorbents in practical applications for pollutants removal for water treatment.

The molecularly imprinted chitosan hydrogel beads were synthesized. The biosorbent offered higher adsorption capacity for Ag(I) and better adsorption selectivity in aqueous solution, as compared with non-imprinted chitosan beads. The imprinted biosorbent also offered higher uptake rate for template ion Ag(I) and slower adsorption rate for other ion (Cu(II)) under Ag(I)/Cu(II) competitive adsorption conditions, due to the enhanced adsorption affinity towards template ion after imprinting.

In this project, the as prepared carbonaceous and chitosan based adsorbents present promising application potential in wastewater treatment. Many efforts are still needed in future to develop and application of adsorbents. The following future studied are recommended for development and improvement of the adsorbent,

For the TAC adsorbent, the following study are recommended,

- (1) Modifying the surface of the TAC with either HNO_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, or H_2O_2 to attach functional group on the TAC surface to understand the role of surface functional groups in sorption process of AC in aqueous solutions.

For templated activated carbon, the following suggestions may be considered,

- (1) Synthesizing of silica templated mesoporous activated carbons for adsorption of bulky molecule of dyes.

For the CNS adsorbent, the following studies are recommended in future,

- (1) Synthesizing of magnetic carbon nanosphere by encapsulation or coating magnetic nano- and nanoparticles in/onto the carbon nanosphere for magnetic field-based separations of carbon nanosphere from aqueous solution.
- (2) Grafting the carbon nanosphere on supporting materials such as micro glass beads for practical application in continuous adsorption mode in fixed bed column to decrease the pressure drop and prevent clogging of the column.
- (3) Adsorption properties of the activated carbon nanosphere to other metal ion such as Cu(II) , Cd(II) , and Hg(II) , and acid dyes etc in aqueous solution. And the adsorption property of the carbon nanosphere in practical wastewater.
- (4) Supporting efficient catalysts such as cobalt oxide on the carbon nanosphere for degradation of organic dyes in aqueous solution.

For the molecularly imprinted chitosan adsorbent, the following studies are recommended,

- (1) Multi-component adsorption properties of metal ions on the bio-sorbent.
- (2) Further improve the molecularly imprinted method, by such as decreasing or avoiding formation of sodium hydroxide formation in the phase inversion procedure, to further enhance the imprinting efficiency.

REFERENCE

- [1] B.H. Hameed, M.I. El-Khaiary, Equilibrium, kinetics and mechanism of malachite green adsorption on activated carbon prepared from bamboo by K₂CO₃ activation and subsequent gasification with CO₂, *J. Hazard. Mater.* 157 (2008) 344-351.
- [2] Q. Sun, L. Yang, The adsorption of basic dyes from aqueous solution on modified peat-resin particle, *Water Res.* 37 (2003) 1535-1544.
- [3] E.C. Eysenbach, Task force on pretreatment of Industrial Wastes; Pretreatment of Industrial Wastes, W.E. Federation (Ed.), Alexandria, VA, 1994.
- [4] N.L.D. Nemerow, Industrial and Hazardous Waste Treatment, Van Nostrand Reinhold, New York, 1991.
- [5] F. Banat, S. Al-Asheh, L. Al-Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, *Process Biochem.* 39 (2003) 193-202.
- [6] M.K. Purkait, A. Maiti, S. DasGupta, S. De, Removal of congo red using activated carbon and its regeneration, *J. Hazard. Mater.* 145 (2007) 287-295.
- [7] F. Rodrigues-Reinoso, Introduction to Carbon Technologies, Publicaciones de la Universidad de Alicante, Spain (Chapter 2), 1997.
- [8] M. Streat, J.W. Patrick, M.J.C. Perez, Sorption of phenol and para-chlorophenol from water using conventional and novel activated carbons, *Water Res.* 29 (1995) 467-472.
- [9] L. Walid K, Production of activated carbon from acorns and olive seeds, *Biomass Bioenergy* 20 (2001) 57-62.
- [10] O. Ioannidou, A. Zabaniotou, Agricultural residues as precursors for activated carbon production—A review, *Renewable Sustainable Energy Rev.* 11 (2007) 1966-2005.
- [11] G.-P. Hao, W.-C. Li, S. Wang, S. Zhang, A.-H. Lu, Tubular structured ordered mesoporous carbon as an efficient sorbent for the removal of dyes from aqueous solutions, *Carbon* 48 (2010) 3330-3339.
- [12] C.O. Ania, V. Khomenko, E. Raymundo-Pinero, J.B. Parra, F. Beguin, The large electrochemical capacitance of microporous doped carbon obtained by using a zeolite template, *Adv. Funct. Mater.* 17 (2007) 1828-1836.
- [13] H. Nishihara, P.-X. Hou, L.-X. Li, M. Ito, M. Uchiyama, T. Kaburagi, A. Ikura, J. Katamura, T. Kawarada, K. Mizuuchi, T. Kyotani, High-pressure hydrogen storage in zeolite-templated carbon, *J. Phys. Chem. C* 113 (2009) 3189-3196.
- [14] X. Yuan, S.-P. Zhuo, W. Xing, H.-Y. Cui, X.-D. Dai, X.-M. Liu, Z.-F. Yan, Aqueous dye adsorption on ordered mesoporous carbons, *J. Colloid Interface Sci.* 310 (2007) 83-89.
- [15] S. Kubo, Z.-Z. Gu, K. Takahashi, A. Fujishima, H. Segawa, O. Sato, Tunable Photonic Band Gap Crystals Based on a Liquid Crystal-Infiltrated Inverse Opal Structure, *J. Am. Chem. Soc.* 126 (2004) 8314-8319.
- [16] X. Sun, Y. Li, Colloidal Carbon Spheres and Their Core/Shell Structures with Noble-Metal Nanoparticles, *Angew. Chem. Int. Ed.* 43 (2004) 597-601.
- [17] H. Zhu, M.J. McShane, Loading of hydrophobic materials into polymer particles: Implications for fluorescent nanosensors and drug delivery, *J. Am. Chem. Soc.* 127 (2005) 13448-13449.
- [18] Y. Shin, L.-Q. Wang, I.-T. Bae, B.W. Arey, G.J. Exarhos, Hydrothermal

- syntheses of colloidal carbon spheres from cyclodextrins, *J. Phys. Chem. C* 112 (2008) 14236-14240.
- [19] X. Sun, Y. Li, Hollow carbonaceous capsules from glucose solution, *J. Colloid Interface Sci.* 291 (2005) 7-12.
- [20] D.H. Cho, E.Y. Kim, *Bioprocess. Biosyst. Eng.* 25 (2003) 271-277.
- [21] P.A. Marques, H.M. Pinheiro, J. Teixeira, M.F. Rosa, Removal efficiency of Cu^{2+} , Cd^{2+} and Pb^{2+} by waste brewery biomass: pH and cation association effects, *Desalination* 124 (1999) 137-144.
- [22] A. Ozer, D. Ozer, H.I. Ekiz, The equilibrium and kinetic modelling of the biosorption of copper(II) ions on *Cladophora crispata*, *Adsorption* 10 (2005) 317-326.
- [23] P.K. Dutta, M.N.V. Ravikumar, J. Dutta, Chitin and chitosan for versatile applications, *J. Macromol. Sci., Polym. Rev.* 42 (2002) 307-354.
- [24] S. Hirano, Chitin and chitosan as novel biotechnological materials, *Polym. Int.* 48 (1999) 732-734.
- [25] R. Jayakumar, N. Nwe, S. Tokura, H. Tamura, Sulfated chitin and chitosan as novel biomaterials, *Int. J. Biol. Macromol.* 40 (2007) 175-181.
- [26] B. Krajewska, Application of chitin- and chitosan-based materials for enzyme immobilizations: A review, *Enzyme Microb. Technol.* 35 (2004) 126-139.
- [27] B. Krajewska, Membrane-based processes performed with use of chitin/chitosan materials, in, *Selected Papers presented at PERMEA 2003, Membrane Science and Technology Conference of Visegrad Countries*, Elsevier, 2005, pp. 305-312.
- [28] M.N.V.R. Kumar, R.A.A. Muzzarelli, C. Muzzarelli, H. Sashiwa, A.J. Domb, Chitosan chemistry and pharmaceutical perspectives, *Chem. Rev.* 104 (2004) 6017-6084.
- [29] P. Kumar, K.C. Gupta, Novel conditions for rapid and clean deprotection of oligodeoxyribonucleotides from universal polymer supports, *React. Funct. Polym.* 41 (1999) 197-204.
- [30] M. Prabakaran, J.F. Mano, Chitosan-Based Particles as Controlled Drug Delivery Systems, *Drug Delivery* 12 (2005) 41-57.
- [31] F. Shahidi, J.K.V. Arachchi, Y.-J. Jeon, Food applications of chitin and chitosans, *Trends Food Sci. Technol.* 10 (1999) 37-51.
- [32] P.C. Srinivasa, R.N. Tharanathan, Chitin/Chitosan — Safe, Ecofriendly Packaging Materials with Multiple Potential Uses, *Food Reviews International* 23 (2007) 53-72.
- [33] J. Kim, J.E. Lee, J. Lee, J.H. Yu, B.C. Kim, K. An, Y. Hwang, C.-H. Shin, J.-G. Park, J. Kim, T. Hyeon, Magnetic fluorescent delivery vehicle using uniform mesoporous silica spheres embedded with monodisperse magnetic and semiconductor nanocrystals, *J. Am. Chem. Soc.* 128 (2006) 688-689.
- [34] X. Sun, Y. Li, Ga_2O_3 and GaN semiconductor hollow spheres, *Angew. Chem. Int. Ed.* 43 (2004) 3827-3831.
- [35] M. Zheng, J. Cao, X. Chang, J. Wang, J. Liu, X. Ma, Preparation of oxide hollow spheres by colloidal carbon spheres, *Mater. Lett.* 60 (2006) 2991-2993.
- [36] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, *J. Hazard. Mater.* 97 (2003) 219-243.
- [37] E. Guibal, Interactions of metal ions with chitosan-based sorbents: A review, *Sep. Purif. Technol.* 38 (2004) 43-74.
- [38] E. Guibal, M. Van Vooren, B.A. Dempsey, J. Roussy, A review of the use of chitosan for the removal of particulate and dissolved contaminants, *Sep. Sci.*

