Sorption mechanisms of divalent cations with titanate nanotube

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**SORPTION MECHANISMS OF DIVALENT CATIONS
WITH TITANATE NANOTUBE**

**A thesis submitted to the School of Civil and Environmental Engineering of Nanyang
Technological University in partial fulfilment of the requirements for the degree of
Doctor of Philosophy**

Du Jianhong

2011

Abstract

The occurrence of heavy metal ions in industrial wastewater discharges is a pertinent issue. Discharges that are not properly treated causes pollution to the downstream river and groundwater which are often used for drinking and irrigation in the rural area. This thesis explores the feasibility of titanate nanotube as an industrial sorbent to remove cadmium and other divalent cations from water.

Nanotubes, synthesized via alkali hydrothermal process, were characterized using microscopic techniques. Empirical approaches (Langmuir equation, Kurbatov equation and hard and soft acids and bases) were used to understand the sorption behaviour of titanate nanotube on seven divalent cations. It was found that the sorbent had high selectivity for lead and cadmium. In descending order, the affinity for titanate nanotube: lead >> cadmium > copper > zinc > calcium > strontium > nickel. For each cation, its sorption capacity was correlated with intrinsic parameters (hydrolysis constant, electronegativity, hardness and charge-size function). From linear regression analyses of six cations, with the exception of nickel, it was found that sorption capacity can be adequately correlated with hydrolysis constant and electronegativity.

Due to the toxicity of cadmium, the effects of solution chemistry on cadmium uptake were studied. Sorption efficiency increased at higher pH condition, other parameters being held constant. This, in part, was due to the surface charge of titanate nanotube. Metal oxide being amphoteric had negative charge when $\text{pH} > \text{point of zero charge}$, thereby attracting the positively charge cadmium ions. Varying ionic strength at low order of magnitude ($10^{-3} - 10^{-2} \text{ M}$), did not have significant effect on sorption uptake. At 0.1 M, significant decrease in cadmium sorbed can be observed. The sorption of cadmium was due to a combination of electrostatic forces and covalent bonding.

Two complementary spectroscopic techniques were utilized to investigate the mechanisms involved in sorption of cadmium. X-ray photoelectron spectroscopy (XPS) showed an increase in cadmium at higher pH which was in accordance with behaviour exhibited in the sorption edges. In open system, cadmium precipitated to

form otavite, $\text{CdCO}_3(\text{s})$. Samples equilibrated at pH 7 and 9 showed a shoulder in Cd $3d_{5/2}$ peak which were contributed by Cd- CO_3 . From Na 1s spectra, it was found that there was a decrease in sodium for samples after sorption equilibrium. This was due to the release of sodium ions while cadmium ions were being sorbed onto titanate nanotubes. X-ray absorption spectroscopy (XAS) studies of cadmium K-edge found that samples equilibrated at 0.001 and 0.1 M ionic strength had Fourier transformed peaks similar to that of CdO standards. Fitting processes showed that these peaks can be described by electron scattering paths of Cd-O and Cd-Ti.

Cadmium sorption edges were simulated using charge distribution multisite ion complexation (CDMUSIC) model. This model made use of crystallographic details of titanate nanotube and also evidence from prior spectroscopic analyses. From parameter optimization program, it was found that the acid-base behaviour and cadmium sorption behaviour can be satisfactorily described by invoking the interlayer sites and weak and strong surface sites. Sorption edges were well-fitted when considering both inner-sphere complexation at surface and ion-exchange at the interlayer.

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Zhang, X.W., **Du, A.J.**, Lee, P.F., Sun, D.D. and Leckie, J.O. (2008) "Grafted multifunctional titanium dioxide nanotube membrane: Separation and photodegradation of aquatic pollutant". *Applied Catalysis B: Environmental*. 84 (1-2), 262-267.

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List of Symbols and Terms

%sorbed	Sorption efficiency (%)
§	Section
χ	Electronegativity
ϵ	Relative dielectric constant
ϵ_0	Permittivity of free space (8.85×10^{-12} F/m)
η	Pearson Hardness
κ	Reciprocal Debye length
λ	X-ray wavelength (Å)
θ_B	Angle of the most intense peak (radians)
σ_i	Charge at i plane (C/m ²)
ΔG_{ads}°	Change in Gibbs free energy for sorption
ψ_i	Potential at i plane (V)
a	Sorbent concentration (g/L)
A	Bond valence constant (19.8)
b	CDMUSIC constant (0.37 Å)
B	Full width at half maximum of most intense peak (radians)
BET	Brunauer Emmett Teller
BJH	Barrett Joyner Halenda
C_i	Capacitance at i layer (F/m ²)
C_A	Concentration of acid (mol/L)
C_B	Concentration of base (mol/L)
CCM	Constant Capacitance Model
CDMUSIC	Charge Distribution Multisite Ion Complexation
C_e	Equilibrium concentration of solution sorbate (mol/L)
CN	Coordination number
D	Distribution ratio
DLM	Diffuse Layer Model
e	Elementary charge of an electron (1.6×10^{-19} C)
f	Distribution factor
F	Faraday constant (96,490 C/mol)

IS	Ionic strength (mol/L)
IUPAC	International Union of Pure and Applied Chemistry
JCPDF	Joint Committee on Powder Diffraction File
k	Boltzmann constant (1.38×10^{-23} J/K)
K or K_{ads}	Langmuir sorption binding constant (L/mol)
K_i	Equilirbium constant
K_d	Distribution coefficient
m	Number of proton-donating bond
n	Number of proton-accepting bond
pC	Negative logarithm of species molarity (pC = -log [C])
pH ₅₀	pH value when %sorbed = 50%
pH _{initial}	pH before sorption equilibrium
pH _{final}	pH after sorption equilibrium
P _{CO2}	Partial pressure of carbon dioxide gas
PZC	Point of zero charge
q	Sorption uptake (mol/g)
q _m	Langmuir sorption capacity (mol/g)
Q	Surface charge (mol/g)
R	Ideal gas constant (8.314 J/mol.K)
R	Bond length
R _o	Element-specific distance
s	Specific surface area (m ² /g)
s _i	Charge contribution by i
SAED	Selected area electron diffraction
t	Crystal size (Å)
T	Temperature (K)
TEM	Transmission electron microscopy
TLM	Triple Layer Model
TNT	Titanate nanotube
USEPA	United States Environmental Protection Agency
v	Bond valence
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

z	Valence of ion
Z^2/r	Charge-size function

Chapter 1 Introduction

1.1 Background

World's cadmium production increased from 17,500 tonnes in 2002 to 21,100 tonnes in 2006 (Hetherington et al. 2008). World's primary production of cadmium is Asia (China, Japan, South Korea), Pacific, North America and Europe. Another major source of cadmium production is NiCd battery recycling factories (Tolcin 2010).

Cadmium is widely used in industries such as plastics manufacturing, batteries, pigments, metal alloys and pesticides (Posselt and Weber 1971). It is estimated that 75% of total cadmium consumption was for the production of rechargeable nickel cadmium (NiCd) batteries and the remaining 25% distributed among plastics manufacturing (4%), coatings and plating (7%), pigments (13%) and nonferrous alloys (1%) (Plachy 2001). Despite the introduction of lithium-ion and nickel-metal hydride substitutes to consumer electronic products, NiCd batteries remain in demand for industrial applications (Tolcin 2010).

Indeed, cadmium becomes a common occurrence in wastewater of the industry and in view of this, USEPA (<http://www.epa.gov/safewater/contaminants/index.html>) has enforced strict regulations on cadmium levels in industrial discharges. Cadmium is non-essential to humans and should not be present in human tissues. The heavy metal has a long biological half-life in humans and is able to accumulate in the human long after the exposure period (Waalkes 2003). Symptoms of cadmium poisoning are characterized by kidney damage (renal tubular dysfunction) and softening of bones (osteomalacia) in the victims (Kasuya 2000). Moreover, cadmium is a human carcinogen causing cancer of the lung, kidney and prostate. Due to its high toxicity to humans, cadmium pollution is of significant concern. In Japan, the infamous itai-itai disease is the result of using cadmium-tainted river water for irrigation purposes.

Treatment methods to separate heavy metals from the wastewater include coagulation-precipitation, sorption, electrolysis and nanofiltration. Despite emerging technologies, sorption remains a cost-effective and widely-studied method for the removal of heavy metals from water (Bailey et al. 1999; Reddad et al. 2002; Gerente et al. 2007). Commercial ion-exchange resins are often used to sorb heavy metals. Matrix are usually styrene divinylbenzene copolymer grafted with sulfonate (Demirbas et al. 2005) iminodiacetate or thiol (Brower et al. 1997) groups. They have high capacity for heavy metals but low selectivity.

Cadmium, however, often coexists with many other cations in wastewater and the non-selective sorption of every cations present becomes operationally inefficient. It results in depletion of sites for partitioning of more toxic ions and impedes the process of recovering the more precious metal. In order to recover valuable metals of high purity from spent sorbent, the sorbent itself needs to have high selectivity in addition to high capacity.

Recently, inorganic titanate nanotubes have received increasing attention as a sorbent for removal of various pollutants. Monocrystalline titanate nanotube has high surface area and dimensions comparable to that of multiwalled carbon nanotube. Application-wise the morphology of nanotube allows itself to have better separation/recovery efficiency over nanoparticle. Ou et al. applied titanate nanotube to sorbed aqueous ammonium species (Ou et al. 2008). Niu and co-workers investigated the feasibility of titanate nanotubes as sorbents for arsenic removal (Niu et al. 2009). Liu et al. used titanate nanotube for the removal of copper(II) ions from water (Liu et al. 2009).

There is a lack of information regarding the sorption capacities of titanate nanotubes on various divalent cations and the sorbent's selectivity for each cation. More understanding of sorption behaviour is warranted in order to apply titanate nanotube to remediation of industrial wastewater. Secondly, from above-mentioned literatures, sorption mechanism of cadmium on titanate nanotube was either attributed

exclusively to the ion-exchange at the interlayer of the nanotube or not stated at all. Details concerning sorption mechanisms of titanate nanotubes are either inconclusive or lacking. The sorption behaviour is poorly understood and there are room for more rigorous studies such as computer modelling and advanced spectroscopic techniques.

1.2 Research Objectives

Overall objective of this study is to synthesize and characterize titanate nanotubes. The nano-sized sorbent were applied for the removal of cadmium ions from water. Batch tests to elucidate sorption mechanism of cadmium onto titanate nanotube. Systems should allowed sufficient duration to achieve pseudo-equilibrium. Effect of solution composition (pH, ionic strength and competing cations) on sorption behaviour has to be elucidated. The objectives of this work are to:

- (i). synthesize titanate nanotubes and characterize the sorbent using various microscopic techniques
- (ii). investigate the sorption behavior of titanate nanotubes under different solution compositions
- (iii). utilize spectroscopic techniques to elucidate the mechanisms behind the sorption processes
- (iv). simulate experimental data using a theoretical model

1.3 Thesis Overview

This thesis comprises of 9 chapters and 3 appendices. **Chapters 1, 2 and 3** are the introduction, literature review and methodology, respectively.

Chapter 4 explains the synthesis protocol of titanate nanotube (TNT). It is followed by reporting the crystallographic, textural and surface properties of the synthesized sorbent. Characterization techniques include x-ray diffraction (XRD), field-

emission scanning electron microscope (FESEM), transmission electron microscope (TEM), nitrogen gas sorption-desorption and acid-base titration.

Chapter 5 reports sorption uptakes for seven different divalent cations. Empirical approaches (Langmuir equation, Kurbatov plot and theory of hard and soft acids and bases) were employed to explain and correlate the TNT sorption behaviour and selectivity. Kinetic studies were performed to determine the pseudo-equilibrium duration.

Chapter 6 describes findings from two complementary spectroscopic studies (x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS)). The sorption mechanisms of cadmium on titanate were elucidated based on the results and analyses.

Chapter 7 discusses the simulation of sorption behaviour using a theoretical model. Surface complexation model, specifically charge distribution multisite ion complexation model (CDMUSIC), is used to model the sorption behavior of cadmium-TNT. Input file is written with the consideration of TNT crystallography.

Chapter 8 investigates the sorption behaviour of cadmium on titanate from batch tests experiments. Equilibrium batch tests were conducted to determine the effects of solution composition on sorption behaviour.

Chapter 9 consists of an overall conclusion to this investigation. It also provides recommendations and suggestions for future works.

Appendix A presents derivation of the Gouy-Chapman theory which forms the basis of surface complexation models. **Appendix B** shows the sensitivity of ICP-OES analysis. **Appendix C** gives the raw experimental data required for the construction of figures. **Appendix D** shows PhreePlot input files for the surface complexation modelling of experimental data.

Chapter 2 Literature Review

2.1 Metal Oxide-Water Interface

Metal oxides are ubiquitous in the terrestrial soils. The study of metal oxides/ water interface is important as this interaction can be found in cases of:

- (i). sediment at the river bed
- (ii). soil and groundwater
- (iii). inorganic sorbent used for wastewater treatment.

Due to their low solubility they are present in soils and river sediments often as oxides of Fe, Al, Mn and Ti. Table 2.1 lists some metal oxides commonly found in soils.

The bulk of these metal oxides (titanium dioxide, iron oxides and manganese oxides) are often crystalline and made up of building blocks of octahedrons. That is, the center metal atom is hexagonally bonded to oxygens forming a single octahedron. (Figure 2.1). Various crystal polymorphs arise from different configurations of octahedrons. At the surface of the metal oxides are terminating oxygen atoms. These oxygen atoms have a reduced coordination number and behave as Lewis acid. They are reactive and able form bonds with other ions from the solution.

Table 2.1 Metal oxides commonly found in soils (Sposito 1984).

Name	Chemical Formula	Name	Chemical Formula
Anatase, Rutile	TiO ₂	Hematite	α-Fe ₂ O ₃
Birnessite	Na _{0.7} Ca _{0.3} Mn ₇ O ₁₄ ·2.8H ₂ O	Ilmenite	FeTiO ₃
Boehmite	γ-AlOOH	Lepidocrocite	γ-FeOOH

Ferrihydrite	$\text{Fe}_2\text{O}_3 \cdot 2\text{FeOOH} \cdot 2.6\text{H}_2\text{O}$	Lithiophorite	$(\text{Al}, \text{Li}) \text{MnO}_2(\text{OH}_2)$
Gibbsite	$\gamma\text{-Al}(\text{OH})_3$	Maghemite	$\gamma\text{-Fe}_2\text{O}_3$
Goethite	$\alpha\text{-FeOOH}$	Magnetite	Fe_3O_4

Figure 2.1 Schematic depicting a single octahedron building block and cross section of metal oxide at the solid-water interface.

2.1.1 Acid-Base Chemistry of Metal Oxide

Surface charge of a certain metal oxide can be viewed as the sorption/desorption of protons from the solution. This surface charge can be determined by performing an acid-base titration of the slurry. The surface charge (σ_o) of the sorbent can be calculated using the following (Stumm 1992):

$$\sigma_o = \frac{QF}{s} = \frac{F}{as} (C_A - C_B + [\text{OH}^-] - [\text{H}^+]) \tag{1}$$

where F is Faraday constant (96 490 C/mol), s is the specific surface area (m^2/g), a is sorbent concentration (g/L) and C_A and C_B denote the amount of acid and base added (mol/L)

In general two types of titration curves can be found in the literature. Most minerals have only variable charge at the edge. Solids with only variable charge are characterized by the presence of a common point of zero charge (PZC) (Figure 2.2A).

Figure 2.2 Typical titration curves for minerals (A) with variable charge only (B) with variable charge and permanent charge. Ionic strength (I) is in the descending order $I_1 \gg I_2 \gg I_3$.

The point where curves intersect is also known as point of zero salt effect (PZSE) (Sposito 1999):

$$\left(\frac{\partial \sigma_H}{\partial I} \right)_{T,P} = 0 \quad (\text{pH} = \text{PZSE}) \quad [2]$$

where T is temperature and P is pressure. At point of zero salt effect the surface charge is unaffected by the change in ionic strength (I). At high ionic strength protonation/deprotonation at surface hydroxyl is more prominent than at low ionic strength. Table 2.2 lists different PZCs of minerals with variable charge. Sposito (1998) described the balance of charge of a solid as:

$$\sigma_O + \sigma_H + \Delta q = 0 \tag{3}$$

where σ_O is permanent charge, σ_H is sorbed proton charge and Δq is summation of charge contribution from other ions. Charge contribution to the charge of solid can be from inner-sphere complex (σ_{IS}), outer-sphere complex (σ_{OS}) and the diffuse swarm (σ_d):

$$\Delta q = \sigma_{IS} + \sigma_{OS} + \sigma_d \tag{4}$$

Table 2.2 Point of zero charge values of various minerals (Davis and Kent 1990).

Mineral	PZC	Reference
$\gamma\text{-Al}_2\text{O}_3$	8.5	(Huang and Stumm 1973)
Anatase (TiO_2)	5.8	(Bérubé and de Bruyn 1968)
Birnessite ($\delta\text{-MnO}_2$)	2.2	(Balistrieri and Murray 1982)
Calcite (CaCO_3)	9.5	(Parks 1975)
Corundum ($\alpha\text{-Al}_2\text{O}_3$)	9.1	(Sposito 1984)
Goethite ($\alpha\text{-FeOOH}$)	7.3	(Atkinson et al. 1972)
Hematite ($\alpha\text{-Fe}_2\text{O}_3$)	8.5	(Breeuwsma and Lyklema 1973)
Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$)	7.6	(Bell et al. 1973)
Magnetite ($\alpha\text{-Fe}_3\text{O}_4$)	6.6	(Tewari and McLean 1972)
Rutile (TiO_2)	5.8	(Yates and Healy 1980)
Quartz ($\alpha\text{-SiO}_2$)	2.9	(Sposito 1984)

2.2 Empirical Isotherms

In order to describe observed experimental results with known theories, various empirical isotherms had been formed. Table 2.3 lists the equations which were commonly used to describe a wider range of sorption reactions.

Table 2.3 General sorption isotherms, modified from literature (Kinniburgh 1986; Hayes 1987).

Sorption Isotherm	Equation	No. of Unknown Parameter	Asymptotic Properties	
			Linear at Low Concentration	Maximum Sorption Capacity at High Concentration
Single-Site Langmuir	$q = \frac{q_m K_{ads} C_e}{1 + K_{ads} C_e}$	2	Yes	Yes = q_m
Multisite Langmuir	$q = \sum_i^k \frac{q_{m,i} K_{ads,i} C_e}{1 + K_{ads,i} C_e}$	2k	Yes	Yes = $q_{m,i}$
Freundlich	$q = (KC)^n$	2	No	No
Sum of Freundlichs	$q = \sum_i^k (K_i C)^{n,i}$	2k	No	No
Langmuir-Freundlich	$q = \frac{q_m (K_{ads} C_e)^n}{1 + (K_{ads} C_e)^n}$	3	No	Yes = q_m
Redlich-Peterson	$q = \frac{K_{ads} C_e}{1 + (K_{ads} C_e)^n}$	3	Yes	No
Toth	$q = \frac{q_m K_{ads} C_e}{[1 + (K_{ads} C_e)^n]^{1/n}}$	3	Yes	Yes = q_m

Dubinin-Radushkevich	$\log q = -n \log^2 (K_{ads} C_e) + \log q_m$	3	No	No
Modified Dubinin-Radushkevich ^a	$\log q = \log q^* - \log C_e^* + \log C_e$ (when $C_e \leq C_e^*$) $\log q = -n \log^2 \left(\frac{K_{ads} C_e}{1 + K_{ads} C_e} \right) + \log q_m$ (when $C_e \geq C_e^*$)	3	Yes	Yes = q_m

q is the amount of sorbate bounded per unit mass of sorbent, q_m is the maximum sorption capacity, C_e is sorbate concentration at equilibrium and n is empirical constant which is dependent on the degree of heterogeneity.

^a The point (q^*, C_e^*) is the point where $\frac{\partial \log q}{\partial \log C_e} = 1$. C_e^* cannot be calculated explicitly but is given to a good approximation by

$$\log C_e^* \approx \left(-\frac{1}{2n} \right) - \log K_{ads}.$$

2.2.1 Langmuir Isotherm

The Langmuir sorption process can be described by the mass law equation (Stumm and Morgan 1996):

where S is the surface site of sorbent, A is sorbate and SA is the sorbate-bounded surface site

Like any other chemical reactions, Equation [1] is governed by laws of thermodynamics defined by reaction constant K_{ads} :

$$\frac{[SA]}{[S][A]} = K_{ads} = \exp\left(-\frac{\Delta G_{ads}^{\circ}}{RT}\right) \quad [6]$$

And total number of sites can be defined by the sum of occupied and unoccupied sites:

$$[S_T] = [S] + [SA] \quad [7]$$

Combining Equations [2] and [3]:

$$[SA] = [S_T] \frac{K_{ads}[A]}{1 + K_{ads}[A]} \quad [8]$$

Equation [4] can be written in a more familiar form:

$$q = \frac{q_m K_{ads} C_e}{1 + K_{ads} C_e} \quad [9]$$

where q is sorption capacity, q_m is maximum sorption capacity and C_e is concentration of sorbate in solution at equilibrium

Typically q and q_m are expressed in (moles bound sorbate per grams sorbent) or (grams bound sorbate per grams sorbent) and C_e in (moles free sorbate per liter solution) or (grams free sorbate per liter solution). The constants q_m and K_{ads} can be solved by plotting the linearized form of Equation [9]. Table 2.4 lists four linearized Langmuir equations that are commonly utilized to fit experimental data.

Table 2.4 Linear transformation of Langmuir isotherm (Kinniburgh 1986).

Linearized Equation	Plot		K_{ads}	q_m
	Abcissa	Ordinate		
(i) Double Reciprocal (Lineweaver-Burk)				
$\frac{1}{q} = \frac{1}{q_m K_{ads}} \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q}$	$\frac{1}{C_e}$	intercept/slope	1/intercept
(ii) Reciprocal (Langmuir)				
$\frac{C_e}{q} = \frac{1}{q_m} C_e + \frac{1}{K_{ads} q_m}$	$\frac{C_e}{q}$	C_e	slope/intercept	1/slope
(iii) (Eadie-Hofstee)				
$q = -\frac{1}{K_{ads}} \frac{q}{C_e} + q_m$	q	$\frac{q}{C_e}$	-1/slope	intercept
(iv) Distribution Coefficient (Scatchard)				
$\frac{q}{C_e} = -K_{ads} q_m + K_{ads} q_m$	$\frac{q}{C_e}$	q	-slope	-intercept/slope

Sposito (1984) pointed out that the most accurate is the one which involves distribution coefficient (i.e. Table 2.4(iv)). By definition distribution coefficient is the ratio of sorbate sorbed versus sorbate in aqueous phase:

$$K_d = \frac{q}{C_e}$$

[10]

By multiplying both sides of Equation [9] with $\left(K_{ads} + \frac{1}{C_e}\right)$ and replacing $K_d = \frac{q}{C_e}$ yields:

$$K_d = -K_{ads}q + K_{ads}q_m \quad [11]$$

Hence sorption is said to be Langmuirian if plot K_d against q yields a straight line. Single-site Langmuir isotherm (Equation [9]) is based on assumption that the molar ratio of site to sorbate is 1:1 i.e. for each site only one sorbate occupies it. Hayes (1987) pointed out that K_d is empirical and dependent on solution compositions (such as variation in ionic strength, pH, dissolved carbonate content etc.).

For simplicity let us write the sorption of monovalent cation (M^+) onto metal oxide surface ($\equiv\text{SOH}$):

Applying mass law to Equation [12] we get:

$$K_M = \frac{[\equiv\text{SOM}][H^+]}{[\equiv\text{SOH}][M^+]} \quad [13]$$

Invoking the definition of distribution coefficient, K_d , Equation [13] becomes:

$$K_M = K_d \frac{[H^+]}{[\equiv\text{SOH}]} \quad [14]$$

Equation [14] exemplifies the limitation of using distribution coefficient in describing the sorption process of Equation [12]. The overall sorption process, K_M , is dependent on not only K_d but also pH and sorbent concentration. Hence K_d has limited use in simulating sorption behavior of systems that are affected by

variations in pH, ionic strengths, sorbent concentrations or presence of competing sorbate. The assumption of distribution coefficient is that all dissolved sorbate ions have same affinity for the sorbent surface. Moreover it does not account any possible surface site heterogeneity.

It cannot describe (i) a system with more than one sorbate (i.e. competitive sorption) or (ii) a system in which the sorbent has more than one sites (i.e. site heterogeneity). The assumption of distribution coefficient is that all dissolved sorbate ions have same affinity for the sorbent surface. Moreover it does not account any possible surface site heterogeneity.

The two-site Langmuir isotherm can be applied to describe an additional component in the system. It was found appropriate in describing data of ion sorption on mineral surfaces (Sposito 1984; Kinniburgh 1986; Dzombak and Morel 1990). Theoretical calculation of the two-site Langmuir isotherm is beyond scope of this thesis. A detailed analysis of two-site Langmuir isotherm can be found in Sposito (1984).

2.2.2 Empirical Surface Precipitation Model

Another empirical model was proposed based on system different from the single-site binding. In solution where sorbate concentration increases, the sites on the sorbent become insufficient and more than one sorbate molecules will bind to one site. Higher concentrations of sorbate would inadvertently result in accumulation of the molecules forming a surface precipitate on the sorbent.

It was suggested that the amount of molecules being sorbed to follow (Benjamin 2002):

$$q_{sp} = \frac{\phi C_e / C'_e}{1 - C_e / C'_e} = \frac{\phi K' C_e}{1 - K' C_e} \quad [15]$$

where ϕ is mass of sorbent that contributes to the mixed solid phase, normalized to the adsorbent surface area (e.g. mg/m^2), C'_e is the sorbate concentration that would be in equilibrium with the pure precipitated solid (e.g. if precipitate is metal hydroxide, $C'_e = K_{\text{sp,Me(OH)}_2(s)} / [\text{(Bencheikh-Latmani)}^2]$) and $K' = 1/C'_e$.

Benjamin (2002) pointed out the above equation is similar to the single-site Langmuir isotherm (Equation 9) with the exception of the sign convention in the denominator. Both ϕ and K' are analogous to q_m and K_{ads} in its single-site counterpart. Benjamin (2002) elaborated that at low C_e , Equation 15 reduces to a linear equation:

$$q_{\text{sp}} = \phi K' C_e \quad [16]$$

where the amount of sorbate is linearly related to C_e . Interestingly, as C_e approaches $1/K'$, the amount of sorbate becomes very large. This indicates that the surface precipitate forms a pure solid precipitate of the sorbate.

2.3 Surface Complexation Models

2.3.1 Constant Capacitance Model (CCM)

The earliest complexation model was the CCM. It is a single layer model and developed by Schindler and Kamber (1968) and Hohl and Stumm (1976). Details of CCM model can be found in other reviews as well (Sposito 1984; Davis and Kent 1990). The CCM is a special case of diffuse layer model, which will be discussed subsequently. The assumptions of CCM are (Hayes 1987; Davis and Kent 1990):

(i). The surface of sorbent consist of hydroxyl groups ($\equiv\text{SOH}$) which are amphoteric:

These protonation/deprotonation reactions are governed by equilibrium constants, K_{a1} , K_{a2} . These sites are able to react with metal cations to form surface complexes:

For simplicity metal divalent cations (Me^{2+}) are used as an example. Altogether there are 4 equilibrium constants in CCM in which these constants are unique for a particular ionic strength.

(ii). Only specific sorption (i.e. inner-sphere complexation) can occur on the single layer. Certain ions (H^+ , metal cations and ligand anions) will be sorbed into this layer while electrolyte ions (Na^+ , K^+ , NO_3^- , ClO_4^- , etc.) do not sorbed onto the surface and does not affect the charge balance

(iii). The surface charge (σ_o) is directly proportional to the surface potential (ψ_o):

$$\sigma_o = C\psi_o \quad [19]$$

where C is the capacitance of the only layer. The value of surface potential is hence obtained from the above equation.

Figure 2.3A illustrates the possible ions sorbed onto the surface of the oxide and the decay of potential with respect to the distance from the surface. The application of CCM is limited to high ionic strength conditions. The CCM was used by various literatures to describe sorption of metal cations, anions onto surface of metal oxides. Hohl and Stumm applied CCM to study $Pb(II)$ onto $\gamma-Al_2O_3$ (Hohl and Stumm 1976). Sigg and Stumm used CCM to model anions on goethite (Sigg and Stumm 1981). Manning and Goldberg employ CCM for sorption of arsenic on various

minerals (Manning and Goldberg 1997). Recently, Tan et al. used CCM to fit sorption data of Eu(III) onto titania (Tan et al. 2009).

2.3.2 Diffuse Layer Model (DLM)

The DLM theory originated from Stumm et al. (1970) and Huang and Stumm (1973). DLM has two layers at the solid-water interface, each accounting for different types of ions. This model is similar to the CCM model in which surface hydroxyl groups are amphoteric and protonation/deprotonation are defined likewise in Equations [15,16]. Equations for metal cation complexation are similar to Equations [17,18] too. Both protonation and specific sorption are located at the surface plane.

The DLM has an additional diffuse layer which accounts for the effects of electrolyte ions (Figure 2.3B). This enables DLM greater versatility in describing systems with variable ionic strength. The Gouy-Chapman theory was used to describe the charge (σ_d) and potential (ψ_d) at the d-plane (James and Parks 1982):

$$\sigma_d = -0.1174\sqrt{I} \sinh \frac{ze\psi_d}{2kT} \quad [20]$$

where I is molarity of electrolyte, z is the valence of electrolyte, e is elementary charge of electron (1.6×10^{-19} C) and k is the Boltzmann constant and T is temperature (K).