- Technol. 41 (2006) 2487-2514.
- [39] A.J. Varma, S.V. Deshpande, J.F. Kennedy, Metal complexation by chitosan and its derivatives: A review, *Carbohydr. Polym.* 55 (2004) 77-93.
 - [40] E. Guibal, I. Saucedo, J. Roussy, P. Le Cloirec, Uptake of uranyl ions by new sorbing polymers: discussion of adsorption isotherms and pH effect, *React. Polym.* 23 (1994) 147-156.
 - [41] M. Jansson-Charrier, E. Guibal, J. Roussy, B. Delanghe, P. Le Cloirec, Vanadium (IV) sorption by chitosan: kinetics and equilibrium, *Water Res.* 30 (1996) 465-465.
 - [42] I.N. Jha, L. Iyengar, A.V.S. Prabhakara Rao, Removal of cadmium using chitosan, *J. Environ. Eng.* 114 (1988) 962-974.
 - [43] Y.B.a.K. Katsutoshi Inoue, Adsorption of Metal Ions on Chitosan and Crosslinked Copper(II)-Complexed Chitosan, *Bull. Chem. Soc. Jpn.* 66 (1993) 2915-2921.
 - [44] I. Saucedo, E. Guibal, C. Roulph, P. Le Cloirec, Sorption of uranyl ions by a modified chitosan: Kinetic and equilibrium studies, *Environ. Technol.* 13 (1992) 1101-1115.
 - [45] I. Saucedo, E. Guibal, J. Roussy, C. Roulph, P. Le Cloirec, Uranium sorption by glutamate glucan. A modified chitosan. Part I. Equilibrium studies, *Water SA* 19 (1993) 113-118.
 - [46] M.L. Arrascue, H.M. Garcia, O. Horna, E. Guibal, Gold sorption on chitosan derivatives, in, *Biohydrometallurgy: Fundamentals, Technology and Sustainable*, September 16, 2001 - September 19, 2001, Elsevier, Ouro Preto, Brazil, 2003, pp. 191-200.
 - [47] E. Guibal, M. Ruiz, T. Vincent, A. Sastre, R. Navarro-Mendoza, Platinum and palladium sorption on chitosan derivatives, 36 (2001) 1017-1040.
 - [48] C.L. Lasko, M.P. Hurst, An investigation into the use of Chitosan for the removal of soluble silver from industrial wastewater, *Environ. Sci. Technol.* 33 (1999) 3622-3626.
 - [49] C. Peniche-Covas, L.W. Alvarez, W. Arguelles-Monal, Adsorption of mercuric ions by chitosan, *J. Appl. Polym. Sci.* 46 (1992) 1147-1150.
 - [50] E. Piron, A. Domard, Formation of a ternary complex between chitosan and ion pairs of strontium carbonate, *Int. J. Biol. Macromol.* 23 (1998) 113-120.
 - [51] S. Qian, G. Huang, J. Jiang, F. He, Y. Wang, Studies of adsorption behavior of crosslinked chitosan for Cr(VI), Se(VI), *J. Appl. Polym. Sci.* 77 (2000) 3216-3219.
 - [52] M.T. Vasconcelos, M.F.C. Leal, H.M.V.M. Soares, Influence of the ratio copper(II) to ligand concentrations and the nature of entering and leaving ligands on the lability of copper(II) complexes, *Anal. Chim. Acta* 330 (1996) 273-273.
 - [53] A. Ozer, D. Ozer, Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: Determination of biosorption heats, *J. Hazard. Mater.* 100 (2003) 219-229.
 - [54] M.C.B. Andrade, A.E. Santana, J.D.M. Vianna, Poincare-Lie algebra and relativistic phase space, *J. Phys. A: Math. Gen.* 33 (2000) 4015-4024.
 - [55] E. Guibal, L. Dambies, C. Milot, J. Roussy, Influence of polymer structural parameters and experimental conditions on metal anion sorption by chitosan, *Polym. Int.* 48 (1999) 671-680.
 - [56] K. Kurita, H. Akao, J. Yang, M. Shimojoh, Erratum: Nonnatural branched polysaccharides: Synthesis and properties of chitin and chitosan having

- disaccharide maltose branches (Biomacromolecules (1264-1268)), Biomacromolecules 4 (2003) 1868-1868.
- [57] I.M.N. Vold, K.M. Vårum, E. Guibal, O. Smidsrød, Binding of ions to chitosan—selectivity studies, Carbohydr. Polym. 54 (2003) 471-477.
- [58] H. Ishii, M. Minegishi, B. Lavitpichayawong, T. Mitani, Synthesis of chitosan-amino acid conjugates and their use in heavy metal uptake, Int. J. Biol. Macromol. 17 (1995) 21-23.
- [59] O.A.C. Monteiro Jr, C. Airoidi, Some Thermodynamic Data on Copper–Chitin and Copper–Chitosan Biopolymer Interactions, J. Colloid Interface Sci. 212 (1999) 212-219.
- [60] M.G. Peter, Applications and environmental aspects of chitin and chitosan, J. Macromol. Sci., Pure Appl. Chem. A32 (1995) 629-629.
- [61] E. Piron, M. Accominotti, A. Domard, Interaction between Chitosan and Uranyl Ions. Role of Physical and Physicochemical Parameters on the Kinetics of Sorption, Langmuir 13 (1997) 1653-1658.
- [62] K. Kurita, T. Sannan, Y. Iwakura, Studies on chitin. VI. Binding of metal cations, J. Appl. Polym. Sci. 23 (1979) 511-515.
- [63] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresour. Technol. 97 (2006) 1061-1085.
- [64] A. Domard, pH and c.d. measurements on a fully deacetylated chitosan: Application to Cull-polymer interactions, J. Macromol. Sci., Pure Appl. Chem. 9 (1987).
- [65] L. Raymond, F.G. Morin, R.H. Marchessault, Degree of deacetylation of chitosan using conductometric titration and solid-state NMR, Carbohydr. Res. 246 (1993) 331-336.
- [66] H. Sashiwa, H. Saimoto, Y. Shigemasa, R. Ogawa, S. Tokura, Distribution of the acetamide group in partially deacetylated chitins, Carbohydr. Polym. 16 (1991) 291-296.
- [67] H. Sashiwa, H. Saimoto, Y. Shigemasa, S. Tokura, N-acetyl group distribution in partially deacetylated chitins prepared under homogeneous conditions, Carbohydr. Res. 242 (1993) 167-172.
- [68] K.M. Vårum, M.W. Anthonsen, H. Grasdalen, O. Smidsrød, ¹³C-N.m.r. studies of the acetylation sequences in partially N-deacetylated chitins (chitosans), Carbohydr. Res. 217 (1991) 19-27.
- [69] P. Chassary, T. Vincent, E. Guibal, Metal anion sorption on chitosan and derivative materials: A strategy for polymer modification and optimum use, React. Funct. Polym. 60 (2004) 137-149.
- [70] E. Piron, A. Domard, Interaction between chitosan and uranyl ions: Part 1. Role of physicochemical parameters, Int. J. Biol. Macromol. 21 (1997) 327-335.
- [71] E. Guibal, C. Milot, J.M. Tobin, Metal-anion sorption by chitosan beads: Equilibrium and kinetic studies, Ind. Eng. Chem. Res. 37 (1998) 1454-1463.
- [72] M.T. Qurashi, H.S. Blair, S.J. Allen, Studies on modified chitosan membranes. II. Dialysis of low molecular weight metabolites, J. Appl. Polym. Sci. 46 (1992) 263-269.
- [73] G.W. Urbanczyk, B. Lipp-Symonowicz, Influence of processing terms of chitosan membranes made of differently deacetylated chitin on the crystalline structure of membranes, J. Appl. Polym. Sci. 51 (1994) 2191-2194.
- [74] B. Krajewska, Diffusion of metal ions through gel chitosan membranes, React. Funct. Polym. 47 (2001) 37-47.

- [75] N. Kubota, Permeability properties of chitosan-transition metal complex membranes, *J. Appl. Polym. Sci.* 64 (1997) 819-822.
- [76] M.T. Qurashi, H.S. Blair, S.J. Allen, Studies on modified chitosan membranes. I. Preparation and characterization, *J. Appl. Polym. Sci.* 46 (1992) 255-261.
- [77] V. Veimam, The precipitation Laws, *Chemical Reviews* 2, 1925.
- [78] T. Vincent, E. Guibal, Cr(VI) extraction using Aliquat 336 in a hollow fiber module made of chitosan, *Ind. Eng. Chem. Res.* 40 (2001) 1406-1411.
- [79] H. Yoshida, A. Okamoto, T. Kataoka, Adsorption of acid dye on cross-linked chitosan fibers: equilibria, *Chem. Eng. Sci.* 48 (1993) 2267-2272.
- [80] J.R. Evans, W.G. Davids, J.D. MacRae, A. Amirbahman, Kinetics of cadmium uptake by chitosan-based crab shells, *Water Res.* 36 (2002) 3219-3226.
- [81] E. Guibal, M. Jansson-Charrier, I. Saucedo, P. Le Cloirec, Enhancement of metal ion sorption performances of chitosan. Effect of the structure on the diffusion properties, *Langmuir* 11 (1995) 591-598.
- [82] M. Jansson-Charrier, E. Guibal, J. Roussy, R. Surjous, P. Le Cloirec, Dynamic removal of uranium by chitosan: Influence of operating parameters, in, *Proceedings of the 1996 18th Biennial Conference of the International Association on Water Quality. Part 6, June 23, 1996 - June 28, 1996*, Elsevier Science Inc., Singapore, Singapore, 1996, pp. 169-177.
- [83] C. Milot, J. McBrien, S. Allen, E. Guibal, Influence of physicochemical and structural characteristics of chitosan flakes on molybdate sorption, *J. Appl. Polym. Sci.* 68 (1998) 571-580.
- [84] L.-Q. Wu, A.P. Gadre, H. Yi, M.J. Kastantin, G.W. Rubloff, W.E. Bentley, G.F. Payne, R. Ghodssi, Voltage-dependent assembly of the polysaccharide chitosan onto an electrode surface, *Langmuir* 18 (2002) 8620-8625.
- [85] S. Kawamura, Effectiveness of natural polyelectrolytes in water treatment, *J. Am. Water Works Assn* 83 (1991) 88-91.
- [86] G.L. Rorrer, T.Y. Hsien, J.D. Way, Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from wastewater, *Ind. Eng. Chem. Res.* 32 (1993) 2170-2178.
- [87] G.A.F. Roberts, *Chitin Chemistry*, MacMillan, London, UK, 1992.
- [88] Z. Cao, H. Ge, S. Lai, Studies on synthesis and adsorption properties of chitosan cross-linked by glutaraldehyde and Cu(II) as template under microwave irradiation, *Eur. Polym. J.* 37 (2001) 2141-2143.
- [89] K. Inoue, H. Hirakawa, Y. Ishikawa, T. Yamaguchi, J. Nagata, K. Ohto, K. Yoshizuka, Adsorption of metal ions on gallium(III)-templated oxine type of chemically modified chitosan, *Sep. Sci. Technol.* 31 (1996) 2273-2285.
- [90] M. Shafiqul Alam, I. Katsutoshi, Y. Kazuharu, I. Hideaki, Adsorptive separation of rhodium (III) using Fe(III)-templated oxine type of chemically modified chitosan, *Sep. Sci. Technol.* 33 (1998) 655-666.
- [91] P.O. Osifo, A. Webster, H. van der Merwe, H.W.J.P. Neomagus, M.A. van der Gun, D.M. Grant, The influence of the degree of cross-linking on the adsorption properties of chitosan beads, *Bioresour. Technol.* 99 (2008) 7377-7382.
- [92] Y. Koyama, A. Taniguchi, STUDIES ON CHITIN X. HOMOGENEOUS CROSS-LINKING OF CHITOSAN FOR ENHANCED CUPRIC ION ADSORPTION, *J. Appl. Polym. Sci.* 31 (1986) 1951-1954.
- [93] T.-Y. Hsien, G.L. Rorrer, Heterogeneous cross-linking of chitosan gel beads: Kinetics, modeling, and influence on cadmium ion adsorption capacity, *Ind. Eng. Chem. Res.* 36 (1997) 3631-3638.