Units of σ_d and potential ψ_d are C/m² and V, respectively. The charge balance condition for DLM is:

$$\sigma_o + \sigma_d = 0 \quad [21]$$

The summation of charges at the surface (o-plane) and d-plane should be zero. For DLM, potentials at o-plane and d-plane are equal ($\psi_o = \psi_d$). Hence ψ_o can be calculated from Equation [20, 21]:

$$\sigma_o = -\sigma_d = 0.1174\sqrt{I} \sinh \frac{ze\psi_o}{2kT} \quad [22]$$

σ_o can be yielded from titration of sorbent (Equation [1]). At low surface potential ($\psi_o \ll 25$ mV), Equation [22] can be reduced to (Stumm and Morgan 1996):

$$\sigma_o \approx (2.3\sqrt{I})\psi_o \quad [23]$$

From experiment data, it is known that ionic strength (I) is inversely proportional to surface potential (ψ_o) (Dzombak and Morel 1990). Hence given the boundary conditions of high I and low ψ_o , DLM can be theoretically approximated to CCM (Equation [19]).

The DLM was first applied by Huang and Stumm (1973) on sorption of alkaline earth cations on γ -Al₂O₃. Subsequent researchers have also used DLM to model experimental data (Harding and Healy 1985; Harding and Healy 1985; Dzombak and Morel 1986). Dzombak and Morel (1990) used DLM to modeled vast amount of experimental data from literatures. The book also summarized the prior works done on sorption of inorganic ions onto hydrous ferric oxide. Recently, Appelo et al. used the DLM to study the effect of Fe(II) and carbonates on As sorption on ferrihydrite (Appelo et al. 2002).

Figure 2.3 Schematic representations of (A) Constant Capacitance Model (B) Diffuse Layer Model (C) Triple Layer Model (Hayes 1987).

2.3.3 Triple Layer Model (TLM)

The TLM concept was developed by Yates et al. (1974) and applied by Davis (1978) and then modified by Hayes (1987). Essentially the difference between TLM and the previous two models is that TLM incorporates an additional plane, β -plane, to describe outer-sphere complexation (Figure 2.3C). As such only protonation/deprotonation can occur at the o-plane (inner-sphere complexation) while β -plane is for metal cations, ligands and electrolyte ions. The charge balance of the mineral becomes:

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \quad [24]$$

The charge-potential relationship between σ_d and ψ_d is still described by Gouy-Chapman theory (Equation [20]), whereas potential at o-plane, ψ_o , is now:

$$\psi_o - \psi_\beta = \frac{\sigma_o}{C_1} \quad [25]$$

and potential at β -plane, ψ_β , is:

$$\psi_\beta - \psi_d = \frac{\sigma_o + \sigma_\beta}{C_2} = -\frac{\sigma_d}{C_2} \quad [26]$$

where C_1 and C_2 are the capacitances (C/m^2) of inner and outer Stern layers, respectively. In addition to Equations [15-18], TLM has an addition set of equations to account for electrolyte ions at the d-plane:

where C^+ and A^- represent the cation and anion of the 1:1 electrolyte, respectively. Hence TLM uses 6 equilibrium constants to describe a set of data.

In a modified version of TLM, metal cations are allowed to form complexation at both o-plane and β -plane (Hayes and Leckie 1987). Metal cations at the o-plane are inner-sphere complexation and β -plane outer-sphere complexation. The modified TLM is more accurate at the molecular level as many heavy metal cations forms inner-sphere bonding with the metal oxide surface (Hayes and Leckie 1987; Strawn and Sparks 1999; Hizal and Apak 2006). Davis and Leckie applied the original TLM to fit Cr(VI) and Se(VI) sorption onto iron oxyhydroxide (Davis and Leckie 1980). Hayes and Leckie used the modified TLM on sorption of Cd(II) and Pb(II) (Hayes and Leckie 1987). Dyer utilized the modified TLM to fit sorption data of Pb(II) on ferrihydrite (Dyer et al. 2003).

2.3.4 Multisite Ion Complexation (MUSIC) Model

The MUSIC framework was introduced by Hiemstra et al. (Hiemstra et al. 1989; Hiemstra et al. 1989; Hiemstra et al. 1996). In MUSIC model, the surfaces sites were directly derived from the crystal structure of the mineral.

The first version of MUSIC was based on the Pauling bond valance principle (Pauling 1929). In order for electroneutrality to occur in the bulk of metal oxide, the charge of metal, S, in the metal oxide should be neutralized by that of surrounding oxygens (O). The charge valence can be interpreted in terms of the charge on each S-O bonds. Hence the valence (v) of each S-O bond can be defined as:

$$v = \frac{z}{CN} \quad [29]$$

where z is the charge of the metal ion, and CN is the coordination number of metal ion. The equation suggests that the charge of the amphoteric sites would not be generically defined as in the case of CCM, DLM and TLM (Equations [15-16]). For

example, in iron oxide (goethite, ferrihydrite etc.), Fe has charge of 3+ and hexa-coordinated with oxygens. Hence the valence of the Fe-O bond would be 0.5+ and the resulting equations for the surface sites are:

where $\equiv \text{FeO}$ represents a singly coordinated site (i.e. oxygen is bonded to one Fe atom). Structurally iron oxide would have doubly-coordinated and triply-coordinated sites at the surfaces as well (Hiemstra et al. 1989). Hence equations for doubly-coordinated sites would be:

and for triply-coordinated site:

In the second version of MUSIC, Hiemstra et al. correlated the proton affinity of surface sites with the bond valence surrounding the exposed oxygen (Hiemstra et al. 1996). The relationship is said to be linear and the equilibrium constants for protonation/deprotonation can be thus be calculated directly (Hiemstra et al. 1996):

$$\log K_a = -A \left(\sum_j s_j + V \right) \quad [36]$$

where A is a constant predefined as 19.8, V is the valence of the oxygen atom (-2) and s is the contribution of j bond valence charges from the surrounding atoms/ions.

Arithmetically s can be defined as:

$$\sum_j s_j = \sum_i s_{S,i} + ms_H + n(1 - s_H) \quad [37]$$

where $s_{S,i}$ is the charge contribution from surrounding metal ions, s_H is the bond valence of H-donating bond (0.8), $(1 - s_H)$ denotes the bond valence of H-accepting bond and m and n are the number of each type of bonds, respectively

At the solid-water interface, a singly-coordinated oxygen ($\equiv\text{SO}$) is able to form two bonds with protons in the solution, i.e. $m + n = 2$, whereas a triply-coordinated oxygen ($\equiv\text{S}_3\text{O}$) is allowed to form only a single bond with solution proton ($m + n = 1$). In doubly-coordinated sites ($\equiv\text{S}_2\text{O}$), bonding with hydrogen can be either 1 or 2, depending on the type of mineral (Hiemstra et al. 1996). The ambiguity of this version of MUSIC lies in the number of bonds for doubly-coordinated sites, usually the parameter is determined by the goodness-of-fit with the experimental data and the user's prerogative (Gaboriaud and Ehrhardt 2003; Tournassat et al. 2004).

The contribution by surrounding metal ions (s_S) is calculated in accordance to Brown and Altermatt (Brown and Altermatt 1985):

$$s_S = \exp\left(\frac{R_o - R}{b}\right) \quad [38]$$

where R is the bond length of S-O, R_o is an element-specific distance (Brown and Altermatt 1985) and b is a constant set to 0.37 Å.

Hiemstra et al. have applied MUSIC to wide range of minerals such as gibbsite, goethite, hematite, lepidocrocite, magnetite, silica, rutile and anatase (Hiemstra et al. 1989; Hiemstra et al. 1996; Venema et al. 1998; Hiemstra and Van Riemsdijk 1999; Hiemstra et al. 1999; Bourikas et al. 2001).

2.3.5 Charge Distribution (CD)

This concept also introduced by Hiemstra et al. is departure from treating sorbed ions as point charges (Hiemstra and Van Riemsdijk 1996). Due to the compactness of the double layer, inner-sphere complexes, especially large sorbate (such as carbonates and oxyanions), may occupy both the o-plane and the β -plane concurrently. The resulting charge should therefore be distributed to both planes. Hiemstra extended the application of Pauling bond valence principle into CD concept by providing scenario of silicic acid sorption onto goethite (Figure 2.4).

Figure 2.4 Schematic depicting sorption of silicic acid onto goethite at the o- and β -plane in a bidentate configuration. Ratio of charge allocated to o-plane : β -plane is denoted by distribution factor, f (Hiemstra and Van Riemsdijk 1996).

Where f is the fraction of charge in Si (+4) allocated to the β -plane. Using Pauling bond valence concept, the charge of Fe-O bond is +0.5. If the charge of Si is

distributed equally between both planes Figure 2.4A, each Si-O would have a charge of +1. The resulting charge of o-plane (-1) would be yielded by the arithmetic sum of the charges of Fe-O, Si-O and oxygen (-2). And charge at the β -plane is zero. However if the distribution factor is 0.75, the Si-O bonds would have charge of +1.5 each and Si-OH bonds each +0.5. The resulting o-plane and β -plane would have charge of zero and -1, respectively (Figure 2.4B). The CD concept was particularly useful in achieving fit for sorption of larger multivalent ions. Villalobos et al. and Appelo et al. incorporated CD in TLM to model sorption of carbonate on goethite and ferrihydrite, respectively (Villalobos et al. 2001; Appelo et al. 2002). Stachowicz et al. applied CD model to As(III) and As(V) sorption onto goethite !!! INVALID CITATION !!!).

2.3.6 Minerals with Permanent Charge

Thus far literatures reported discussed applying SCMs on minerals with variable charge only (Figure 2.2A). Modelling minerals with additional permanent charge are more complex and requires extra unknown parameter to account for sorption via permanent charge. Typically permanent charge can be found in basal plane of clays such as smectite, kaolinite, illite etc. Clays have layered structures and permanent charges occurred at the interlayer region (also known as basal plane). They are usually negatively-charged because of isomorphic substitution in the crystal structure (Sposito 1984). Lyklema termed permanent charge as polarized or non-relaxed as it is independent of changes in solution chemistry whereas variable charge is relaxed and charge can be altered by adsorption of other charged ions (such as protons, metals or ligands) (Lyklema 1995). With the presence of permanent charge, the titration curves are parallel to one another as illustrate in Figure 2.2B. There is a PZC for every ionic strength and the point of zero salt effect is notably absent from the graph. PZC decreases with increasing ionic strength. Protonation is higher at low ionic strength and deprotonation higher at higher ionic strength.

Sorption via permanent charge can result in either specified sorption or hydrogen bonding. As illustrated in Figure 2.5, formation of either inner-sphere or outer-sphere complexes at the interlayer region depends on the type of isomorphous substitution (Sposito 1984). James and Parks applied incorporated an exchange constant into TLM to model Marshall and Krinbill data of putnam clay (Marshall and Krinbill 1942; James and Parks 1982). Charlet used TLM to model sorption behaviour on oxisol clays (Charlet 1986). Recently MUSIC model was used to fit titration data of minerals with permanent charge. Gustafsson used the MUSIC model to explain the charging effect of imogolite (Gustafsson 2001). Tournassat et al. compared the fits of a non-electrostatic model with MUSIC model based on the titration data of montmorillonite (Tournassat et al. 2004).

Figure 2.5 Distinct surface complexation of metal cations at the interlayer region of different clays. (A) Inner-sphere (B) Outer-sphere (Sposito 1984).

2.4 Titanium Dioxide

Titanium dioxide (TiO_2) or titania is a naturally occurring mineral. As shown in Table 2.1, the predominant crystal phases found in nature are anatase and rutile. Titania has many advantageous properties. It is widely known to be a good

photocatalyst, absorbing ultraviolet light to form reactive radicals (Hoffmann et al. 1995). Moreover, TiO_2 is resilient to acidic and alkaline conditions. Due to these unique characteristics, TiO_2 can be found in consumer products such as cosmetics, paint and sunscreen. Apart from photocatalytic oxidation, studies have been made to investigate TiO_2 as a sorbent (Yates et al. 1980; Weng et al. 1997; Vohra and Davis 1998; Jakobsson 1999; Yang and Davis 1999; El Shafei et al. 2001; Dutta et al. 2004; Janusz and Matysek 2006; Pena et al. 2006; Tan et al. 2009). The study of TiO_2 as sorbent is important due to its omnipresence in nature. Specifically, they affect the fate and transport of ions and causes attenuation of certain pollutants in nature. Evidently, titanium dioxide is a good candidate for the removal of certain pollutants from water. Naturally occurring bulk TiO_2 , however, has low specific surface areas. This intuitively results in a lower capacity for the uptake of target pollutant. In order to achieve desirable sorption efficacies, there is a need to synthesize a TiO_2 sorbent with high specific surface area. Generally, materials such as nanoparticle and quantum dots would have superior surface area than its other counterparts (nanowires, nanotubes and microspheres). In the field of water treatment and remediation, however, catalysts or sorbents with small dimensions pose another engineering problem. The recovery of these nanoparticles or quantum dots would be very difficult.

As such, studies have been conducted on fabrication of titania microspheres to overcome the separation/recovery problem. Li et al. fabricated TiO_2 microspheres for photocatalytic oxidation (Li et al. 2003). They claimed that these porous microspheres have high settling velocity which aids in the separation of material from treated water. In a separate study, microsphere was tested for separation efficiency by membrane filtration (Pan et al. 2008). It was found that, as compared to using P25 nanoparticles, higher permeate flux can be achieved during separation of TiO_2 microsphere (Figure 2.6A). Studies have shown that the one-dimensional materials can also be efficiently separated by membrane filtration (Zhang et al. 2009) (Figure 2.6B). One-dimensional nanomaterials are often used to describe structures with high aspect ratios as such the smaller dimension is in the nano-range. Among the one-dimensional nanomaterials, tubular morphology has the highest

surface area. Both outer and inner wall of the tube can be possible sites for reactions. Therefore, titanium nanotube is a good candidate as a sorbent due to its high BET surface area and its non-toxicity.

Figure 2.6 Higher permeate flux achieved during membrane separation of (A) microspheres (Pan et al. 2008) and (B) nanowires (Zhang et al. 2009).

2.4.1 Fabrication of Titanium Dioxide Nanotubes

There are many methods in producing TiO₂ nanotubes. Subsequent review gives an introduction to more commonly-used techniques. In general, synthesis of TiO₂ nanotubes can be categorized into 3 methods:

(i). Template-assisted. This method utilized an existing “mould” and filling it with TiO₂ precursor. A commonly used template in nanotube fabrication is the AAO (anodized aluminium oxide) membrane (Imai et al. 1999; Chen et al. 2005; Zhang et al. 2008). This method enables production of anatase nanotubes without calcination at high temperature. However, diameter of the nanotube is limited by the pore-size of AAO, usually 20 – 200 nm. Figure 2.7A shows anatase nanotubes fabricated from an AAO with 200 nm pores. In addition, templates are sacrificial articles and often cannot be re-used; they are usually removed before the nanotubes can be applied. Moreover, the purity of nanotubes may be compromised. Complete

removal of template from nanotubes is, in fact, not possible. Consequently residues may contaminate the nanotubes.

Figure 2.7 Titanium dioxide nanotubes fabricated from (A) template-assisted synthesis (Imai et al. 1999) and (B) anodization synthesis (Mor et al. 2005).

(ii). Anodization. Nanotube also can be produced by oxidizing of titanium metal. A well-reported method involves using titanium foil as an anode in a redox cell (Mor et al. 2005). The TiO_2 nanotubes are formed as a result of electric voltage and corrosive electrolyte. Anodization is versatile in that the diameter of tube can be adjusted from 15 to 120 nm (Bauer et al. 2006) (Figure 2.7B). These nanotubes are highly aligned and supported by the remaining Ti foil.

(iii). Hydrothermal. This is a straightforward method which involves heating TiO_2 precursor under moderate temperatures in a sealed vessel. The air-tight apparatus thereby creates an environment with relatively high pressure. Various morphologies, such as sheet, wire and tube, have been reported using this technique (Wu et al. 2006; Bavykin and Walsh 2009). The method of fabricating TiO_2 nanotube was discovered by Kasuga et al. (Kasuga et al. 1998). Hydrothermal is useful for large-scale production, it is limited only by the size of the vessel. Its energy consumption is minimal as the temperature for nanotubes formation is only 150 °C.

Among the discussed methods of fabricating nanotubes, hydrothermal is able to achieve the tube with the smallest diameter. The as-produced nanotube can have an

outer diameter of 10 nm or less. Its BET surface area can be as high as 250 m²/g (Bavykin et al. 2004). Due to its small diameter and high surface area, hydrothermal was the preferred synthesis method for this study.

Chapter 3 Methodology

3.1 Chemicals

All chemicals are reagent grade unless otherwise stated. Sodium hydroxide (NaOH) pellets were supplied by VWR BDH. Nitric acid (HNO₃) and sodium nitrate (NaNO₃) were supplied by Sigma Aldrich. Titanium dioxide powder was from Merck. Stock solutions of all divalent cations were prepared from reagent grade nitrate salts. The rationale of choosing nitrate is to ensure interference of anion to sorption is minimal. Nitrate is known to bind weakly to surface of metal oxides (Hayes 1987). Thereby, most, if not all, sites were made available for Cd-sorption studies.

3.2 Synthesis

Titanium dioxide powder was used as precursor for the synthesis of sodium titanate nanotubes (TNT). The powder was used as-received and no pre-treatment was conducted. Synthesis procedure was a modified version of Kasuga et al. (Kasuga et al. 1998). Typically, 4 g of TiO₂ powder was weighed using mass balance (Mettler Toledo, Precision Balance) and added to 50 mL NaOH solution (10 M). The mixture was stirred for 1 day and loaded into an acid digestion bomb (125 mL) for hydrothermal treatment at 150 °C, 2 days. As-synthesized TNT were retrieved from the Teflon cup and washed with 0.001 M HCl in a 1 L HDPE bottle. After 1 day, the TNT were separated (centrifuged at 10 000 rpm for 30 min) and washed with de-ionized water. The washing process was repeated until solution has neutral pH and a conductivity of 10⁻⁶ S/cm.

The TNTs were freeze dried and added into de-ionized water to form slurry of known concentration. The slurry was subjected to conditioning in an end-over-end mixer for 2 weeks. To ensure homogenous TNT stock the slurry was transferred to

a settling column to separate larger aggregates. After 30 min the supernatant in the column was retrieved and the concentration of TNT in supernatant was calculated by determining the dry weight of the settled particles. The supernatant suspension was stored and used for subsequent experiments.

3.3 Experiments

3.3.1 Titration

Discontinuous batch titration was conducted in this work (Sigg and Stumm 1981). Suspension of 12.5 g/L TNT with appropriate ionic strength (IS) was prepared and divided into aliquots of 20 mL. pH were adjusted with 0.25 M HNO_3 and/or NaOH. In order to avoid the presence of carbonate at high pH, all solutions involved in titration were evacuated under vacuum for 2 days before transferring into nitrogen atmosphere. The pH value was measured using a Horiba pH meter/electrode. The values were recorded after stabilizing for 5 – 10 min.

3.3.2 Kinetics

Kinetic studies were performed to determine the duration required to achieve a pseudo-equilibrium. Two 1 L HDPE bottles containing 0.05 g/L TNT were adjusted to pH 3 and 4.8. Third bottle of DI water (without TNT) were adjusted to pH 3. At various time intervals 10 mL sample were collected, filtered (0.2 μm Nylon, Sartorius) and preserved with 20 μL HNO_3 (70%). Samples were measured for Cd, Na and Ti using ICP-OES.

3.3.3 Batch Tests

Sorption edge and isotherm studies were conducted with samples of 50 mL each containing appropriate concentrations of TNT and ionic strength. This was followed by pH adjustment using HNO_3 and/or NaOH. Finally, the target divalent cation was spiked into the suspension prior to equilibrium mixing for 24 hr. The pH values

before and after equilibration were recorded. Unless otherwise state, all pH values in subsequent figures should be taken as final pH (i.e. after equilibration). The solids were separated from solution by centrifuging at 10 000 rpm, 30 min and passing the supernatant through a syringe filter (0.2 μ m Nylon, Sartorius). The equilibrium concentrations (C_e) in the filtrates were analysed using ICP-OES. Sorption efficiency which is the percentage of divalent cation being sorbed by TNT was calculated by:

$$\%_{\text{sorbed}} = \frac{C_o - C_e}{C_o} \times 100\% \quad [39]$$

A blank sample (i.e. without TNT) was prepared for each set of test to determine the real C_o . All equilibration were performed in the dark.

3.4 Equipments

3.4.1 Field-Emission Scanning Electron Microscope (FESEM)

In this work, morphology of TNT was viewed using Jeol JSM-6340F which has a cold-emission source. Electrons are produced by a cold cathode field-emission gun. All micrographs are obtained from secondary electrons and accelerating voltage of 15 kV. In order to prevent surface charging during capturing of image, samples were sputtered-coated with platinum for 60 seconds prior to loading into FESEM.

3.4.2 Transmission Electron Microscope (TEM)

TEM with a field-emission source (Jeol JEM 2100F) were used for observation TNT. Accelerating voltage of electron source was fixed at 200 kV. TEM samples were prepared by dispersing TNT sample in ethanol using ultrasound bath. After 1 min of ultrasonication, few drops of the suspension were dripped onto a carbon holey grid, allowing each drop to dry before applying the next.

3.4.3 X-Ray Diffraction (XRD)

X-ray diffractometer (XRD, Bruker AXS D8 Advance) with Cu K α ($\lambda = 1.5418 \text{ \AA}$) was used to analyze crystal phase of the samples. Scanning speed was 0.05°/s, 40 kV, 40 mA.

3.4.4 Nitrogen Sorption-Desorption

Nitrogen sorption was performed on a Quantachrome Autosorb-1 Analyzer. To avoid any change in crystallinity and morphology of TNT, samples were freeze-dried and transferred for out-gassing at 100 °C for 24 hours.

3.4.5 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Cadmium and other cations were measured using ICP-OES (PerkinElmer Optima 2000). Five-point calibration using standards were performed prior to each measurement. All calibration curves had best-fit values of at least 0.999. Each sample was measured thrice and reported value was the mean. The sensitivity of ICP measurement was given in Appendix B. Measurement 50 replicates of same cadmium solution ($2 \times 10^{-6} \text{ M}$) was conducted.

3.4.6 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analyses were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below $2.66 \times 10^{-7} \text{ Pa}$ at room temperature. Photoemission spectra were recorded by a Kratos Axis Ultra spectrometer equipped with a standard monochromatic Al K α excitation source ($h\nu = 1486.71 \text{ eV}$). The pass energy and step size of low-resolution XPS scan were performed at 160 and 1 eV, respectively. For the high-resolution XPS scan, the parameters above were adjusted to 40 and 0.1 eV. Due to surface charge effects, the binding energy (BE) scale was calibrated using C 1s peak at 284.8 eV. Background were corrected with Shirley and peaks were fitted with Gaussian-Lorentzian (GL) function. XPS samples were lightly dust onto a double-sided carbon tape (Moulder 1995).

3.4.7 X-Ray Absorption Spectroscopy (XAS)

Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University.

Synchrotron radiation was used for XAS studies. Absorption spectra of cadmium K-edge (26,711 eV) were collected at wiggler beam line 4-1. Double-crystal monochromator Si(220) was liquid nitrogen cooled and positioned at 90° to detune incident x-rays to desired energy. Data were collected at room temperature in transmission mode. Ionization chambers (I_0 , I_1 and I_2) were filled with argon gas. The samples and standard (cadmium foil) were placed 90° vertically from incidence x-ray (Figure 3.1).

Figure 3.1 Side view schematic of XAS setup in transmission mode (not according to scale).

During transportation to SSRL, the centrifuged solids were kept moist in a wet paste form to simulate in-situ condition. Shallow well was made by taping scotch tapes onto a strip of Kapton tape. Wet pastes of cadmium-sorbed TNT were spread into the cavity. It is important to ensure EXAFS sample is smooth and homogeneous and no pinholes should be present inside. Single scan often results in noisy and distorted spectrum at high k . In order to avoid noisy data, at least four replicate scans were performed for each sample.

3.5 Modelling Programme and Fixed Parameters

In this work, computations involving speciation, titration and sorption were performed using PhreePlot (Kinniburgh and Cooper 2009). Equilibrium constants used for calculations were obtained from minteq.v4.dat (Allison et al. 1991). For the modelling of titration and sorption edges data a charge distribution multisite ion complexation model (CDMUSIC) was chosen (Hiemstra and Van Riemsdijk 2006). Samples of the programming language used in this work can be found in Appendix D.

CDMUSIC was used to fit experimental data from titration and sorption tests. The basal plane of the nanotube is the solid-water interface and its singly and doubly coordinated oxygen atoms were identified as potential sites for ion complexation. From crystallographic calculation the density of each site is 2.9 nm^{-2} . In addition the ion-exchange can occur at the interlayer of basal planes and cation exchange capacity from crystallographic calculation is 6.629 meq/g. The capacitances of inner and outer Stern layers were fixed at 0.9 F/m^2 (Hiemstra and Van Riemsdijk 2006).

Chapter 4 Characterization of Titanate Nanotube

4.1 Introduction to Material Characterization

In order to understand the interaction of divalent cations with titanate nanotube, we would first need to understand the intrinsic properties of the sorbent. Various characterization technique was exploited to probe titanate nanotubes. The more widely used equipments are transmission electron microscopy (TEM) and x-ray diffraction (XRD) (Chen et al. 2002; Ma et al. 2003; Yang et al. 2003). Other powerful techniques such as, x-ray absorption spectroscopy (XAS) from synchrotron radiation and x-ray electron microscopy (XPS), was also used to determine the inter-atomic distances of TNT (Ma et al. 2005; Gateshki et al. 2007).

Using electron and x-ray diffraction patterns, Chen et al. (2002), proposed that TiO_2 based nanotubes fabricated from alkaline hydrothermal reaction are multi-walled nanotubes and is asymmetrical. The formation of nanotube is due to the scrolling of TiO_2 based sheets which resulted in the asymmetric morphology (Figure 4.1).

Figure 4.1 Structure of titanate nanotube as proposed by Chen et al. (2002)

On the other hand, Ma et al. (2005) suggested a different lattice configuration to that of Chen et al. (2002). Using identical characterization tools (electron and x-ray diffractions), the former authors claimed that the nanotubes should be of lepidocrocite arrangement (Figure 4.2) rather than the tritanate nanotube as proposed by Chen et al. (2002).

Figure 4.2 Different lattice configurations of TiO₂ based nanotubes as proposed by (A) Chen et al. (2002) and (B) Ma et al. (2005).

As such material characterization techniques (such as XRD, SAED, FESEM, TEM, gas sorption-desorption and acid-alkali titration) were performed on virgin TNT to understand its crystallinity, textural morphology and surface properties. The synthesis of TNT was explained in §3.2. Details of equipments and operating conditions were described in the following §4.2.

4.2 Methodology

4.2.1 Field-Emission Scanning Electron Microscope (FESEM)

In this work, morphology of TNT was viewed using Jeol JSM-6340F which has a cold-emission source. Electrons are produced by a cold cathode field-emission gun.

All micrographs are obtained from secondary electrons and accelerating voltage of 15 kV. In order to prevent surface charging during capturing of image, samples were sputtered-coated with platinum for 60 seconds prior to loading into FESEM.

4.2.2 Transmission Electron Microscope (TEM)

TEM with a field-emission source (Jeol JEM 2100F) were used for observation TNT. Accelerating voltage of electron source was fixed at 200 kV. TEM samples were prepared by dispersing TNT sample in ethanol using ultrasound bath. After 1 min of ultrasonication, few drops of the suspension were dripped onto a carbon holey grid, allowing each drop to dry before applying the next.

4.2.3 X-Ray Diffraction (XRD)

X-ray diffractometer (XRD, Bruker AXS D8 Advance) with Cu K α ($\lambda = 1.5418 \text{ \AA}$) was used to analyze crystal phase of the samples. Scanning speed was 0.05°/s, 40 kV, 40 mA.

4.2.4 Nitrogen Sorption-Desorption

Nitrogen sorption was performed on a Quantachrome Autosorb-1 Analyzer. To avoid any change in crystallinity and morphology of TNT, samples were freeze-dried and transferred for out-gassing at 100 °C for 24 hours.

4.3 Crystallographic Information

4.3.1 X-Ray Diffraction (XRD)

To ensure that phase change occurred during hydrothermal synthesis, x-ray diffraction (XRD) was performed on both TNT product and Merck TiO₂ precursor (Figure 4.4A and B). The as-prepared TNT has relatively less distinct peaks (Figure 4.4A). The structure of as-prepared titanate is still a controversy and various atomic

configuration of this material have been put forward, including monoclinic trititanate, $H_2Ti_3O_7$ (Chen et al. 2002), tetratitanates, $H_2Ti_4O_9$ (Nakahira et al. 2004), lepidocrocite titanate, $H_xTi_{2-x/4}\square_{x/4}O_4$ (Ma et al. 2003) and orthorhombic titanate, $H_2Ti_2O_4(OH)_2$ (Yang et al. 2003). After comparisons of our patterns with the JCPDF database, we found that our patterns matched closely with that of $Na_2Ti_3O_7$ (JCPDF 72-0148). Depending of the procedures of washing, Na and proton are inter-changeable:

From the left hand side of the above equation, as-synthesized TNT are often in Na^+ form due to the basic condition of the hydrothermal process (§3.1). Under acid washing, the TNT loses Na^+ for H^+ to form hydrogen titanate, $H_2Ti_3O_7$. It is noted that the structures of TNT and hydrogen titanate are similar but differs in its lattice cell orientation (Figure 4.3). The former has a stacking sequence of AAA and space group $P2_1/m$ whereas latter is ABA-stacked and space group $C2/m$ (Feist and Davies 1992).