- [94] P. Baroni, R.S. Vieira, E. Meneghetti, M.G.C. da Silva, M.M. Beppu, Evaluation of batch adsorption of chromium ions on natural and crosslinked chitosan membranes, *J. Hazard. Mater.* 152 (2008) 1155-1163.
- [95] A.-H. Chen, S.-C. Liu, C.-Y. Chen, C.-Y. Chen, Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin, *J. Hazard. Mater.* 154 (2008) 184-191.
- [96] N. Li, R. Bai, A novel amine-shielded surface cross-linking of chitosan hydrogel beads for enhanced metal adsorption performance, *Ind. Eng. Chem. Res.* 44 (2005) 6692-6700.
- [97] V.E. Tikhonov, L.A. Radigina, Y.A. Yamskov, Metal-chelating chitin derivatives via reaction of chitosan with nitrilotriacetic acid, *Carbohydr. Res.* 290 (1996) 33-41.
- [98] C.B. Li, S. Hein, K. Wang, Biosorption of chitin and chitosan, *Mater. Sci. Technol.* 24 (2008) 1088-1099.
- [99] L. Dobetti, F. Delben, Binding of metal cations by N-carboxymethyl chitosans in water, *Carbohydr. Polym.* 18 (1992) 273-282.
- [100] R.A.A. Muzzarelli, F. Tanfani, The N-permethylation of chitosan and the preparation of N-trimethyl chitosan iodide, *Carbohydr. Polym.* 5 (1985) 297-307.
- [101] R.A.A. Muzzarelli, F. Tanfani, M. Emanuelli, S. Mariotti, N-(carboxymethylidene)chitosans and N-(carboxymethyl)chitosans: Novel chelating polyampholytes obtained from chitosan glyoxylate, *Carbohydr. Res.* 107 (1982) 199-214.
- [102] a.A. K.S. Choi, H.S., A study of synthesis of crosslinked chitosan phosphate and adsorption characteristics of metallic ions, *Pollimo* 14 (1990).
- [103] I. T. Asakawa, K., and Tanaka, T., Adsorption of silver on dithiocarbamate type of chemically modified chitosan, *Kag Kog Ronbunsbu* 26 (2000) 321.
- [104] C. Peng, Y. Wang, Y. Tang, Synthesis of crosslinked chitosan-crown ethers and evaluation of these products as adsorbents for metal ions, *J. Appl. Polym. Sci.* 70 (1998) 501-506.
- [105] S. Tan, Y. Wang, C. Peng, Y. Tang, Synthesis and adsorption properties for metal ions of crosslinked chitosan acetate crown ethers, *J. Appl. Polym. Sci.* 71 (1999) 2069-2074.
- [106] Z. Yang, Y. Wang, Y. Tang, Preparation and adsorption properties of metal ions of crosslinked chitosan azacrown ethers, *J. Appl. Polym. Sci.* 74 (1999) 3053-3058.
- [107] M. Ruiz, A.M. Sastre, E. Guibal, Palladium sorption on glutaraldehyde-crosslinked chitosan, *React. Funct. Polym.* 45 (2000) 155-173.
- [108] K. Sreenivasan, Synthesis and preliminary studies on a -cyclodextrin-coupled chitosan as a novel adsorbent matrix, *J. Appl. Polym. Sci.* 69 (1998) 1051-1055.
- [109] T. Tojima, H. Katsura, M. Nishiki, N. Nishi, S. Tokura, N. Sakairi, Chitosan beads with pendant -cyclodextrin: Preparation and inclusion property to nitrophenolates, *Carbohydr. Polym.* 40 (1999) 17-22.
- [110] R.-S. Juang, C.-Y. Ju, Kinetics of sorption of Cu(II)-ethylenediaminetetraacetic acid chelated anions on cross-linked, polyaminated chitosan beads, *Ind. Eng. Chem. Res.* 37 (1998) 3463-3469.
- [111] Y. Kawamura, M. Mitsuhashi, H. Tanibe, H. Yoshida, Adsorption of metal ions on polyaminated highly porous chitosan chelating resin, *Ind. Eng. Chem. Res.* 32 (1993) 386-391.

- [112] J. Ruey-Shin, J. Ching-Yun, Equilibrium sorption of copper(II)-ethylenediaminetetraacetic acid chelates onto cross-linked, polyaminated chitosan beads, *Ind. Eng. Chem. Res.* 36 (1997) 5403-5409.
- [113] K. Dill, R.D. Carter, A.R. Katritzky, Structural elucidation of the reductive methylation by-product of glycophorin AM, *Int. J. Biol. Macromol.* 8 (1986) 318-320.
- [114] N. Nishi, Y. Maekita, S.-i. Nishimura, O. Hasegawa, S. Tokura, Highly phosphorylated derivatives of chitin, partially deacetylated chitin and chitosan as new functional polymers: metal binding property of the insolubilized materials, *Int. J. Biol. Macromol.* 9 (1987) 109-114.
- [115] V.M. Ramos, N.M. Rodriguez, M.S. Rodriguez, A. Heras, E. Agullo, Modified chitosan carrying phosphonic and alkyl groups, *Carbohydr. Polym.* 51 (2003) 425-429.
- [116] M. Ruiz, A. Sastre, E. Guibal, Pd and Pt recovery using chitosan gel beads. II. Influence of chemical modifications on sorption properties, *Sep. Sci. Technol.* 37 (2002) 2385-2403.
- [117] M. Ruiz, A. Sastre, E. Guibal, Osmium and iridium sorption on Chitosan derivatives, *Solvent Extr. Ion Exch.* 21 (2003) 307-329.
- [118] C. Ni, Y. Xu, Studies on syntheses and properties of chelating resins based on chitosan, *J. Appl. Polym. Sci.* 59 (1996) 499-504.
- [119] S. Sun, A. Wang, Adsorption kinetics of Cu(II) ions using N,O-carboxymethyl-chitosan, *J. Hazard. Mater.* 131 (2006) 103-111.
- [120] W.S.W. Ngah, S. Fatinathan, Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan-GLA beads and chitosan-alginate beads, *Chem. Eng. J.* 143 (2008) 62-72.
- [121] W.S. Wan Ngah, C.S. Endud, R. Mayanar, Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads, *React. Funct. Polym.* 50 (2002) 181-190.
- [122] S.-T. Lee, F.-L. Mi, Y.-J. Shen, S.-S. Shyu, Equilibrium and kinetic studies of copper(II) ion uptake by chitosan-tripolyphosphate chelating resin, *Polymer* 42 (2001) 1879-1892.
- [123] L. Zhou, Y. Wang, Z. Liu, Q. Huang, Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres, *J. Hazard. Mater.* 161 (2009) 995-1002.
- [124] N. Li, R. Bai, Copper adsorption on chitosan-cellulose hydrogel beads: Behaviors and mechanisms, *Sep. Purif. Technol.* 42 (2005) 237-247.
- [125] F. Zhao, B. Yu, Z. Yue, T. Wang, X. Wen, Z. Liu, C. Zhao, Preparation of porous chitosan gel beads for copper(II) ion adsorption, *J. Hazard. Mater.* 147 (2007) 67-73.
- [126] V.M. Boddu, K. Abburi, A.J. Randolph, E.D. Smith, Removal of copper (II) and nickel (II) ions from aqueous solutions by a composite chitosan biosorbent, *Sep. Sci. Technol.* 43 (2008) 1365-1381.
- [127] S. Verbych, M. Bryk, G. Chornokur, B. Fuhr, Removal of copper(II) from aqueous solutions by chitosan adsorption, *Sep. Sci. Technol.* 40 (2005) 1749-1759.
- [128] H.S.B. G.M. A. Findon, *J. Environ. Sci. Health., Part A* 28 (1993) 173.
- [129] R.W. Coughlin, M.R. Deshaies, E.M. Davis, Chitosan in crab shell wastes purifies electroplating wastewater, *Environ. Prog.* 9 (1990) 35-39.
- [130] M. Rhazi, J. Desbrieres, A. Tolaimate, M. Rinaudo, P. Vottero, A. Alagui, M. El Meray, Influence of the nature of the metal ions on the complexation with