Figure 4.3 of Na₂Ti₃O₇ unit cell (2×2) as projected down the [010] axis. Dimensions of the monoclinic unit cell are $a = 8.571 \text{ \AA}$, $b = 3.804 \text{ \AA}$, $c = 9.135 \text{ \AA}$ and $\beta = 101.57^\circ$ (Andersson and Wadsley 1961). Lines in bold denote position at $y = \frac{3}{4}$ and normal lines at $y = \frac{1}{4}$.

The peaks of precursor were similar to the diffraction patterns of anatase crystal (JCPDF 21-1272). By using diffracted peaks, the Scherrer's equation can be used to estimate the crystal size, t :

$$t = \frac{0.9\lambda}{B \cos \theta_B} \quad [41]$$

where λ is the wavelength of x-ray ($\text{\AA}$), B can be obtained by measuring full width half maximum of the most intense peak (radians, 2θ), and θ_B is the angle of the peak (radians).

From Figure 4.4B, the most intense peak, (101) plane at 25.3° , has a narrow full width half maximum distance. Thereby indicating this powder has a relatively large crystal size. Evidently, the TNT produced from alkaline hydrothermal treatment was different from the precursor. The peak positions of TNT are different from that of anatase. This showed that TiO₂ anatase powder has undergone a change in crystallinity after hydrothermal treatment for 2 days at 150°C .

Figure 4.4 X-ray diffraction patterns of (A) TNT and (B) Merck TiO₂. Peaks are indexed according to JCPDF 72-0148 and 21-1272, respectively.

4.3.2 Selected Area Electron Diffraction (SAED)

Figure 4.5 shows the ring patterns as result of electron diffraction by the lattice planes of TNT. Each ring represents a crystal plane present in the TNT. Some intense rings which can be clearly observed from Figure 4.5 were indexed according to Na₂Ti₃O₇, titanate phase. Crystal planes indices and d-spacings were obtained from JCPDF 72-0148:

Figure 4.5 Selected area electron diffraction patterns of TNT. Indices and d-spacings were obtained from JCPDF 72-0148.

4.4 Morphological and Textural Information

4.4.1 FESEM Micrographs

FESEM images were captured as a preliminary characterization technique. This tool is useful for observation of sample surface morphology at the micro and nano scales. Figure 4.6 shows an image of as-synthesized TNT at x1,500 magnification. It is clear that TNT exists as particles possibly due to the agglomeration of nanotubes. Size of each particle varies from 2 – 5 μm . Tubular morphology is unable to be observed at this magnification.

Figure 4.6 Low magnification FESEM image of as-synthesized TNT. The nanotubes evidently agglomerate *in vacuo*. Samples were coated with Pt.

At higher magnifications (Figure 4.7 and Figure 4.8), it is evident that each particle consists of many individual tubes aggregating together. The dimensions of each tube can be clearly estimated from Figure 4.8. It is however important to note that these TNT have been coated with Pt nanoparticles for 60 sec and consequentially, actual dimensions of nanotubes cannot be determined from these images.

Figure 4.7 FESEM image of as-synthesized TNT at high magnification. Samples were coated with Pt.

Figure 4.8 FESEM image of as-synthesized TNT at high magnification. Samples were coated with Pt.

4.4.2 TEM Micrographs

Due to the limitation of the FESEM equipment, TEM was used to determine the dimensions and crystallography of the nanotubes. As observe from Figure 4.9, the nanotubes have high aspect ratio with lengths in the range of sub-micrometer. The aspect ratio observed here is in accordance with the morphology seen in FESEM images. A typical nanotube has inner diameter of 5 nm and outer diameter of 10 nm (Figure 4.10). According to IUPAC (Sing et al. 1985), pores with diameters ranging from 2 to 5 nm were catagorized as mesopores.

Figure 4.10 shows an edited high-resolution TEM micrograph of a single nanotube. Each tube is the result of scrolling of the titanate sheets along its y or [010] axis. The sheets are parallel to the (100) plane and each anionic sheet was said to have a structural formula of $\text{Ti}_3\text{O}_7^{2-}$ (Andersson and Wadsley 1961; Feist and Davies 1992).

Figure 4.9 TEM image of as-synthesized TNT.

Figure 4.10 High resolution TEM image of TNT. Image was modified to indicate the spacing of the titanate sheets and the longitudinal axis of the nanotube.

During the hydrothermal process, these $\text{Ti}_3\text{O}_7^{2-}$ sheets actually scrolled along the [010] axis forming an asymmetrical nanotube (Chen et al. 2002). Distance between each sheet is the d-spacing of (100) plane ($d_{(100)} = 0.84 \text{ nm}$). While the ends of the tube are defined as (020) plane (Chen et al. 2002). It has been reported that sodium atoms which are intercalated within the sheets are capable of exchanging their places with various divalent cations. Sun and Li found that sodium was absent after uptake of various transition metals ions (Sun and Li 2003). Bavykin and Walsh reported possibility of simultaneous intercalation of monovalent ions and release of protons (Bavykin and Walsh 2007).

4.4.3 Sorption-Desorption Isotherm

Figure 4.11 shows the sorption-desorption isotherm. With reference to IUPAC the curves is categorized as a Type IV isotherm with Type H3 loop (Sing et al. 1985).

In Type IV isotherm, the hysteresis of sorption-desorption suggests the phenomenon of capillary condensation occurring in mesopores while the Type H3 loop resulted from slit-shaped pores of sample. This is in accordance with the morphology of the nanotubes observed in §4.4.2 in which the longitudinal pores were created from scrolling of titanate sheets.

Figure 4.11 Sorption-desorption isotherm of TNT. BET surface area of triplicate samples was found to be $206 \pm 2.4 \text{ m}^2/\text{g}$.

4.4.4 Pore-Size Distribution and Surface Area

From the micrograph observation and isotherm analysis, we should expect a peak at mesopore range (2–5 nm). Figure 4.12 shows the BJH desorption pore size distribution. Clearly, a distinct peak can be observed at 2-3 nm which could be attributed to the pore channel of the nanotubes which is in the same order as the diameter observed in the TEM micrographs (§4.4.2). In addition, a broad second peak at 10-20 nm was found in the pore-size distribution curve. Formation of macropores was attributed to the agglomeration of the nanotubes (Sun and Li 2003). The presence of bimodal pore size distribution indicates possible modes of mass transfer pathways in aqueous condition. Firstly, sorbate will diffuse from the bulk solution to the outer surface of nanotubes relatively quickly. In contrast, solute

entering the pore of tube will have a longer reaction time. Rate-limiting step would be the putative solid diffusion on solute into the interlayer of anionic titanate sheets. This process would be discussed with reference to the kinetics data (§5.7).

Figure 4.12 Desorption portion of BJH pore-size distribution. Bimodal-type distribution is attributed to the pore of the nanotube and the intra-pores formed from the agglomeration of tubes.

4.5 Surface Charge

The surface charge of TNT was obtained by performing acid-base titration at three ionic strengths (0.001, 0.01 and 0.1 M). The understanding of TNT surface charge is pertinent prior to studying the cations sorption behaviours. The apparent proton surface charge density (σ_H) was calculated from Stumm and Morgan (Stumm and Morgan 1996):

$$\sigma_H = \frac{QF}{s} = \frac{F}{as}(C_A - C_B + [OH^-] - [H^+]) \quad [42]$$

where F is Faraday constant (96490 C/mol), s is the specific surface area (m^2/g), and a is sorbent concentration (g/L). C_A and C_B denote the amount of acid and base added (M). The protocol for titration studies was described in §3.3.1. Figure 4.13 shows titration curves conducted at different ionic strength (IS). It is evident that TNT is positively-charged at acidic condition and negatively-charged at basic condition. Each curve has a point of zero charge (PZC) unique to the particular ionic strength. The curves are parallel and do not intersect. Increasing IS causes left-shift of titration curve and reduces PZC. In addition when $\text{pH} < \text{PZC}$, TNT is less protonated at higher ionic strength. High concentration of Na^+ ion competes with and reduces the amount of protons being sorbed. When $\text{pH} > \text{PZC}$, effect of deprotonation is lesser at lower ionic strength. These characteristics of TNT titration curves are similar to clays reported in literature (Kraepiel et al. 1998). The shape of titration curves can be explained by the origin of the charges. Titanate nanotube is different from bulk anatase or rutile. The titanate nanotube has a layered structure and two types of charges. At the solid-water interface hydroxyl groups ($\equiv\text{TiOH}$) are variably-charged and permanently-charged sites ($\equiv\text{Ti}_3\text{O}_7^{2-}$) are located within the interlayer which is also the walls of the tube. Sodium ions intercalated at the interlayer can be exchanged with other monovalent ions (Izawa et al. 1985; Bavykin and Walsh 2007).

Figure 4.13 Titration curves of TNT under different ionic strengths. Each point represent aliquot of 20 mL. TNT = 12.5 g/L. Discontinuous batch titration is performed under nitrogen atmosphere.

4.6 Conclusion

From this chapter, FESEM characterizations have shown that sample produced from hydrothermal at 150 °C for 2 days had tubular morphology. From SAED and TEM, the nanotubes had a distinct titanate crystal phase. More importantly, nitrogen sorption-desorption shown that titanate nanotubes had high specific surface area of 206 m²/g. This suggests a potentially high capacity being available for the uptake of target divalent cations. As such, in-depth batch tests were conducted to substantiate the above hypothesis.

Chapter 5 Sorption Capacity and Selectivity of Titanate Nanotube

5.1 Introduction to Theory of Hard and Soft Acids and Bases (HSAB)

In order to know the feasibility of TNT in the removal of heavy metals from water, the sorbent was tested on seven target divalent cations (calcium, nickel, copper, zinc, strontium, cadmium and lead).

The HSAB method, which is used for describing reactions between metal ions and ligands, was developed by Pearson (Pearson 1963). HSAB theory can be used to predict the stability of the bond formed by these reactions. The assumptions of theory are that:

- (i). electrons are involved in the bonding
- (ii). in the resulting product, one component will act as acid and the other as base.

Acid is the electron acceptor and positively charged whereas base is the electron donor and negatively charged. Pearson used terms “hard” and “soft” to describe the bonding nature of the acids and bases. From Table 5.1 and Table 5.2, it can be observed that acids and bases that are hard, tend to have relatively smaller sizes and slightly polarizable. The converse is true for the soft species. Pearson proposed a rule to predict the binding behaviour of acids and bases: hard acids bind strongly to hard bases and soft acids bind strongly to soft bases (Pearson 1963). In general the hard-hard interactions tend to form bonds of ionic nature (electrostatic) while soft-soft binding tend to result in covalent bonds.

Table 5.1 Characteristics of hard and soft acids (Leckie and Tang 2010).

Acids Property	Hard Acids	Soft Acids
Polarizability	Low	High
Electropositivity	High	Low
Positive charge or oxidation state	Large	Small
Size	Small	Large
Types of bonds	Ionic	Covalent
Outer electrons on donor atoms	Few and not easily excited	Several and easily excited

Table 5.2 Characteristics of hard and soft bases (Leckie and Tang 2010).

Bases Property	Hard Bases	Soft Bases
Polarizability	Low	High
Electronegativity	High	Low
Negative charge	Large	Small
Size	Small	Large
Types of bonds	Ionic	Covalent
Empty orbitals on acceptor atoms	High energy and inaccessible	Low lying energy and accessible

5.2 Methodology

5.2.1 Kinetics

Kinetic studies were performed to determine the duration required to achieve a pseudo-equilibrium. Two 1 L HDPE bottles containing 0.05 g/L TNT were adjusted to pH 3 and 4.8. Third bottle of DI water (without TNT) were adjusted to pH 3. At various time intervals 10 mL sample were collected, filtered (0.2 µm Nylon, Sartorius) and preserved with 20 µL HNO₃ (70%). Samples were measured for Cd, Na and Ti using ICP-OES.

5.2.2 Batch Tests

Sorption edge and isotherm studies were conducted with samples of 50 mL each containing appropriate concentrations of TNT and ionic strength. This was followed by pH adjustment using HNO_3 and/or NaOH . Finally, the target divalent cation was spiked into the suspension prior to equilibrium mixing for 24 hr. The pH values before and after equilibration were recorded. The solids were separated from solution by centrifuging at 10 000 rpm, 30 min and passing the supernatant through a syringe filter (0.2 μm Nylon, Sartorius). The equilibrium concentrations (C_e) in the filtrates were analysed using ICP-OES. Sorption efficiency which is the percentage of divalent cation being sorbed by TNT was calculated by:

$$\% \text{ sorbed} = \frac{C_o - C_e}{C_o} \times 100\% \quad [39]$$

A blank sample (i.e. without TNT) was prepared for each set of test to determine the real C_o . All equilibration were performed in the dark.

5.2.3 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Cadmium and other cations were measured using ICP-OES (PerkinElmer Optima 2000). Five-point calibration using standards were performed prior to each measurement. All calibration curves had best-fit values of at least 0.999. Each sample was measured thrice and reported value was the mean. The sensitivity of ICP measurement was given in Appendix B. Measurement 50 replicates of same cadmium solution ($2 \times 10^{-6} \text{ M}$) was conducted.

5.3 Sorption Isotherm

Figure 5.1 shows the respective sorption isotherms. The sorption data were fitted using Langmuir isotherm:

$$q = \frac{q_m K_{ads} C_e}{1 + K_{ads} C_e}$$

[43]

where q is the amount of cation sorbed at equilibrium (mol/g), q_m is the sorption capacity of TNT (mol/g), K_{ads} is Langmuir sorption constant (L/mol), and C_e is the concentration of solution cation at equilibrium (mol/L). Langmuir isotherm describes sorbate forming monolayer on the sorbent surface. In this work the experiments were conducted at pH 3 and the values before and after equilibrium did not fluctuate by more than 0.02 pH units.

Figure 5.1 Sorption isotherms of divalent cations on TNT. Lines are Langmuir isotherms. Error bars represents standard deviation of triplicates. TNT = 0.05 g/L, IS = 0.1 M, pH_{final} 3 ±0.02.

The sorption capacity of TNT for divalent cations is $\text{Pb} \gg \text{Cd} > \text{Cu} > \text{Zn} > \text{Ca} > \text{Sr} > \text{Ni}$. Surface hydroxyl groups of TNT are amphoteric and positively charge under acidic condition. At pH 3, nonetheless, TNT exhibits high capacities for Pb, Cd and Cu. Sequences of sorption capacities are unique to each sorbent. Hydrous manganese oxide has order of $\text{Pb} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Cd} > \text{Sr} > \text{Ca}$ (Stumm and Morgan 1996) while hydrous ferric oxide has binding sequence of $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni} > \text{Ca}$ (Tonkin et al. 2004). Generally, transition and post-transition cations tend to have better binding affinity than alkaline earth cations. According to the hard and soft acids and bases (HSAB) theory, transition and post-transition cations are either soft or borderline acids whereas alkaline earth cations are hard acids (Huheey et al. 1993). Soft acids have higher acidity and bind more readily to metal oxides than hard acids. They are unaffected by surface charge of sorbent and can bind at low pH even when sites are protonated. In contrast, hard acids such as Ca and Sr, are able to bond only when pH is higher and surface is deprotonated (Hayes 1987). Despite aqueous hydroxyl (OH^-) being labeled as a hard base (Huheey et al. 1993), the hydroxyl functional groups on TNT is different. This is because the oxygen in OH^- sites has additional coordination to titanium atom(s). These local coordinations (singley, doubley or tripley), consequentially, increases the affinity for metal cations. As shown in Figure 5.1, TNT shows higher affinity for relatively softer acids (Pb, Cd, Cu and Zn). Therefore TNT should be considered a soft base. In addition, the increasing trend of experimental data suggests that the Langmuir Isotherm is unable to fully describe the data points as the equilibrium concentration has not plateau.

5.4 Kurbatov Plot

Figure 5.2 show the sorption efficiencies of TNT on seven divalent cations as a function of pH. The edges are spread across the pH range from 4–11. Qualitatively all cations have lower uptake at acidic condition than basic condition. The selectively order of cations can somewhat be observed from this plot. However cations precipitate at different pH and high uptake of certain cation (nickel at pH 10)

may be due to both sorption and precipitation. A more precise method of illustrating the sorption behaviour would be to convert data in Figure 5.2 into a Kurbatov plot.

Figure 5.2 Sorption edges of divalent cations. TNT = 0.005 g/L, IS = 0.1 M, $C_o = 10^{-5}$ M.

This empirical method was first presented by Kurbatov et al. (Kurbatov et al. 1950) to describe sorption behavior as a function of pH. Essentially, it is a transformation of sorption edge into a linear curve by plotting distribution ratio versus pH in a semi-logarithmic plot. Distribution ratio, D , is the proportion of cation on TNT to cation in solution:

$$D = \frac{\%sorbed}{100 - \%sorbed} = \frac{C_o - C_e}{C_e} \quad [44]$$

where %sorbed denotes the sorption efficiency, C_o and C_e are the initial and equilibrium concentrations of cation (mol/L). It was said that the slope of Kurbatov plot describes the ratio of protons and cations exchanged (Kinniburgh and Jackson 1981). Intersection of curve with $\log D = 0$ is known as pH_{50} , the point where $\log D$

is zero and sorption efficiency is 50%. Table 5.3 list the value of pH_{50} for the divalent cations. Among the divalent cations, Pb is highest (Figure 5.3) and, logically, the selectivity is similar to the order observed trend in Langmuir isotherms (Figure 5.1). From Figure 5.3, it is evident the plots are grouped together according to their position in the periodic table. Post-transition Pb which has the highest log D for a given pH, is above the plots of transition cations (Cd, Cu and Zn). The alkaline earth cations (Ca and Sr), which have the least affinity for TNT, is position towards the bottom right corner of the graph. Generally the slope of each plot (Table 5.3) is in the decreasing order of post-transition cation > transition cations > alkaline earth cations. The order is in accordance with reported trend (Kinniburgh and Jackson 1981).

Figure 5.3 Effect of pH on distribution coefficient, D (Kurbatov plot). TNT = 0.005 g/L, IS = 0.1 M, $C_o = 10^{-5}$ M. Data points with more than 90% sorption or pH exceeding precipitation were not included in the plot. Linear regression parameters listed in Table 5.3.

Table 5.3 Linear regression parameters of Kurbatov plot.

Divalent Cation	log D = m × pH + C		R ²	pH ₅₀ ^a
	slope, m	intercept, C		
Pb	0.502	-1.678	0.995	3.34
Cd	0.209	-1.217	0.989	5.82
Cu	0.272	-1.732	0.989	6.37
Zn	0.363	-2.469	0.991	6.80
Ni	0.320	-3.242	0.917	10.13
Ca	0.174	-1.927	0.922	11.07
Sr	0.187	-2.312	0.999	12.36

^a define as the pH value when %sorbed = 50%

5.5 Correlation of Sorption Capacity

To understand the effect of intrinsic cation parameters have on the sorption capacities, the Langmuir parameters (q_m and K_{ads}) were plotted against the intrinsic parameters listed in Table 5.4.

Table 5.4 Langmuir and intrinsic parameters for selected divalent cations

Divalent Cation	Langmuir Parameters		pK _{MeOH} ^a	Electro- negativity, χ ^b	Pearson Hardness, η ^c	Charge-Size Function, Z^2/r ^d
	log q_m	log K_{ads}				
Pb	-2.896	6.051	7.60	1.87	8.46	10.30
Cd	-3.412	5.821	10.10	1.69	10.29	9.40
Cu	-3.474	5.034	7.50	2.00	8.27	11.80
Zn	-3.814	4.557	9.00	1.65	10.88	11.70
Ni	-4.708	4.310	9.90	1.91	8.50	12.40

Ca	-3.997	4.377	12.70	1.00	19.52	9.00
Sr	-4.323	4.817	13.18	0.95	16.30	7.80

^a $pK_{MeOH} = -\log K_{MeOH}$ and K_{MeOH} is hydrolysis constant
 $Me^{2+} + H_2O \leftrightarrow MeOH^+ + H^+$. From minteq.v4.dat (Allison et al. 1991).

^b From Table 5.6 of (Huheey et al. 1993).

^c From Table I of (Pearson 1988).

^d $\times 10^{28}$ C²/m. From Table 9.3 of (Huheey et al. 1993).

It was found that $\log q_m$ varies linearly with first hydrolysis constant, pK_{MeOH} , and electronegativity, χ , of the cation. Figure 5.4 displays the relationship between $\log q_m$ and pK_{MeOH} . In the semilog plot, the sorption capacity of TNT increases with higher hydrolysis constants. As hydrolysis constants describe the affinity of the cation to bond with OH⁻ and is related to the binding constants of cation onto metal oxide (Dzombak and Morel 1990) it is reasonable to apply correlation of $\log q_m$ - pK_{MeOH} to predict sorption capacities of other divalent cations. Various studies have tried to linearly correlate experimental or modeling results with intrinsic parameters of cations. Dzombak and Morel (Dzombak and Morel 1990) used linear-free energy relationship to associate hydrous ferrous oxide binding constants with hydrolysis constants. Reddad et al. (Reddad et al. 2002) obtained good fits for linear regression of sorption rate and sorption capacity with hydrolysis constants of heavy metal cations.

Figure 5.4 Correlation of sorption capacity with hydrolysis constant. Linear regression (solid line) and 95% confidence intervals (dotted lines) are shown. Ni was not considered in regression.

In general, electronegativity increases across the periodic table from left to right; alkaline earth cations have lower electronegativities than heavier transition cations. From Figure 5.5, TNT has higher capacities for cations with high electronegativities. Electronegativity is defined as the power of an element to attract electrons to itself (Huheey et al. 1993). Having higher electronegativities, the post-transition and transition cations are preferentially sorbed than alkaline earth cations. The relationship was also observed by other researchers (Allen and Brown 1995; Faur-Brasquet et al. 2002).

Figure 5.5 Correlation of sorption capacity with electronegativity. Linear regression (solid line) and 95% confidence intervals (dotted lines) are shown. Ni was not considered in regression.

Figure 5.6 Correlation of sorption capacity with hardness. Linear regression (solid line) and 95% confidence intervals (dotted lines) are shown. Ni was not considered in regression.

It was found that the charge-size function (Z^2/r) cannot be linearly correlated with data from this work (Figure 5.7). Linear regression of seven data points resulted in a horizontal trend line which suggests sorption capacity of TNT is not a dependent variable of this parameter.

Figure 5.7 Correlation of sorption capacity with charge-size function (Z^2/r). Linear regression (solid line) and 95% confidence intervals (dotted lines) are shown. Ni was not considered in regression.

5.6 Anomaly of Nickel

In linear correlations with hydrolysis constant, electronegativity and hardness, Ni fell outside the 95% confidence intervals suggesting the unusual sorption behavior of Ni on TNT. The sorption capacity for Ni is in the same order of magnitude with alkaline earth cations (cf. Table 5.4) and the HSAB theory is unable to describe its behavior. Being defined as a soft acid, it should bind strongly to OH sites on TNT regardless of pH. On the contrary, Kurbatov plot (Figure 5.8) shows that Ni sorption

was observed only when pH exceeds the PZC of TNT. Using extrapolation, other transition cations (Cd, Cu and Zn) have $\text{pH}_{50} < \text{pK}_{\text{MeOH}}$ (Table 5.3 and Table 5.4). That is, sorption efficiency of more than 50% is achieved before the first hydrolysis constant. For Ni, substantial uptake occurred only when pH exceeds the pK_{MeOH} . It is plausible that sorption mechanism of Ni on TNT is different from the other transition cations. Superposition Figure 5.3 and Figure 5.8 reveals Ni curve to be located nearer to Ca and Sr curves than its transition cations. It is plausible that the transition metal ion is present as NiOH^+ . And the nickel species is binded to surface TNT via weak electrostatic forces. This would explains nickel's apparent weak affinity in Figure 5.2 and also the fact that substantial uptake occurs only when $\text{pH} > \text{PZC}$. This counter-intuitive behaviour of Ni, however, was not observed on other metal oxides (Kinniburgh and Jackson 1981; Dzombak and Morel 1990). With reference to sorption data presented in this chapter and literature suggest that low affinity of nickel to surface hydroxyl is unique to TNT. The resulting data suggest that TNT can be a potential industrial sorbent to treat wastewater of NiCd battery manufacturing.

Figure 5.8 Kurbatov plot of transition cations. TNT = 0.005 g/L, IS = 0.1 M, Cation = 10^{-5} M. Data points with sorption more than 90% or pH exceeding

precipitation were not included in the plot. Linear regression parameters listed in Table 5.3.

5.7 Kinetics

5.7.1 Dissolution Kinetics

It is important to monitor the rate and extent of dissolution occurring to the mineral during the sorption process. Detailed procedures of the experiment can be found in §3.3.2. Depending on the type of metal being dissolved from the metal oxide, it may alter the overall solution pH by either consuming H^+ or OH^- (Tournassat et al. 2004). The structure of TNT is similar to anatase and rutile. The building blocks of TiO_2 based minerals are TiO_6 octahedra and they are resilient under acid and basic condition. It was found that at pH 3, the amount of Ti^{4+} detected in the solution is in the order of 10^{-7} M. Dissolution was not considered in this study as it was found that, during the sorption of cadmium, aqueous titanium at pH 3 was negligible (Figure 5.9).

Figure 5.9 60-day kinetic studies of aqueous Ti. TNT = 0.05 g/L, IS = 0. pH indicated are prior to equilibrium.

5.7.2 Sorption Kinetics

To determine the pseudo-equilibrium duration for sorption, kinetic studies was conducted (Figure 5.10 and Figure 5.11). Concentration of TNT was in excess to ensure the sufficient sites were available for Cd bonding. In spite of this, maximum Cd sorption at pH 3 was only about 80%.

The duration to reach maximum uptake was about 2 hr, relatively slower than the duration to reach equilibrium at pH 4.8 (less than 12 min). This can be explained by the nature of the sorption sites. Essentially two types of free sites are (i) the surface hydroxyl groups (external surface and the ends) and (ii) internal layers. It is possible that at pH 3, protons compete with Cd for the former sites thereby restricting the uptake of Cd. The less accessible interlayer sites are still available and more time is required for the larger divalent cation to reach those sites. There is no such problem for Cd at pH 4.8 as the surface hydroxyl groups are readily available to bind with Cd ions.

It is interesting to note that solution Cd increased as the time proceeds. At pH 3 desorption occurs readily and equilibrium was not achieved during the 60 days. The trend is not uncommon and has been reported in literature (Backes et al. 1995; McLaren et al. 1998). It has been pointed out that, at a given pH, contact time affects the sorption efficiency (Sparks 2005).

Nevertheless, equilibration duration of 24 h was chosen for batch tests. Na^+ concentrations remained constant throughout the experiment. At pH 3, protons replace sodium ions held at the interlayer of TNT. Hence Na molarity is higher at pH 3 than at pH 4.8. In a sorption process involving only ion-exchange the uptake of Cd^{2+} should release a stoichiometrically-equivalent amount of Na^+ as shown in Equation (45) (i.e. for every 1 Cd^{2+} ion, 2 Na^+ ions should be released):

Hence in Figure 5.10 and Figure 5.11, the sorption of Cd should not involve solely ion-exchange mechanism because it would result in sodium-cadmium ratio of 2:1. Indeed, at pH 4.8, uptake of 10^{-5} M Cd^{2+} did not result in stoichiometric release of 2×10^{-5} M Na^+ into bulk solution. From Figure 5.10, it is observed that the ratio of sodium released to cadmium sorbed is only ca. 0.35:1. This indicate that ion-exchange mechanism is no the main phenomenon in the sorption of cadmium onto TNT. Indeed it is possible that due to solution pH the fresh sorbent, prior to sorption kinetic study, is in form of $\text{H}_x\text{Na}_{2-x}\text{Ti}_3\text{O}_7$:

Thus the overall equation describing the exchange of Cd^{2+} with TNT under various pH conditions is:

where X denotes the proportion of Na and protons in the TNT.

Alternatively the release of Cd during prolonged mixing can be argued due to the dissolution of TNT at low pH. As discussed shown in Figure 5.9, the concentration of Ti indeed is higher at pH 3 than pH 4.8. However, Ti molarity remained stable throughout the 60-day study which is inconsistent with the gradual release of Cd as illustrated in Figure 5.11.

Another plausible scenario is due to the morphological and crystallinity change in TNT. The chemical stability of TNT has not been as widely investigated in the literature as its structural formula and configuration. There is however evidence that the crystallinity of TNT is unstable under 0.1 M H₂SO₄ (Bavykin et al. 2006). It is reported that TNT undergoes morphological and crystallinity changes under acidic condition to form rutile particles. It is plausible that at pH 3, the formation of rutile nanoparticles resulted in the gradual release of Cd which was initially binded onto the interlayers of TNT. At pH 4.8, however, TNT is stable and not subjected to the crystal change. Hence no desorption of Cd was observed in Figure 5.11.