- chitosan. Application to the treatment of liquid waste, *Eur. Polym. J.* 38 (2002) 1523-1530.
- [131] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, *J. Colloid Interface Sci.* 255 (2002) 64-74.
- [132] R.-S. Juang, H.-J. Shao, A simplified equilibrium model for sorption of heavy metal ions from aqueous solutions on chitosan, *Water Res.* 36 (2002) 2999-3008.
- [133] M.M. Beppu, E.J. Arruda, R.S. Vieira, N.N. Santos, Adsorption of Cu(II) on porous chitosan membranes functionalized with histidine, *J. Membr. Sci.* 240 (2004) 227-235.
- [134] C. Liu, R. Bai, Adsorptive removal of copper ions with highly porous chitosan/cellulose acetate blend hollow fiber membranes, *J. Membr. Sci.* 284 (2006) 313-322.
- [135] G.C. Steenkamp, K. Keizer, H.W.J.P. Neomagus, H.M. Krieg, Copper(II) removal from polluted water with alumina/chitosan composite membranes, *J. Membr. Sci.* 197 (2002) 147-156.
- [136] N. Sankararamakrishnan, A.K. Sharma, R. Sanghi, Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater, *J. Hazard. Mater.* 148 (2007) 353-359.
- [137] M.S. Dzul Erosa, T.I. Saucedo Medina, R. Navarro Mendoza, M. Avila Rodriguez, E. Guibal, Cadmium sorption on chitosan sorbents: Kinetic and equilibrium studies, *Hydrometallurgy* 61 (2001) 157-167.
- [138] W.L. Yan, R. Bai, Adsorption of lead and humic acid on chitosan hydrogel beads, *Water Res.* 39 (2005) 688-698.
- [139] Y. Tao, L. Ye, J. Pan, Y. Wang, B. Tang, Removal of Pb(II) from aqueous solution on chitosan/TiO₂ hybrid film, *J. Hazard. Mater.* 161 (2009) 718-722.
- [140] A.T. Paulino, M.R. Guilherme, A.V. Reis, E.B. Tambourgi, J. Nozaki, E.C. Muniz, Capacity of adsorption of Pb²⁺ and Ni²⁺ from aqueous solutions by chitosan produced from silkworm chrysalides in different degrees of deacetylation, *J. Hazard. Mater.* 147 (2007) 139-147.
- [141] D. Chauhan, N. Sankararamakrishnan, Highly enhanced adsorption for decontamination of lead ions from battery wastewaters using chitosan functionalized with xanthate, *Bioresour. Technol.* 99 (2008) 9021-9024.
- [142] C.A. Eiden, C.A. Jewell, J.P. Wightman, INTERACTION OF LEAD AND CHROMIUM WITH CHITIN AND CHITOSAN, *J. Appl. Polym. Sci.* 25 (1980) 1587-1599.
- [143] N. Li, R. Bai, Highly enhanced adsorption of lead ions on chitosan granules functionalized with poly(acrylic acid), *Ind. Eng. Chem. Res.* 45 (2006) 7897-7904.
- [144] S. Sun, L. Wang, A. Wang, Adsorption properties of crosslinked carboxymethyl-chitosan resin with Pb(II) as template ions, *J. Hazard. Mater.* 136 (2006) 930-937.
- [145] H. Su, Z. Wang, T. Tan, Preparation of a surface molecular-imprinted adsorbent for Ni²⁺ based on *Penicillium chrysogenum*, *J. Chem. Technol. Biotechnol.* 80 (2005) 439-444.
- [146] S. Nagib, K. Inoue, T. Yamaguchi, T. Tamaru, Recovery of Ni from a large excess of Al generated from spent hydrodesulfurization catalyst using picolylamine type chelating resin and complexane types of chemically modified chitosan, *Hydrometallurgy* 51 (1999) 73-85.
- [147] C. Jeon, H.P. Kwang, Adsorption and desorption characteristics of mercury(II)

- ions using aminated chitosan bead, *Water Res.* 39 (2005) 3938-3944.
- [148] R.S. Vieira, M.M. Beppu, Dynamic and static adsorption and desorption of Hg(II) ions on chitosan membranes and spheres, *Water Res.* 40 (2006) 1726-1734.
- [149] A. Shafaei, F.Z. Ashtiani, T. Kaghazchi, Equilibrium studies of the sorption of Hg(II) ions onto chitosan, *Chem. Eng. J.* 133 (2007) 311-316.
- [150] A.M. Donia, A.A. Atia, K.Z. Elwakeel, Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde, *J. Hazard. Mater.* 151 (2008) 372-379.
- [151] A.A. Atia, Studies on the interaction of mercury(II) and uranyl(II) with modified chitosan resins, *Hydrometallurgy* 80 (2005) 13-22.
- [152] J.D. Merrifield, W.G. Davids, J.D. MacRae, A. Amirbahman, Uptake of mercury by thiol-grafted chitosan gel beads, *Water Res.* 38 (2004) 3132-3138.
- [153] R. Maruca, B.J. Suder, J.P. Wightman, Interaction of heavy metals with chitin and chitosan. III. Chromium, *J. Appl. Polym. Sci.* 27 (1982) 4827-4837.
- [154] H. Huo, H. Su, T. Tan, Adsorption of Ag⁺ by a surface molecular-imprinted biosorbent, *Chem. Eng. J.* 150 (2009) 139-144.
- [155] A.M. Donia, A.A. Atia, K.Z. Elwakeel, Recovery of gold(III) and silver(I) on a chemically modified chitosan with magnetic properties, *Hydrometallurgy* 87 (2007) 197-206.
- [156] Y. Yi, Y. Wang, H. Liu, Preparation of new crosslinked chitosan with crown ether and their adsorption for silver ion for antibacterial activities, *Carbohydr. Polym.* 53 (2003) 425-430.
- [157] R.K. Katarina, T. Takayanagi, M. Oshima, S. Motomizu, Synthesis of a chitosan-based chelating resin and its application to the selective concentration and ultratrace determination of silver in environmental water samples, *Anal. Chim. Acta* 558 (2006) 246-253.
- [158] M. Hosoba, K. Oshita, R.K. Katarina, T. Takayanagi, M. Oshima, S. Motomizu, Synthesis of novel chitosan resin possessing histidine moiety and its application to the determination of trace silver by ICP-AES coupled with triplet automated-pretreatment system, *Anal. Chim. Acta* 639 (2009) 51-56.
- [159] J. Guzman, I. Saucedo, R. Navarro, J. Revilla, E. Guibal, Vanadium interactions with chitosan: Influence of polymer protonation and metal speciation, *Langmuir* 18 (2002) 1567-1573.
- [160] E. Guibal, A. Larkin, T. Vincent, J.M. Tobin, Chitosan sorbents for platinum sorption from dilute solutions, *Ind. Eng. Chem. Res.* 38 (1999) 4011-4022.
- [161] Y. Sağ, Y. Aktay, Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin, *Process Biochem.* 36 (2000) 157-173.
- [162] P. Udaybhaskar, L. Iyengar, A.V.S.P. Rao, Hexavalent chromium interaction with chitosan, *J. Appl. Polym. Sci.* 39 (1990) 739-747.
- [163] L. Dambies, E. Guibal, A. Roze, Arsenic(V) sorption on molybdate-impregnated chitosan beads, *Colloids Surf., A* 170 (2000) 19-31.
- [164] L. Dambies, T. Vincent, E. Guibal, Treatment of arsenic-containing solutions using chitosan derivatives: Uptake mechanism and sorption performances, *Water Res.* 36 (2002) 3699-3710.
- [165] V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, R. Haasch, Removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent, *Water Res.* 42 (2008) 633-642.
- [166] C.-Y. Chen, T.-H. Chang, J.-T. Kuo, Y.-F. Chen, Y.-C. Chung, Characteristics of molybdate-impregnated chitosan beads (MICB) in terms of arsenic removal

- from water and the application of a MICB-packed column to remove arsenic from wastewater, *Bioresour. Technol.* 99 (2008) 7487-7494.
- [167] J. F. Derbyshire, M., Andrews, R., Rao, A., Martin-Gullon, I., Grulke, E., Carbon materials in Environmental Applications, Marcel Dekker, New York, 2001.
- [168] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, *Carbon* 42 (2004) 83-94.
- [169] J.-B.D.a.F.S.M.D. R. C. Bansal, Active carbon, Marcel Dekker, New York, 1988.
- [170] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from Terminalia arjuna nuts activated with zinc chloride, *Chem. Eng. Sci.* 60 (2005) 3049-3059.
- [171] S. Ichcho, E. Khouya, S. Fakhi, M. Ezzine, H. Hannache, R. Pallier, R. Naslain, Influence of the experimental conditions on porosity and structure of adsorbents elaborated from Moroccan oil shale of Timahdit by chemical activation, *J. Hazard. Mater.* 118 (2005) 45-51.
- [172] F. Suarez-Garcia, A. Martinez-Alonso, J.M.D. Tascon, Activated carbon fibers from Nomex by chemical activation with phosphoric acid, *Carbon* 42 (2004) 1419-1426.
- [173] Y. Sudaryanto, S.B. Hartono, W. Irawaty, H. Hindarso, S. Ismadji, High surface area activated carbon prepared from cassava peel by chemical activation, *Bioresour. Technol.* 97 (2006) 734-739.
- [174] S. Erdogan, Y. Onal, C. Akmil-Basar, S. Bilmez-Erdemoglu, C. Sarici-Ozdemir, E. Koseoglu, G. IcDuygu, Optimization of nickel adsorption from aqueous solution by using activated carbon prepared from waste apricot by chemical activation, *Appl. Surf. Sci.* 252 (2005) 1324-1331.
- [175] J. Hayashi, N. Yamamoto, T. Horikawa, K. Muroyama, V.G. Gomes, Preparation and characterization of high-specific-surface-area activated carbons from K₂CO₃-treated waste polyurethane, *J. Colloid Interface Sci.* 281 (2005) 437-443.
- [176] I.A. Rahman, B. Saad, S. Shaidan, E.S. Sya Rizal, Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical-thermal process, *Bioresour. Technol.* 96 (2005) 1578-1583.
- [177] C.-F. Chang, C.-Y. Chang, W.-T. Tsai, Effects of Burn-off and Activation Temperature on Preparation of Activated Carbon from Corn Cob Agrowaste by CO₂ and Steam, *J. Colloid Interface Sci.* 232 (2000) 45-49.
- [178] B.S. Girgis, A.-N.A. El-Hendawy, Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid, *Microporous Mesoporous Mater.* 52 (2002) 105-117.
- [179] M.M. Mohamed, Acid dye removal: Comparison of surfactant-modified mesoporous FSM-16 with activated carbon derived from rice husk, *J. Colloid Interface Sci.* 272 (2004) 28-34.
- [180] Y.C. Sharma, Uma, Optimization of parameters for adsorption of methylene blue on a low-cost activated carbon, *J. Chem. Eng. Data* 55 (2010) 435-439.
- [181] M.A. Ahmad, N.K. Rahman, Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon, *Chem. Eng. J.* 170 (2011) 154-161.
- [182] M.C. Baquero, L. Giraldo, J.C. Moreno, F. Suarez-Garcia, A. Martinez-Alonso, J.M.D. Tascon, Activated carbons by pyrolysis of coffee bean husks in presence of phosphoric acid, *J. Anal. Appl. Pyrolysis* 70 (2003) 779-784.