Figure 5.10 2-h kinetic studies of aqueous cadmium and sodium. TNT = 0.05 g/L, IS = 0; $C_0 = 10^{-5}$ M. pH indicated are prior to equilibrium.

Figure 5.11 60-day kinetic studies of aqueous cadmium and sodium. TNT = 0.05 g/L, IS = 0; $C_0 = 10^{-5}$ M. pH indicated are prior to equilibrium.

Pseudo-second-order rate model was fitted to the sorption data (Figure 5.12 and Figure 5.13). The reaction can be described as:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad [48]$$

where q and q_e are the cadmium uptake at time t and equilibrium (mol g^{-1}), q is a function of time, t (h) and k_2 denotes reaction rate constant ($\text{g mol}^{-1} \text{h}^{-1}$). Integrating above equation and applying boundary conditions, $q(0) = 0$ and $q(t) = q$, will give:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad [49]$$

Plotting the linear equation of t/q vs t will yield values of k_2 , q_e and the resulting fits in Figure 5.12 can be generated. From Figure 5.13, it was found that, Cd sorption can be described by the pseudo-second-order equation at pH 3. This model is known to encompass the reactions of external film diffusion, surface adsorption and intra-particle diffusion (Shen et al. 2009). The rate-limiting step is the putative solute diffusion into the bulk sorbent. Firstly, Cd ions can diffuse and adsorb onto outer wall of TNT relatively quickly. Upon the saturation of outer sites, the slower reactions would be the diffusion of cations into the interlayers and the mass transfer to the inner wall of the tube.

Despite the good linear regression analysis (Figure 5.12), the model was unable to fit sorption kinetics at pH 4.8. The reason for this incompatibility could be due to the faster kinetics and different sorption mechanism. Reaction rate models are known to have their inadequacy in modelling sorption data. Regardless of the orders of reaction, all kinetic models are affected by only apparent parameters (e.g. initial concentration, sorbent dosage and type of solute) and failed to consider other equally pertinent conditions (Ho and McKay 2000). In this case, the difference due to effect of pH cannot be simulated using the pseudo-second-order equation.

Figure 5.12 Linear plot of pseudo-second-order reaction. TNT = 0.05 g/L; Cd_{initial} = 10⁻⁵ M. Lines are linear regression analyses.

Figure 5.13 Sorption kinetics of cadmium at pH 3 and 4.8. TNT = 0.05 g/L; Cd_{initial} = 10⁻⁵ M. Lines are pseudo-second-order equation.

5.8 Conclusion

In conclusion for this chapter, TNT showed varying uptakes for the seven cations. Generally, higher affinities can be observed for heavy metals as compared to alkaline earth metal. The sorption capacities were Pb >> Cd > Cu > Zn > Ca > Sr > Ni. It is interesting to note that TNT had a low Ni uptake despite it being in the same period as Cu and Zn on the periodic table. The sorption kinetics of Cd was fast, with the sorption achieving equilibrium in less than 10 min.

Chapter 6 Effects of Solution Chemistry on Cadmium Uptake

6.1 Introduction to Speciation of Cadmium Ions

Among the tested cations, cadmium is toxic and a suspected carcinogen (Kasuya 2000; Waalkes 2003). Therefore an in-depth study of the sorption behaviour of TNT and cadmium is necessary. Currently, the literature lacks an in-depth study of cadmium-TNT interaction. This chapter will illustrate the effects of various solution chemistries have on the interaction of TNT with cadmium. In addition, discussion will be made on the plausible sorption mechanisms involved.

Cadmium belongs to Group IIB transition elements on the Periodic Table. Together with zinc and mercury, they characteristically have 2 electrons in the outer most shell. Cadmium atom has electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$. Cadmium has a valence charge of +1 and +2 and it is known that in aqueous state, cadmium ion exists in the former oxidation state (Posselt and Weber 1971; Baes and Mesmer 1976). In solution, free cadmium ion (Cd^{2+}) is, in fact, associated with water molecules within its hydration sphere. The coordination of cadmium is much discussed and researchers are still debating whether the metal ion is surrounded by six or seven water molecules. Using molecular dynamics and x-ray absorption spectroscopy, D'Angelo et al. suggested hydrated cadmium is heptacoordinated (D'Angelo et al. 2008). While Pye et al. and Marcus concluded a hexacoordination for cadmium ion (Pye et al. 2006; Marcus 2009).

In aqueous state, cadmium ions react with water to form hydroxo complexes (Figure 6.1). In the absence of other ligands (carbonates, halides, sulfates etc.), cadmium occurs predominantly as free cadmium, Cd^{2+} (Figure 6.3). At higher solution pH, cadmium is mainly in the form $Cd(OH)_2^0$. Larger hydrolysis products ($Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$) do not form in conventional range of pH. Total dissolved cadmium (Cd_T) decreases at higher pH due to the precipitation of $Cd(OH)_{2(s)}$ (Log $K = 13.73$) (Figure 6.2).

Figure 6.1 Distribution of hydrolysis species of cadmium at $\text{Cd} = 10^{-5} \text{ M}$, $\text{IS} = 0.1 \text{ M}$ and 25°C . Only mononuclear species are shown. Data generated using Visual MINTEQ (Gustafsson 2009).

Figure 6.2 pC-pH curves of hydrolyzed cadmium species at $\text{IS} = 0.1 \text{ M}$ and 25°C . Solution saturated with $\text{Cd}(\text{OH})_{2(s)}$. Only mononuclear species are shown. Data generated using Visual MINTEQ (Gustafsson 2009).

Known precipitates of cadmium include hydroxide ($\text{Cd}(\text{OH})_{2(s)}$), cadmium carbonate (otavite, $\text{CdCO}_{3(s)}$) and cadmium sulfide (greenockite, $\text{CdS}_{(s)}$). Solubility products of environmentally-relevant cadmium precipitates are presented in Table 6.1.

Table 6.1 Cadmium precipitates of interest. Equilibrium constants taken from minteq.v4.dat (Allison et al. 1991).

Mineral	Chemical Reaction	Log K_{sp}
Cadmium hydroxide	$\text{Cd}(\text{OH})_2 + 2\text{H}^+ = \text{Cd}^{2+} + 2\text{H}_2\text{O}$	13.73
Otavite	$\text{CdCO}_3 = \text{Cd}^{2+} + \text{CO}_3^{2-}$	-12
Greenockite	$\text{CdS} + \text{H}^+ = \text{Cd}^{2+} + \text{HS}^-$	-14.36

Cadmium dissolution/precipitation equilibrium depends on various factors such as:

- (i). concentration of system cadmium
- (ii). ligands availability (OH^- , CO_3^{2-} , S^{2-} etc.)
- (iii). system pH
- (iv). pressure-temperature condition

The influence of carbon dioxide gas on cadmium speciation is of environmental interest. P_{CO_2} (partial pressure of carbon dioxide gas) of systems in equilibrium with atmosphere (such as rivers and lakes) is typically $10^{-3.5}$ atm. Under this condition, aqueous cadmium is likely to precipitate into otavite ($\text{CdCO}_{3(s)}$) rather than cadmium hydroxide ($\text{Cd}(\text{OH})_{2(s)}$).

Figure 6.3 Predominance diagram for Cd²⁺-CO₂-H₂O system at Cd = 10⁻⁵ M, IS = 0 and 25 °C. Data generated using PhreePlot (Kinniburgh and Cooper 2009). NA denotes unknown phase, plausibly soluble carbonate species.

6.2 Methodology

6.2.1 Batch Tests

Sorption edge and isotherm studies were conducted with samples of 50 mL each containing appropriate concentrations of TNT and ionic strength. This was followed by pH adjustment using HNO₃ and/or NaOH. Finally, the target divalent cation was spiked into the suspension prior to equilibrium mixing for 24 hr. The pH values before and after equilibration were recorded. The solids were separated from solution by centrifuging at 10 000 rpm, 30 min and passing the supernatant through a syringe filter (0.2 µm Nylon, Sartorius). The equilibrium concentrations (*C_e*) in

the filtrates were analysed using ICP-OES. Sorption efficiency which is the percentage of divalent cation being sorbed by TNT was calculated by:

$$\%_{\text{sorbed}} = \frac{C_o - C_e}{C_o} \times 100\% \quad [50]$$

A blank sample (i.e. without TNT) was prepared for each set of test to determine the real C_o . All equilibration were performed in the dark.

6.2.2 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Cadmium and other cations were measured using ICP-OES (PerkinElmer Optima 2000). Five-point calibration using standards were performed prior to each measurement. All calibration curves had best-fit values of at least 0.999. Each sample was measured thrice and reported value was the mean. The sensitivity of ICP measurement was given in Appendix B. Measurement 50 replicates of same cadmium solution (2×10^{-6} M) was conducted.

6.3 Effect of pH on Sorption Isotherms

In order to elucidate the effects of pH on sorption capacities of TNT for cadmium, isotherm study was conducted. Similar to §5.3, experimental data were fitted with the empirical Langmuir isotherm (Figure 6.4). It is observed that increasing Cd concentration resulted in increase of Cd uptake up to a saturation point. At higher pH, the uptake of Cd increases and the overall sorption capacity increases with solution pH. By increasing the pH from 3 to 7, the sorption capacity for Cd doubled.

Sorption capacity at neutral pH was ca. 1 mmol/g, which is higher than other sorbents reported (Gao et al. 2004; Gupta and Bhattacharyya 2006). The high sorption capacity is attributed to large BET surface area of TNT. TNT surface is negatively-charged under basic condition and the enhanced Cd uptake suggests that

electrostatic forces are involved during the sorption process. The large deviations for pH 7 samples are likely to the instability of pH meter.

Figure 6.4 Effect of pH on cadmium isotherms. pH values are prior to equilibration. Lines are Langmuir isotherms. Error bars represents standard deviation of triplicates. TNT = 0.05 g/L, IS = 0.1 M. pH indicated are prior to equilibrium.

6.4 Effect of TNT Concentration on Cadmium Uptake

Batch tests were conducted for all sorption edge studies. Detailed steps of experiments were explained in §3.3.3. In this work proportion of sorbent to sorbate is chosen to ensure that removal of Cd from solution is due to sorption of dissolved Cd species rather than precipitation on TNT surface. Figure 6.5 shows a distinct relationship between TNT concentration and Cd uptake. An increased sorbent concentration results in higher uptake of Cd ions with other solution compositions held constant. Increasing sorbent concentration can be interpreted as providing more sites for sorbate (Dzombak and Morel 1990). Graphically, this translates to

left-shifting of sorption edges. Complete sorption of Cd ions at pH 3 was achieved when TNT concentration increased to 0.5 g/L. This can be explained as having excess amount of TNT (i.e. more than enough sites) for the given concentration of Cd ions (Dzombak and Morel 1990). In addition to shifting of edges, the gradient of the sorption edges changes with sorbent dosage. It is observed that higher TNT concentration resulted in sorption edge with a steeper gradient. By considering the PZC of the sorbent, Appelo and Postma relate gradient of sorption edges with the “denticities” of the bond (i.e. whether monodentate or bidentate bonding) (Appelo and Postma 1993). In this study, to determine the bonding mechanisms based on the sorption edge gradient is more complex as there are fixed charge in addition to the variably-charged surface sites. Rather, the bonding of Cd ions to TNT-water interface is determined by selecting the one which best fit the experimental data. This will be discussed later in the manuscript.

It was found that protons were released during the sorption process (Figure 6.6). Higher TNT concentrations (0.05 and 0.5 g/L) resulted in a relatively more stable system. This is because TNT acts as a buffer, stabilizing the pH reading. At higher concentrations, more sites will be available to bind the released protons, thereby reducing the fluctuation before and after equilibrium.

Figure 6.5 Effect of TNT concentration on cadmium uptake. IS = 0.1 M; $C_o = 10^{-5}$ M.

Figure 6.6 Effect of TNT concentration on pH before and after sorption equilibrium. IS = 0.1 M; $C_o = 10^{-5}$ M. pH is more stable at higher TNT concentrations. This is because TNT acts as pH buffer. In general, pH did not deviate significantly during the equilibrium process.

6.5 Effect of Ionic Strength on Cadmium Uptake

Ionic strength (IS) was varied two orders of magnitude to investigate its effect on sorption behavior (Figure 6.7). Cadmium uptake is higher at basic pH than acidic pH and can be viewed in terms of electrostatic charges. From the titration of TNT we know that the points of zero charge range from 6.5 to 8.5. At $\text{pH} > \text{PZC}$, the hydroxyl groups are mainly negatively charged. Negatively charged surface hydroxyl groups are able to sorb cadmium ion more readily than a positively charged group. About 90% of cadmium ions were sorbed at pH 7.5 before the onset of otavite precipitation, indicating only dissolved cadmium ions are sorbed in the process. Cadmium uptake is higher at basic pH than acidic pH. It was observed that change in IS did not affect the position of sorption edges significantly from $\text{IS} = 0.001$ to 0.01 M .

Sorption edges which are independent of IS are characteristic of inner-sphere complex formation. Cadmium ions are directly bonded onto the surface functional groups rather than being bonded as a hydrated form. This can be explained by the nature of the sorbate. In contrast to ions of alkaline earth metals, cadmium is a soft acid and is able to bond strongly onto metal oxides (Posselt and Weber 1971; Hayes 1987; Papelis 1992). Ions can bind onto the surface regardless of the thickness of the electric double layer. This observation of cadmium ion is in accordance with previous studies on other metal oxides (Hayes and Leckie 1987; Papelis et al. 1995). In addition, the presence of inner-sphere complexation can also be observed from the acid-base titration plot of the used sorbent. PZC of inner-sphere-complexed sorbent is lower than the virgin sorbent (Hohl et al. 1980).

Figure 6.7 Effect of ionic strength on cadmium uptake. TNT = 0.005 g/L; C_o = 10⁻⁵ M.

In contrast, when IS was increased to 0.1 M, there was a slight reduction in Cd uptake, indicating that there is more than one sorption mechanism involved, plausibly inner-sphere complexation and ion-exchange. In this study, to determine the bonding mechanisms based on the sorption edge gradient is more complex as there are fixed charge in addition to the variably-charged surface sites. Rather, the bonding of Cd ions to TNT-water interface is determined by selecting the model which best fit the experimental data.

It was observed from Figure 6.8 that pH_{final} is less than pH_{initial}. The fluctuation in pH is due to the release of protons during sorption of cadmium. pH did not fluctuate significantly at acidic condition due to (i) low sorption uptake resulting in release of low amount of protons (ii) high concentration of protons at acidic condition, thereby masking the effect by protons release due to sorption.

Figure 6.8 Effect of ionic strength on pH before and after sorption equilibrium. TNT = 0.005 g/L; $C_o = 10^{-5}$ M. Regardless of ionic strengths, protons were release during sorption resulting in $pH_{final} < pH_{initial}$. pH did not fluctuate significantly at acidic condition due to (i) low sorption uptake resulting in release of low amount of protons (ii) high concentration of protons at acidic condition, thereby masking the effect by protons release due to sorption.