- [183] T. Yang, A.C. Lua, Characteristics of activated carbons prepared from pistachio-nut shells by physical activation, *J. Colloid Interface Sci.* 267 (2003) 408-417.
- [184] A. Bacaoui, A. Dahbi, A. Yaacoubi, C. Bennouna, F.J. Maldonado-Hodar, J. Rivera-Utrilla, F. Carrasco-Marin, C. Moreno-Castilla, Experimental design to optimize preparation of activated carbons for use in water treatment, *Environ. Sci. Technol.* 36 (2002) 3844-3849.
- [185] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, *Bioresour. Technol.* 76 (2000) 63-65.
- [186] R.R. Bansode, J.N. Losso, W.E. Marshall, R.M. Rao, R.J. Portier, Adsorption of volatile organic compounds by pecan shell- and almond shell-based granular activated carbons, *Bioresour. Technol.* 90 (2003) 175-184.
- [187] M. Valix, W.H. Cheung, G. McKay, Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption, *Chemosphere* 56 (2004) 493-501.
- [188] G.G. Stavropoulos, A.A. Zabaniotou, Production and characterization of activated carbons from olive-seed waste residue, *Microporous Mesoporous Mater.* 82 (2005) 79-85.
- [189] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, *Bioresour. Technol.* 87 (2003) 129-132.
- [190] M.D.C.M. Alvim-Ferraz, C.M.T.B. Gaspar, Catalytic activity of active carbons impregnated before activation of pinewood sawdust and nutshells to be used on the control of atmospheric emissions, *J. Hazard. Mater.* 119 (2005) 135-143.
- [191] S. Ismadji, Y. Sudaryanto, S.B. Hartono, L.E.K. Setiawan, A. Ayucitra, Activated carbon from char obtained from vacuum pyrolysis of teak sawdust: Pore structure development and characterization, *Bioresour. Technol.* 96 (2005) 1364-1369.
- [192] M. Lopez de Letona Sanchez, A. Macias-Garcia, M.A. Diaz-Diez, E.M. Cuerda-Correa, J. Ganan-Gomez, A. Nadal-Gisbert, Preparation of activated carbons previously treated with hydrogen peroxide: Study of their porous texture, *Appl. Surf. Sci.* 252 (2006) 5984-5987.
- [193] N.V. Sych, N.T. Kartel, N.N. Tsyba, V.V. Strelko, Effect of combined activation on the preparation of high porous active carbons from granulated post-consumer polyethyleneterephthalate, *Appl. Surf. Sci.* 252 (2006) 8062-8066.
- [194] X. Chen, S. Jeyaseelan, N. Graham, Physical and chemical properties study of the activated carbon made from sewage sludge, *Waste Manage.* 22 (2002) 755-760.
- [195] Z. Liu, L. Ling, W. Qiao, L. Liu, Preparation of pitch-based spherical activated carbon with developed mesopore by the aid of ferrocene, *Carbon* 37 (1999) 663-667.
- [196] E.L.K. Mui, D.C.K. Ko, G. McKay, Production of active carbons from waste tyres - A review, *Carbon* 42 (2004) 2789-2805.
- [197] E. Demirbas, M. Kobya, M.T. Sulak, Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon, *Bioresour. Technol.* 99 (2008) 5368-5373.
- [198] M. Auta, B.H. Hameed, Preparation of waste tea activated carbon using

- potassium acetate as an activating agent for adsorption of Acid Blue 25 dye, *Chem. Eng. J.* 171 (2011) 502-509.
- [199] R. Malik, D.S. Ramteke, S.R. Wate, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, *Waste Manage.* 27 (2007) 1129-1138.
- [200] V.K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, A. Nayak, A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye-Acid Blue 113, *J. Hazard. Mater.* 186 (2011) 891-901.
- [201] K. Vijayaraghavan, S.W. Won, Y.-S. Yun, Treatment of complex Remazol dye effluent using sawdust- and coal-based activated carbons, *J. Hazard. Mater.* 167 (2009) 790-796.
- [202] B.H. Hameed, A.L. Ahmad, K.N.A. Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, *Dyes Pigm.* 75 (2007) 143-149.
- [203] T.C. Chandra, M.M. Mirna, Y. Sudaryanto, S. Ismadji, Adsorption of basic dye onto activated carbon prepared from durian shell: Studies of adsorption equilibrium and kinetics, *Chem. Eng. J.* 127 (2007) 121-129.
- [204] K. Okada, N. Yamamoto, Y. Kameshima, A. Yasumori, Adsorption properties of activated carbon from waste newspaper prepared by chemical and physical activation, *J. Colloid Interface Sci.* 262 (2003) 194-199.
- [205] F. Rozada, L.F. Calvo, A.I. Garcia, J. Martin-Villacorta, M. Otero, Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems, *Bioresour. Technol.* 87 (2003) 221-230.
- [206] Y.-R. Lin, H. Teng, Mesoporous carbons from waste tire char and their application in wastewater discoloration, *Microporous Mesoporous Mater.* 54 (2002) 167-174.
- [207] L. Li, S. Liu, T. Zhu, Application of activated carbon derived from scrap tires for adsorption of Rhodamine B, *J. Environ. Sci.* 22 (2010) 1273-1280.
- [208] K. Anoop Krishnan, T.S. Anirudhan, Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: Kinetics and equilibrium studies, *J. Hazard. Mater.* 92 (2002) 161-183.
- [209] H. Hasar, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk, *J. Hazard. Mater.* 97 (2003) 49-57.
- [210] G. Issabayeva, M.K. Aroua, N.M.N. Sulaiman, Removal of lead from aqueous solutions on palm shell activated carbon, *Bioresour. Technol.* 97 (2006) 2350-2355.
- [211] S. Ricordel, S. Taha, I. Cisse, G. Dorange, Heavy metals removal by adsorption onto peanut husks carbon: Characterization, kinetic study and modeling, *Sep. Purif. Technol.* 24 (2001) 389-401.
- [212] K.A. Krishnan, T.S. Anirudhan, Uptake of heavy metals in batch systems by sulfurized steam activated carbon prepared from sugarcane bagasse pith, *Ind. Eng. Chem. Res.* 41 (2002) 5085-5093.
- [213] O.S. Amuda, A.A. Giwa, I.A. Bello, Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon, *Biochem. Eng. J.* 36 (2007) 174-181.
- [214] K.K. Wong, C.K. Lee, K.S. Low, M.J. Haron, Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions, *Chemosphere* 50 (2003) 23-28.

- [215] V.K. Gupta, A. Mittal, L. Krishnan, V. Gajbe, Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash, *Sep. Purif. Technol.* 40 (2004) 87-96.
- [216] B.H. Hameed, M.I. El-Khaiary, Kinetics and equilibrium studies of malachite green adsorption on rice straw-derived char, *J. Hazard. Mater.* 153 (2008) 701-708.
- [217] A. Mittal, L. Krishnan, V.K. Gupta, Removal and recovery of malachite green from wastewater using an agricultural waste material, de-oiled soya, *Sep. Purif. Technol.* 43 (2005) 125-133.
- [218] T. Santhi, S. Manonmani, T. Smitha, Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of *Ricinus communis* by adsorption, (2010).
- [219] Z.Z. Fabing Su, Wanping Guo, Jiajia Liu, Xiaoning Tian, X.S. Zhao, Template approaches to preparing porous carbon, New York: Marcel Dekker (CRC press), 2008, Vol. 30, Chapter 2, pp.63-128.
- [220] C. Guan, Energy storage in carbon nanoparticles, in, School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore, 2009.
- [221] Z. Yang, Y. Xia, R. Mokaya, Enhanced hydrogen storage capacity of high surface area zeolite-like carbon materials, *J. Am. Chem. Soc.* 129 (2007) 1673-1679.
- [222] Y.J. Kim, Y. Horie, S. Ozaki, Y. Matsuzawa, H. Suezaki, C. Kim, N. Miyashita, M. Endo, Correlation between the pore and solvated ion size on capacitance uptake of PVDC-based carbons, *Carbon* 42 (2004) 1491-1500.
- [223] B. Sakintuna, Y. Yurum, Templated porous carbons: A review article, *Ind. Eng. Chem. Res.* 44 (2005) 2893-2902.
- [224] T. Kyotani, Synthesis of various types of nano carbons using the template technique, *Bull. Chem. Soc. Jpn.* 79 (2006) 1322-1337.
- [225] J. Lee, J. Kim, T. Hyeon, Recent progress in the synthesis of porous carbon materials, *Adv. Mater.* 18 (2006) 2073-2094.
- [226] F. Su, L. Lv, X.S. Zhao, Synthesis of nanostructured porous carbon, *Int. J. Nanosci.* 4 (2005) 261-268.
- [227] T. Kyotani, T. Nagai, S. Inoue, A. Tomita, Formation of New Type of Porous Carbon by Carbonization in Zeolite Nanochannels, *Chem. Mater.* 9 (1997) 609-615.
- [228] C.J. Meyers, S.D. Shah, S.C. Patel, R.M. Sneeringer, C.A. Bessel, N.R. Dollahon, R.A. Leising, E.S. Takeuchi, Templated synthesis of carbon materials from zeolites (Y, beta, and ZSM-5) and a montmorillonite clay (K10): Physical and electrochemical characterization, *J. Phys. Chem. B* 105 (2001) 2143-2152.
- [229] J. Rodriguez-Mirasol, T. Cordero, L.R. Radovic, J.J. Rodriguez, Structural and Textural Properties of Pyrolytic Carbon Formed within a Microporous Zeolite Template, *Chem. Mater.* 10 (1998) 550-550.
- [230] J.H. Knox, B. Kaur, G.R. Millward, Structure and performance of porous graphitic carbon in liquid chromatography, *J. Chromatogr. A* 352 (1986) 3-25.
- [231] R. Ryoo, S.H. Joo, S. Jun, Synthesis of Highly Ordered Carbon Molecular Sieves via Template-Mediated Structural Transformation, *J. Phys. Chem. B* 103 (1999) 7743-7746.
- [232] S.B. Yoon, J.Y. Kim, J.-S. Yu, Synthesis of highly ordered nanoporous carbon molecular sieves from silylated MCM-48 using divinylbenzene as precursor,

- Chem. Commun. (2001) 559-560.
- [233] J. Lee, S. Yoon, S.M. Oh, C.-H. Shin, T. Hyeon, Development of a new mesoporous carbon using an HMS aluminosilicate template, *Adv. Mater.* 12 (2000) 359-362.
- [234] A.B. Fuertes, D.M. Nevskaya, Template synthesis of mesoporous carbons from mesostructured silica by vapor deposition polymerisation, *J. Mater. Chem.* 13 (2003) 1843-1846.
- [235] S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Evidence for general nature of pore interconnectivity in 2-dimensional hexagonal mesoporous silicas prepared using block copolymer templates, *J. Phys. Chem. B* 106 (2002) 4640-4646.
- [236] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, Synthesis of new, nanoporous carbon with hexagonally ordered mesostructure, *J. Am. Chem. Soc.* 122 (2000) 10712-10712.
- [237] D.J. Kim, H.I. Lee, J.E. Yie, S.-J. Kim, J.M. Kim, Ordered mesoporous carbons: Implication of surface chemistry, pore structure and adsorption of methyl mercaptan, *Carbon* 43 (2005) 1868-1873.
- [238] Z. Li, J. Zhang, Y. Li, Y. Guan, Z. Feng, C. Li, Preparation and characterization of ordered mesoporous carbons on SBA-15 template, *J. Mater. Chem.* 16 (2006) 1350-1354.
- [239] Y. Xia, R. Mokaya, Ordered mesoporous carbon hollow spheres nanocast using mesoporous silica via chemical vapor deposition, *Adv. Mater.* 16 (2004) 886-891.
- [240] M. Kruk, B. Dufour, E.B. Celer, T. Kowalewski, M. Jaroniec, K. Matyjaszewski, Synthesis of mesoporous carbons using ordered and disordered mesoporous silica templates and polyacrylonitrile as carbon precursor, *J. Phys. Chem. B* 109 (2005) 9216-9225.
- [241] A.-H. Lu, W. Schmidt, B. Spliethoff, F. Schuth, Synthesis of Ordered Mesoporous Carbon with Bimodal Pore System and High Pore Volume, *Adv. Mater.* 15 (2003) 1602-1606.
- [242] J. Sang Hoon, C. Seong Jae, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, Ordered nanoporous arrays of carbon supporting high dispersions of platinum nanoparticles, *Nature* 412 (2001) 169-172.
- [243] W. Guo, F. Su, X.S. Zhao, Ordered mesostructured carbon templated by SBA-16 silica, *Carbon* 43 (2005) 2423-2426.
- [244] T.-W. Kim, R. Ryoo, K.P. Gierszal, M. Jaroniec, L.A. Solovyov, Y. Sakamoto, O. Terasaki, Characterization of mesoporous carbons synthesized with SBA-16 silica template, *J. Mater. Chem.* 15 (2005) 1560-1571.
- [245] D.D. Asouhidou, K.S. Triantafyllidis, N.K. Lazaridis, K.A. Matis, S.-S. Kim, T.J. Pinnavaia, Sorption of reactive dyes from aqueous solutions by ordered hexagonal and disordered mesoporous carbons, *Microporous Mesoporous Mater.* 117 (2009) 257-267.
- [246] Y. Tian, P. Liu, X. Wang, H. Lin, Adsorption of malachite green from aqueous solutions onto ordered mesoporous carbons, *Chem. Eng. J.* 171 (2011) 1263-1269.
- [247] C. Yan, C. Wang, J. Yao, L. Zhang, X. Liu, Adsorption of methylene blue on mesoporous carbons prepared using acid- and alkaline-treated zeolite X as the template, *Colloids Surf., A* 333 (2009) 115-119.
- [248] F. Caruso, R.A. Caruso, H. Mohwald, Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating, *Science* 282 (1998) 1111-1114.
- [249] H. Hu, R.G. Larson, One-step preparation of highly monodisperse micron-size

- particles in organic solvents, *J. Am. Chem. Soc.* 126 (2004) 13894-13895.
- [250] C. Yao, Y. Shin, L.-Q. Wang, C.F. Windisch Jr, W.D. Samuels, B.W. Arey, C. Wang, W.M. Risen Jr, G.J. Exarhos, Hydrothermal dehydration of aqueous fructose solutions in a closed system, *J. Phys. Chem. C* 111 (2007) 15141-15145.
- [251] J. Ryu, Y.-W. Suh, D.J. Suh, D.J. Ahn, Hydrothermal preparation of carbon microspheres from mono-saccharides and phenolic compounds, *Carbon* 48 (2010) 1990-1998.
- [252] S. Tang, Y. Tang, S. Vongehr, X. Zhao, X. Meng, Nanoporous carbon spheres and their application in dispersing silver nanoparticles, *Appl. Surf. Sci.* 255 (2009) 6011-6016.
- [253] R. Demir-Cakan, N. Baccile, M. Antonietti, M.-M. Titirici, Carboxylate-rich carbonaceous materials via one-step hydrothermal carbonization of glucose in the presence of acrylic acid, *Chem. Mater.* 21 (2009) 484-490.
- [254] Y. Ni, L. Jin, L. Zhang, J. Hong, Honeycomb-like Ni@C composite nanostructures: Synthesis, properties and applications in the detection of glucose and the removal of heavy-metal ions, *J. Mater. Chem.* 20 (2010) 6430-6436.
- [255] R. Demir-Cakan, P. Makowski, M. Antonietti, F. Goettmann, M.-M. Titirici, Hydrothermal synthesis of imidazole functionalized carbon spheres and their application in catalysis, *Catal. Today* 150 (2010) 115-118.
- [256] J. Wu, F. Hu, X. Hu, Z. Wei, P.K. Shen, Improved kinetics of methanol oxidation on Pt/hollow carbon sphere catalysts, *Electrochim. Acta* 53 (2008) 8341-8345.
- [257] X. Chen, K. Zhang, J. Zhou, J. Xuan, W. Yan, L.-P. Jiang, J.-J. Zhu, Electrochemical immunosensor based on colloidal carbon sphere array, *Biosens. Bioelectron.* 25 (2010) 1130-1136.
- [258] R. Cui, C. Liu, J. Shen, D. Gao, J.-J. Zhu, H.-Y. Chen, Gold nanoparticle-colloidal carbon nanosphere hybrid material: Preparation, characterization, and application for an amplified electrochemical immunoassay, *Adv. Funct. Mater.* 18 (2008) 2197-2204.
- [259] R. Cui, J.-J. Zhu, Fabrication of a novel electrochemical immunosensor based on the gold nanoparticles/colloidal carbon nanosphere hybrid material, *Electrochim. Acta* 55 (2010) 7814-7817.
- [260] X. Sun, Y. Li, Ag@C core/shell structured nanoparticles: Controlled synthesis, characterization, and assembly, *Langmuir* 21 (2005) 6019-6024.
- [261] H. Freundlich, *Colloid and Capillary Chemistry*, London, 1926.
- [262] I. Langmuir, THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. PART I. SOLIDS, *J. Am. Chem. Soc.* 38 (1916) 2221-2295.
- [263] L. Jossens, J.M. Prausnitz, W. Fritz, E.U. Schlünder, A.L. Myers, Thermodynamics of multi-solute adsorption from dilute aqueous solutions, *Chem. Eng. Sci.* 33 (1978) 1097-1106.
- [264] O. Redlich, D.L. Peterson, A Useful Adsorption Isotherm, *J. Phys. Chem.* 63 (1959) 1024-1024.
- [265] S. Lagergren, About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens, Handlingar.* 24 (1898) 1.
- [266] Y. Sağ, Y. Aktay, Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and *Rhizopus arrhizus*, *Biochem. Eng. J.* 12 (2002) 143-153.
- [267] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modeling of liquid-phase adsorption

- of reactive dyes and metal ions on chitosan, *Water Res.* 35 (2001) 613-618.
- [268] F.-C. Wu, R.-L. Tseng, R.-S. Juang, Comparative adsorption of metal and dye on flake- and bead-types of chitosans prepared from fishery wastes, *J. Hazard. Mater.* 73 (2000) 63-75.
- [269] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451-465.
- [270] Y.S. Ho, G. McKay, A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents, *Process Saf. Environ. Prot.* 76 (1998) 332-340.
- [271] W. Tanthapanichakoon, P. Ariyadejwanich, P. Japthong, K. Nakagawa, S.R. Mukai, H. Tamon, Adsorption-desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires, *Water Res.* 39 (2005) 1347-1353.
- [272] I. De Marco Rodriguez, M.F. Laresgoiti, M.A. Cabrero, A. Torres, M.J. Chomon, B. Caballero, Pyrolysis of scrap tyres, *Fuel Process. Technol.* 72 (2001) 9-22.
- [273] C. Guan, K. Wang, C. Yang, X.S. Zhao, Characterization of a zeolite-templated carbon for H₂ storage application, *Microporous Mesoporous Mater.* 118 (2009) 503-507.
- [274] J. Sun, T.A. Brady, M.J. Rood, C.M. Lehmann, M. Rostam-Abadi, A.A. Lizzio, Adsorbed Natural Gas Storage with Activated Carbons Made from Illinois Coals and Scrap Tires, *Energy Fuels* 11 (1997) 316-322.
- [275] A.A. Zabaniotou, G. Stavropoulos, Pyrolysis of used automobile tires and residual char utilization, *J. Anal. Appl. Pyrolysis* 70 (2003) 711-722.
- [276] P. Ariyadejwanich, W. Tanthapanichakoon, K. Nakagawa, S.R. Mukai, H. Tamon, Preparation and characterization of mesoporous activated carbon from waste tires, *Carbon* 41 (2003) 157-164.
- [277] P.T. Williams, S. Besler, D.T. Taylor, The pyrolysis of scrap automotive tyres: The influence of temperature and heating rate on product composition, *Fuel* 69 (1990) 1474-1482.
- [278] S.J. Allen, G. McKay, K.Y.H. Khader, Equilibrium adsorption isotherms for basic dyes onto lignite, *J. Chem. Technol. Biotechnol.* 45 (1989) 291-302.
- [279] C. Guan, F. Su, X.S. Zhao, K. Wang, Methane storage in a template-synthesized carbon, *Sep. Purif. Technol.* 64 (2008) 124-126.
- [280] L. Chen, R.K. Singh, P. Webley, Synthesis, characterization and hydrogen storage properties of microporous carbons templated by cation exchanged forms of zeolite Y with propylene and butylene as carbon precursors, *Microporous Mesoporous Mater.* 102 (2007) 159-170.
- [281] T. Kyotani, Z. Ma, A. Tomita, Template synthesis of novel porous carbons using various types of zeolites, in, Elsevier Ltd, 2003, pp. 1451-1459.
- [282] Z. Ma, T. Kyotani, A. Tomita, Preparation of a high surface area microporous carbon having the structural regularity of Y zeolite, *Chem. Commun.* (2000) 2365-2366.
- [283] F. Su, X.S. Zhao, L. Lv, Z. Zhou, Synthesis and characterization of microporous carbons templated by ammonium-form zeolite Y, *Carbon* 42 (2004) 2821-2831.
- [284] Z. Yang, Y. Xia, R. Mokaya, Hollow shells of high surface area graphitic N-doped carbon composites nanocast using zeolite templates, *Microporous Mesoporous Mater.* 86 (2005) 69-80.
- [285] K.P. Gierszal, M. Jaroniec, Large pore volume carbons with uniform

- mesopores and macropores: Synthesis, characterization, and relations between adsorption parameters of silica templates and their inverse carbon replicas, *J. Phys. Chem. C* 111 (2007) 9742-9748.
- [286] F. Su, J. Zeng, X. Bao, Y. Yu, J.Y. Lee, X.S. Zhao, Preparation and characterization of highly ordered graphitic mesoporous carbon as a Pt catalyst support for direct methanol fuel cells, *Chem. Mater.* 17 (2005) 3960-3967.
- [287] Z. Zhou, Q. Yan, F. Su, X.S. Zhao, Replicating novel carbon nanostructures with 3D macroporous silica template, *J. Mater. Chem.* 15 (2005) 2569-2574.
- [288] C. Guan, X. Zhang, K. Wang, C. Yang, Investigation of H₂ storage in a templated carbon derived from zeolite Y and PFA, *Sep. Purif. Technol.* 66 (2009) 565-569.
- [289] P.-X. Hou, H. Orikasa, T. Yamazaki, K. Matsuoka, A. Tomita, N. Setoyama, Y. Fukushima, T. Kyotani, Synthesis of nitrogen-containing microporous carbon with a highly ordered structure and effect of nitrogen doping on H₂O adsorption, *Chem. Mater.* 17 (2005) 5187-5193.
- [290] P.-X. Hou, T. Yamazaki, H. Orikasa, T. Kyotani, An easy method for the synthesis of ordered microporous carbons by the template technique, *Carbon* 43 (2005) 2624-2627.
- [291] P. Srinivasu, A. Vinu, S. Hishita, T. Sasaki, K. Ariga, T. Mori, Preparation and characterization of novel microporous carbon nitride with very high surface area via nanocasting technique, *Microporous Mesoporous Mater.* 108 (2008) 340-344.
- [292] C. Wang, C. Yan, J. Yao, L. Zhang, N. Xu, X. Liu, Preparation of mesoporous carbons using acid- and alkali-treated zeolite X as the template, *J. Porous Mater.* 16 (2009) 699-705.
- [293] H. Wang, Q. Gao, J. Hu, Z. Chen, High performance of nanoporous carbon in cryogenic hydrogen storage and electrochemical capacitance, *Carbon* 47 (2009) 2259-2268.
- [294] Z. Yang, Y. Xia, X. Sun, R. Mokaya, Preparation and hydrogen storage properties of zeolite-templated carbon materials nanocast via chemical vapor deposition: Effect of the zeolite template and nitrogen doping, *J. Phys. Chem. B* 110 (2006) 18424-18431.
- [295] J. Parmentier, V. Valtchev, F. Gaslain, L. Tosheva, C. Ducrot-Boisgontier, J. Moller, J. Patarin, C. Vix-Guterl, Effect of the zeolite crystal size on the structure and properties of carbon replicas made by a nanocasting process, *Carbon* 47 (2009) 1066-1073.
- [296] C. Ducrot-Boisgontier, J. Parmentier, J. Patarin, Influence of the carbon precursors on the structural properties of EMT-type nanocasted-carbon replicas, *Microporous Mesoporous Mater.* 126 (2009) 101-106.
- [297] A. Garsuch, O. Klepel, R.R. Sattler, C. Berger, R. Glaser, J. Weitkamp, Synthesis of a carbon replica of zeolite y with large crystallite size, *Carbon* 44 (2006) 593-596.
- [298] L. Song, J.-I. Miyamoto, T. Ohba, H. Kanoh, K. Kaneko, Novel nanostructures of porous carbon synthesized with zeolite LTA-template and methanol, *J. Phys. Chem. C* 111 (2007) 2459-2464.
- [299] Z. Ma, T. Kyotani, A. Tomita, Synthesis methods for preparing microporous carbons with a structural regularity of zeolite Y, *Carbon* 40 (2002) 2367-2374.
- [300] M. Zhixin, T. Kyotani, L. Zheng, O. Terasaki, A. Tomita, Very high surface area microporous carbon with a three-dimensional nano-array structure: synthesis and its molecular structure, *Chem. Mater.* 13 (2001) 4413-4415.

- [301] Y. Kawabuchi, S. Kawano, I. Mochida, Molecular sieving selectivity of active carbons and active carbon fibers improved by chemical vapour deposition of benzene, *Carbon* 34 (1996) 711-717.
- [302] F. Su, J. Zeng, Y. Yu, L. Lv, J.Y. Lee, X.S. Zhao, Template synthesis of microporous carbon for direct methanol fuel cell application, *Carbon* 43 (2005) 2366-2373.
- [303] H. Wilhelm, M. Lelaurain, E. McRae, B. Humbert, Raman spectroscopic studies on well-defined carbonaceous materials of strong two-dimensional character, *J. Appl. Phys.* 84 (1998) 6552-6558.
- [304] F. Tuinstra, J.L. Koenig, RAMAN SPECTRUM OF GRAPHITE, *J. Chem. Phys* 53 (1970) 1126-1130.
- [305] A.A. Zakhidov, R.H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S.O. Dantas, J. Marti, V.G. Ralchenko, Carbon structures with three-dimensional periodicity at optical wavelengths, *Science* 282 (1998) 897-901.
- [306] Y. Wan, Y.-L. Min, S.-H. Yu, Synthesis of silica/carbon-encapsulated core-shell spheres: Templates for other unique core-shell structures and applications in in situ loading of noble-metal nanoparticles, *Langmuir* 24 (2008) 5024-5028.
- [307] D.D. Duong, Adsorption analysis: Equilibria and kinetics, Imperial College Press, London, 2003.
- [308] I. Novak, P. Sysel, J. Zemek, M. pirkova, D. Velic, M. Aranyosiova, Florian, V. Pollak, A. Kleinova, F. Lednicky, I. Janigova, Surface and adhesion properties of poly(imide-siloxane) block copolymers, *Eur. Polym. J.* 45 (2009) 57-69.
- [309] S. Shin, J. Jang, S.H. Yoon, I. Mochida, A study on the effect of heat treatment on functional groups of pitch based activated carbon fiber using FTIR, *Carbon* 35 (1997) 1739-1743.
- [310] X. Sun, The investigation of chemical structure of coal macerals via transmitted-light FT-IR microspectroscopy, *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* 62 (2005) 557-564.
- [311] P.E. Fanning, M.A. Vannice, A DRIFTS study of the formation of surface groups on carbon by oxidation, *Carbon* 31 (1993) 721-730.
- [312] I. Atamanenko, A. Kryvoruchko, L. Yurlova, E. Tsapiuk, Study of the CaSO₄ deposits in the presence of scale inhibitors, *Desalination* 147 (2002) 257-262.
- [313] X.-h. Guan, G.-h. Chen, C. Shang, ATR-FTIR and XPS study on the structure of complexes formed upon the adsorption of simple organic acids on aluminum hydroxide, *J. Environ. Sci.* 19 (2007) 438-443.
- [314] A. Afkhami, T. Madrakian, Z. Karimi, A. Amini, Effect of treatment of carbon cloth with sodium hydroxide solution on its adsorption capacity for the adsorption of some cations, *Colloids Surf., A* 304 (2007) 36-40.
- [315] J.P. Chen, S. Wu, Acid/Base-Treated Activated Carbons: Characterization of Functional Groups and Metal Adsorptive Properties, *Langmuir* 20 (2004) 2233-2242.
- [316] P. Pendleton, S.H. Wu, A. Badalyan, Activated carbon oxygen content influence on water and surfactant adsorption, *J. Colloid Interface Sci.* 246 (2002) 235-240.
- [317] H. Sis, M. Birinci, Effect of nonionic and ionic surfactants on zeta potential and dispersion properties of carbon black powders, *Colloids Surf., A* 341 (2009) 60-67.
- [318] S.F. Wu, K. Yanagisawa, T. Nishizawa, z-potential on carbons and carbides, *Carbon* 39 (2001) 1537-1541.

- [319] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: A review, *J. Hazard. Mater.* 177 (2010) 70-80.
- [320] E.N. El Qada, S.J. Allen, G.M. Walker, Adsorption of basic dyes from aqueous solution onto activated carbons, *Chem. Eng. J.* 135 (2008) 174-184.
- [321] K. Vasanth Kumar, S. Sivanesan, Equilibrium data, isotherm parameters and process design for partial and complete isotherm of methylene blue onto activated carbon, *J. Hazard. Mater.* 134 (2006) 237-244.
- [322] B.H. Hameed, A.T.M. Din, A.L. Ahmad, Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies, *J. Hazard. Mater.* 141 (2007) 819-825.
- [323] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons - A comparative study, *Dyes Pigm.* 51 (2001) 25-40.
- [324] J. Yamashita, M. Shioya, T. Kikutani, T. Hashimoto, Activated carbon fibers and films derived from poly(vinylidene fluoride), *Carbon* 39 (2001) 207-214.
- [325] C.A.P. Almeida, N.A. Debacher, A.J. Downs, L. Cottet, C.A.D. Mello, Removal of methylene blue from colored effluents by adsorption on montmorillonite clay, *J. Colloid Interface Sci.* 332 (2009) 46-53.
- [326] K. Marungrueng, P. Pavasant, High performance biosorbent (*Caulerpa lentillifera*) for basic dye removal, *Bioresour. Technol.* 98 (2007) 1567-1572.
- [327] O. Gulnaz, A. Kaya, F. Matyar, B. Arikan, Sorption of basic dyes from aqueous solution by activated sludge, *J. Hazard. Mater.* 108 (2004) 183-188.
- [328] B.H. Hameed, Grass waste: A novel sorbent for the removal of basic dye from aqueous solution, *J. Hazard. Mater.* 166 (2009) 233-238.
- [329] C.-H. Weng, Y.-F. Pan, Adsorption of a cationic dye (methylene blue) onto spent activated clay, *J. Hazard. Mater.* 144 (2007) 355-362.
- [330] S. Karagoz, T. Tay, S. Ucar, M. Erdem, Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, *Bioresour. Technol.* 99 (2008) 6214-6222.
- [331] C. Chen, J. Wang, Removal of Pb^{2+} , Ag^{+} , Cs^{+} and Sr^{2+} from aqueous solution by brewery's waste biomass, *J. Hazard. Mater.* 151 (2008) 65-70.
- [332] M.E. Fernandez, G.V. Nunell, P.R. Bonelli, A.L. Cukierman, Effectiveness of *Cupressus sempervirens* cones as biosorbent for the removal of basic dyes from aqueous solutions in batch and dynamic modes, *Bioresour. Technol.* 101 (2010) 9500-9507.
- [333] O. Hamdaoui, F. Saoudi, M. Chiha, E. Naffrechoux, Sorption of malachite green by a novel sorbent, dead leaves of plane tree: Equilibrium and kinetic modeling, *Chem. Eng. J.* 143 (2008) 73-84.
- [334] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH, *Bioresour. Technol.* 97 (2006) 512-521.
- [335] C. Moreno-Castilla, J. Rivera-Utrilla, J.P. Joly, M.V. Lopez-Ramon, M.A. Ferro-Garcia, F. Carrasco-Marin, Thermal regeneration of an activated carbon exhausted with different substituted phenols, *Carbon* 33 (1995) 1417-1423.
- [336] M.K. Purkait, S. DasGupta, S. De, Adsorption of eosin dye on activated carbon and its surfactant based desorption, *J. Environ. Manage.* 76 (2005) 135-142.
- [337] K. Okawa, K. Suzuki, T. Takeshita, K. Nakano, Regeneration of granular activated carbon with adsorbed trichloroethylene using wet peroxide oxidation, *Water Res.* 41 (2007) 1045-1051.

- [338] R.V. Shende, V.V. Mahajani, Wet oxidative regeneration of activated carbon loaded with reactive dye, *Waste Manage.* 22 (2002) 73-83.
- [339] N.W. Brown, E.P.L. Roberts, A.A. Garforth, R.A.W. Dryfe, Electrochemical regeneration of a carbon-based adsorbent loaded with crystal violet dye, *Electrochim. Acta* 49 (2004) 3269-3281.
- [340] J. Wang, X. Peng, Z. Luan, C. Zhao, Regeneration of carbon nanotubes exhausted with dye reactive red 3BS using microwave irradiation, *J. Hazard. Mater.* 178 (2010) 1125-1127.
- [341] X. Chen, J. Chen, X. Qiao, D. Wang, X. Cai, Performance of nano-Co₃O₄/peroxymonosulfate system: Kinetics and mechanism study using Acid Orange 7 as a model compound, *Appl. Catal., B* 80 (2008) 116-121.
- [342] W. Zhang, H.L. Tay, S.S. Lim, Y. Wang, Z. Zhong, R. Xu, Supported cobalt oxide on MgO: Highly efficient catalysts for degradation of organic dyes in dilute solutions, *Appl. Catal., B* 95 (2010) 93-99.
- [343] ATSDR, Toxicological profile for silver, in, US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, 1990.
- [344] M.J. Eckelman, T.E. Graedel, Silver emissions and their environmental impacts: A multilevel assessment, *Environ. Sci. Technol.* 41 (2007) 6283-6289.
- [345] A. Dabrowski, Adsorption - From theory to practice, *Adv. Colloid Interface Sci.* 93 (2001) 135-224.
- [346] A. Demirbas, Agricultural based activated carbons for the removal of dyes from aqueous solutions: A review, *J. Hazard. Mater.* 167 (2009) 1-9.
- [347] A.M. El-Menshawly, I.M. Kenawy, A.A. El-Asmy, Modification of chloromethylated polystyrene with 2-mercaptobenzothiazole for application as a new sorbent for preconcentration and determination of Ag⁺ from different matrices, *J. Hazard. Mater.* 173 (2010) 523-527.
- [348] L. Wang, R. Xing, S. Liu, H. Yu, Y. Qin, K. Li, J. Feng, R. Li, P. Li, Recovery of silver (I) using a thiourea-modified chitosan resin, *J. Hazard. Mater.* 180 (2010) 577-582.
- [349] C.Y. Yin, M.K. Aroua, W.M.A.W. Daud, Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions, *Sep. Purif. Technol.* 52 (2007) 403-415.
- [350] M.R. Mostafa, Adsorption of mercury, lead and cadmium ions on modified activated carbons, *Adsorpt. Sci. Technol.* 15 (1997) 551-557.
- [351] D. Zhou, L. Zhang, J. Zhou, S. Guo, Development of a fixed-bed column with cellulose/chitin beads to remove heavy-metal ions, *J. Appl. Polym. Sci.* 94 (2004) 684-691.
- [352] X.-G. Li, H. Feng, M.-R. Huang, Redox sorption and recovery of silver ions as silver nanocrystals on poly(aniline-co-5-sulfo-2-anisidine) nanosorbents, *Chem. Eur. J.* 16 (2010) 10113-10123.
- [353] X.-G. Li, R. Liu, M.-R. Huang, Facile synthesis and highly reactive silver ion adsorption of novel microparticles of sulfodiphenylamine and diammononaphthalene copolymers, *Chem. Mater.* 17 (2005) 5411-5419.
- [354] X.-G. Li, X.-L. Ma, J. Sun, M.-R. Huang, Powerful reactive sorption of Silver(I) and Mercury(II) onto Poly(o-phenylenediamine) microparticles, *Langmuir* 25 (2009) 1675-1684.
- [355] J. Hanzlik, J. Jehlicka, O. ebek, Z. Weishauptova, V. Machovic, Multi-component adsorption of Ag(I), Cd(II) and Cu(II) by natural carbonaceous materials, *Water Res.* 38 (2004) 2178-2184.

- [356] H.L.Z. J.L. Niu, J. Zhang, Z.F. Liu, Tracing the chemical oxidation process of single-walled carbon nanotubes by silver nanoparticles, *Acta Phys. Chim. Sin.* 20 (2004) 1-4.
- [357] C. Luo, Y. Zhang, X. Zeng, Y. Zeng, Y. Wang, The role of poly(ethylene glycol) in the formation of silver nanoparticles, *J. Colloid Interface Sci.* 288 (2005) 444-448.
- [358] Z.R. Yue, W. Jiang, L. Wang, H. Toghiani, S.D. Gardner, C.U. Pittman Jr, Adsorption of precious metal ions onto electrochemically oxidized carbon fibers, *Carbon* 37 (1999) 1607-1618.
- [359] P. Gunawan, R. Xu, Direct assembly of anisotropic layered double hydroxide (LDH) nanocrystals on spherical template for fabrication of drug-LDH hollow nanospheres, *Chem. Mater.* 21 (2009) 781-783.
- [360] B. Hai, J. Wu, X. Chen, J.D. Protasiewicz, D.A. Scherson, Metal-ion adsorption on carboxyl-bearing self-assembled monolayers covalently bound to magnetic nanoparticles, *Langmuir* 21 (2005) 3104-3105.
- [361] Y. Jiang, Q. Gao, H. Yu, Y. Chen, F. Deng, Intensively competitive adsorption for heavy metal ions by PAMAM-SBA-15 and EDTA-PAMAM-SBA-15 inorganic-organic hybrid materials, *Microporous Mesoporous Mater.* 103 (2007) 316-324.
- [362] L. Yang, Y. Li, X. Jin, Z. Ye, X. Ma, L. Wang, Y. Liu, Synthesis and characterization of a series of chelating resins containing amino/imino-carboxyl groups and their adsorption behavior for lead in aqueous phase, *Chem. Eng. J.* 168 (2011) 115-124.
- [363] H.A. Shawky, Synthesis of ion-imprinting chitosan/PVA crosslinked membrane for selective removal of Ag(I), *J. Appl. Polym. Sci.* 114 (2009) 2608-2615.

PUBLICATIONS

1. Song X.H., R. Xu, A. Lai, H. L. Lo, F. L. Neo, K. Wang, Preparation and characterization of mesoporous activated carbons from waste tyre, Asia-Pacific Journal of Chemical Engineering, 2011, DOI: 10.1002/apj.544
2. Song. X. H., Teo. W. S., Wang, K., Synthesis and characterization of activated carbons prepared from benzene CVD on zeolite Y, Journal of porous materials, January, 2011, P1-5, DOI 10.1007/s10934-011-9462-0.
3. Song, Xianghua, Guanwan, Poernomo, Jiang Rongrong, Leong, Susanna Su Jan, Wang Kean, Xu Rong, Surface activated carbon nanospheres for fast adsorption of silver ions from aqueous solutions, Journal of Hazardous Materials, 194, 2011, 162-168.
4. Gunawan, Poernomo; Guan, Cong; Song, Xianghua; Zhang, Quanyuan; Leong, Susanna; Tang, Chuyang; Chen, Yuan; Chan-Park, Mary; Chang, Matthew; Wang, Kean; Xu, Rong, Hollow Fiber Membrane Decorated with Ag/MWNTs: Towards Effective Water Disinfection and Biofouling, ACS Nano, v 5, n 12, p 10033-10040, Decembr 27, 2011.
5. X. Song, R. Xu, K. Wang, High capacity adsorption of malachite green in a mesoporous tyre-derived activated carbon, Asia-Pacific Journal of Chemical Engineering, 10 MAY 2012, DOI: 10.1002/apj.1658.
6. Xianghua Song, Kean Wang and Rong Xu, Adsorption properties of basic dyes

using surface activated carbon nanospheres in aqueous solutions. Submitted to Industrial & Engineering Chemistry Research.

Conference Presentation

1. Song X.H., Wang, K., Sorption behavior of chitosan and modified chitosan hydrogel beads with Ag(I) in aqueous solutions, The International Symposium on Exploring the Frontiers of Chemical and Biomedical Engineering, Singapore, May 2010.