6.6 Effect of Competing Divalent Cation on Cadmium Uptake

Cations often coexist in industrial wastewater. Due to their toxicity and wide occurrence, this portion of work is undertaken to understand the effects of competing divalent cations have on cadmium sorption.

6.6.1 Lead-Cadmium System

Pb has the most pronounce effect on Cd uptake (Figure 6.9). At equimolar concentrations the post-transition cation is preferred over Cd. When Pb is reduced

by an order of magnitude, fractional uptake of Cd can be observed. At molar ratio of 1:1 Pb competes with Cd for the limited sites available of TNT and with the change in molar ratio to 1:0.1 sites become available for sorption of both Pb and Cd. Figure 6.9, evidently suggests that TNT binds preferentially to Pb than Cd. This is in accordance with results reported in Figure 5.2. According to HSAB theory, both cations are considered soft acid and the bonds form with surface hydroxyl groups are covalent in nature (Pearson 1963).

Figure 6.9 Competitive sorption between lead and cadmium as a function of pH.
TNT = 0.005 g/L, IS = 0.1 M.

6.6.2 Zinc-Cadmium and Copper-Cadmium Systems

Systems of Zn-Cd and Cu-Cd have similar sorption behaviors (Figure 6.10 and Figure 6.11). At equimolar ratio, Cd is preferred over Zn and Cu. Under acidic condition (pH < 5), sorption efficiencies of Cd were the same with and without competing cations. TNT preferentially sorbs Cd even when Cu or Zn molarity is increased fivefold. At higher pH, however, the affinity for Cd decreases and increased uptakes of Zn and Cu were observed. Maximum uptake of Cd occurred at pH 6-7 for both systems.

Sorption edges of Cd, Cu and Zn are situated adjacent to one other (Figure 5.2). As such, both scenarios (Figure 6.10 and Figure 6.11) tend to suggest that TNT bonding preference is dependent on solution pH. It is important to note that sorption edges can aid in inferring the empirical sorption behaviours of sorbent and sorbate, however elucidation of coordination number formed with the surface hydroxyl groups require more advanced spectroscopic studies.

Figure 6.10 Competitive sorption between zinc and cadmium as a function of pH.
TNT = 0.005 g/L, IS = 0.1 M.

Figure 6.11 Competitive sorption between copper and cadmium as a function of pH.
TNT = 0.005 g/L, IS = 0.1 M.

6.6.3 Nickel-Cadmium System

Nickel, despite being a transition metal, did not have significant effect on uptake of Cd (Figure 6.12). Sorption edges of Ni-Cd are different from Zn-Cd and Cu-Cd systems. The presence of Ni did not impede TNT uptake of Cd. Five fold increment of Ni did not affect the uptake of Cd significantly either. Uptake of Ni was not observed in competitive sorption systems and while the sudden increase at pH > 8 is attributed to the precipitation of nickel hydroxide. It is interesting to note that sorption edges of Ni resemble that of alkaline earth cations. The presence of free nickel ions (Ni^{2+}) would result in high uptake by TNT. The data, however, suggested otherwise. As such Ni species present would be similar to that of calcium and strontium species. It is plausible that the transition metal ion is present as NiOH^+ .

Figure 6.12 Competitive sorption between nickel and cadmium as a function of pH.
TNT = 0.005 g/L, IS = 0.1 M.

6.6.4 Calcium-Cadmium and Strontium-Cadmium Systems

In systems of Ca-Cd and Sr-Cd (Figure 6.13 and Figure 6.14), TNT was more selective towards Cd and its uptake was not affected by Ca or Sr. Effects of alkaline earth cations were insignificant on the uptake of Cd. It was found that increasing either Ca or Sr five fold did not lead to significant change in the sorption efficiency of Cd. The sorption sites on TNT were binded by Cd and uptakes of Ca and Sr are negligible. This is explained by the outer-sphere complexes formed on TNT by alkaline earth cations (Rietra et al. 2001). Group II cations binding occurs when surface of TNT is negatively-charged (i.e. pH > PZC). Their bondings with hydroxyl group are outer-sphere complexation due to ionic charges whereas heavy metal cations form inner-sphere complexation, a covalent bonding mechanism (Hayes 1987).

Figure 6.13 Competitive sorption between calcium and cadmium as a function of pH. TNT = 0.005 g/L, IS = 0.1 M.

Figure 6.14 Competitive sorption between strontium and cadmium as a function of pH. TNT = 0.005 g/L, IS = 0.1 M.

6.7 Conclusion

It was found that the uptake of cadmium by TNT was not affected by low ionic strength. This indicates cadmium plausibly forms inner-sphere complexes on the surface of TNT. However, at high ionic strength, the cadmium uptake decreased significantly. It is plausible that sorption of cadmium on TNT involved more than one mechanism. The experimental data from batch tests can only give an indication of the type of bonding. Advanced spectroscopic studies are needed to substantiate and complement the findings from this chapter.

Chapter 7 X-Ray Spectroscopic Analyses of Cadmium Complexes

7.1 Introduction to X-Ray Photoelectron Spectroscopy (XPS)

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is a surface sensitive technique and useful in quantifying surface constituents, knowing the valence of sample. This method involves bombarding sample with x-ray source of known energy and measuring amount of electrons escaped from the sample. The process is performed under ultra-high vacuum (UHV) range of $10^{-8} - 10^{-10}$ mbar. This is due mainly to the interference of residual air or other gases. Electrons emitted from samples can be scattered by presence of any gas molecules. Concentration of gases must be kept reasonably low to obtain a good signal-to-noise ratio and high spectral intensity. In addition, the presence of any residual gas inside vacuum chamber will be adsorbed by sample forming a monolayer of gas. As a result, for a given acquisition time, the sensitivity of technique will be reduced (Watts 1990).

For an incident x-ray source, each element has a unique set of binding energies. This set of energies can be used to identify the elements and semi-quantify its concentration at the surface (Moulder 1995). By measuring the kinetic energy (KE) of electron emitted during bombardment, the orbital binding energy (BE) from which electron originates can be calculated by:

$$KE = h\nu - BE - \phi_s$$

where $h\nu$ is the energy of the x-ray and ϕ_s is the work function of the spectrometer. In XPS, only the electrons which did not undergo inelastic scattering are measured. This means only electrons ejected from the surface atoms are detected (i.e. typically 1 – 5 nm depth (Papelis 1992)). For a given homogeneous sample, the intensity of a peak, I , (number of electrons s^{-1}) is given by (Moulder 1995):

$$I = nf\sigma\theta y\lambda AT$$

where n (number of atoms of the element cm^{-3} sample), f is the incident x-ray flux (photons $\text{cm}^{-2} \text{s}^{-1}$), σ is the photoelectric cross-section for the atomic orbital of interest (cm^2), θ is an angular efficiency factor for the instrumental arrangement based on the angle between the photon path and detected electron, y is the efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy, λ is the mean free path of the photoelectrons in the sample, A is the surface area of the sample analyzed and T is the detection efficiency for electrons emitted from the sample (Moulder 1995).

From the above equation, all parameters all considered as constant except σ and λ . The couple are considered to be element-specific. In a comparison study between two elements, the above equation can be simplified into:

$$\frac{n_1}{n_2} = \frac{I_1}{S_1} \frac{S_2}{I_2}$$

where S_i is atomic sensitivity factor (ASF). Hence relative quantification requires only the measurement of intensities of both peaks and knowledge of ASF. For a given spectrometer with fixed configurations, it is possible to derive the S values empirically from measuring well-defined crystalline samples. Wagner et al. collected and calculated ASF of various elements (Wagner et al. 1981) and Moulder corrected the values for system's transmission function (Moulder 1995). The mentioned semi-quantitative method, however, has limitations:

- (i). care must be taken in dealing with heterogeneous samples. The distribution of element of interest affects the quantification process.
- (ii). first series transition metals, in contrast to other elements, has low and significantly different y values. For a given element, the S value calculated from a chemical state may not be valid for another chemical state.

- (iii). substitute has to be used when the main peak overlaps another element peak. For spin doublets, the pairs of peaks are proportional (except 4d) and weaker intensity of the couple may be used as the substitute. For instance, 3d doublet ($3d_{5/2}$ and $3d_{3/2}$) has an intensity ratio of 3:2. Alternatively, the interfering peak can be subtracted mathematically to estimate the intensity of the peak of interest

XPS is a versatile tool use to understand the elemental composition at the surface of environmental particles. Stipp et al. applied to study the uptake of cadmium by calcite (Stipp et al. 1992). XPS was also used to study the sorption of uranyl on montmorillonite (Kowal-Fouchard et al. 2004).

7.1.1 Survey Scans

The details for operating conditions and peak analyses can be found in §3.4.6. For sample preparations, three aliquots of TNT (0.05 g/L) were equilibrated with Cd (10^{-4} M) at pH 3, 7 and 9. After equilibrium, the solid TNT was separated from solution and freeze-dried prior to XPS analysis. For comparison and control, an additional blank sample not tainted with Cd was scanned. All XPS peaks shown were that after calibration, unless otherwise stated. Figure 7.1 shows the survey scans of the samples and control. Spectrum of as-synthesized TNT showed an intense Na 1s peak at 1070 eV.

In comparison with TNT after sorption at different pH, there is a reduced in Na when sorption is performed at pH 3. The reduction of Na 1s suggests protons replaced Na ions since concentration of H^+ is high at pH 3. Exchange of Na^+ with Cd^{2+} is unlikely due to the low uptake of Cd as shown in from the spectrum and sorption edges (Figure 6.7). Presence of Cd in TNT can be observed when sorption is performed at pH 7 and 9. Higher Cd uptakes resulted in relatively more intense peaks than sample equilibrate at pH 3.

Figure 7.1 Survey scans of control and samples after equilibration. Spectra were offset for clarity. TNT = 0.05 g/L; IS = 0.1 M; $C_0 = 10^{-4}$ M. Monochromatic Al K α as x-ray source.

7.1.2 Cadmium 3d Peaks

It is known that 2+ is the only valence state of aqueous cadmium (Posselt and Weber 1971; Baes and Mesmer 1976). Despite the minor peaks in Figure 7.1, survey scans already qualitatively suggested that surface cadmium increased as solution pH increased. Comparisons of detail Cd 3d peaks showed that, indeed, the area of peaks increases when TNT was equilibrated at higher pH (Figure 7.2 and Table 7.1). Cadmium measured from XPS should include solutes sorbed both at the surface of TNT and also at the interlayer sites. This is reasonable assumption as the analytical depth of this technique is, at least, 1 to 5 nm while the first interlayer spacing is 0.8 nm from surface (cf. §4.4.2 and Figure 4.10) meaning that XPS is capable of measuring 5 – 6 layers of titanate sheets.

Figure 7.2 Cadmium 3d peaks of control and samples after equilibration. Spectra were offset for clarity. TNT = 0.05 g/L; IS = 0.1 M; $C_o = 10^{-4}$ M.

In addition, shifting of peaks was observed in the high resolution spectra of Cd 3d peaks. At pH 3, Cd 3d_{5/2} and Cd 3d_{3/2} peaks were found at 405.4 eV and 412.1 eV respectively. Under neutral and basic conditions, peaks of Cd 3d_{5/2} and Cd 3d_{3/2} were shifted to 405.0 eV and 411.6 eV, respectively (Figure 7.2). Shifting of Cd 3d peaks from pH 3 to pH 7 was attributed to the additional Cd bond present on TNT at pH 7 and 9. The de-convolution of Cd 3d_{5/2} peaks (Figure 7.3) reveals there a primary curve for pH 3 whereas two primary curves for pH 7 and 9. Curve 1 corresponds to Cd-O bond in which oxygen originates from the surface hydroxyl groups of TNT rather than the solution species, CdOH⁺. This is because from the speciation curves (Figure 6.1), Cd²⁺ is the predominant species at pH 7 and 9, not CdOH⁺. Cd²⁺ is sorbed onto surface hydroxyl resulting in the Cd-O bond. Curve 2 is attributed to the presence of CdCO_{3(s)}, otavite or soluble carbonato species. It is known that Cd-CO₃ bond has a higher binding energy position than Cd-O

(Hammond et al. 1975; Moulder 1995) and also otavite precipitation starts at pH 7. It is, hence, expected that Cd-CO₃ curve at TNT surface is due to CdCO₃(s).

Figure 7.3 Cadmium 3d_{5/2} peak de-convoluted. TNT = 0.05 g/L; IS = 0.1 M; C₀ = 10⁻⁴ M. Note that otavite precipitates at pH 7 and 9 for this set of solution composition.

Table 7.1 quantifies the raw areas of all the Cd 3d_{5/2} peaks. Evidently, increasing pH of sorption equilibrium increases the Cd uptake. Binding energy at Curve 1 is attributed to the Cd-OH bond resulting from the sorption of Cd onto hydroxyl groups. Curve 2 is the result of Cd-CO₃ which likely is due to the soluble carbonate species or otavite precipitate. Curve 2 is absence at low pH as significant amount of carbonate form carbonic acid. As pH increases, the acid releases protons to form cadmium carbonate species. It was suggested that at higher C_T, cadmium forms a multi-nuclear complexes or precipitate (Papelis et al. 1995).

Table 7.1 Quantification of Cd 3d_{5/2} peak with respect to Figure 7.3

pH	Peak	Binding Energy (eV)	FWHM (eV)	Raw Area (cps)	Ratio of Curve 1: Curve 2
3	Cd 3d _{5/2} 1	405.074	1.602	332.20	-
7	Cd 3d _{5/2} 1	404.803	1.347	1737.2	14.6
	Cd 3d _{5/2} 2	406.545	1.407	118.75	
9	Cd 3d _{5/2} 1	404.845	1.315	3844.7	18.9
	Cd 3d _{5/2} 2	406.516	1.395	203.59	

7.1.3 Carbon 1s Peak

As mentioned in §3.4.6, the carbon 1s peak were used for calibration purpose. Calibration involves shifting the lowest binding energy peak to position of 284.8 eV. All elemental peaks were calibrated by the exact binding energy the C 1s peak was moved. Figure 7.4 shows the C 1s peaks after calibration. The major peak at 284.8 eV has visible shoulders at higher binding energies. There is also a standalone peak at ca. 288.7 eV.

Figure 7.4 Carbon 1s peak of control and samples after equilibration at different pH condition. Spectra were offset for clarity. TNT = 0.05 g/L; IS = 0.1 M; $\text{Cd}_{\text{initial}} = 10^{-4}$ M.

The presence of $\text{CdCO}_{3(s)}$ on sample pH 7 and 9, in theory, should be reflected in C 1s spectrum and this would give a qualitative confirmation of the onset of otavite precipitation. This hypothesis, however, is not practical due to the strong signals emitted from adventitious carbon and the adhesive carbon tape which was used to secured the TNT powder. Adventitious carbon is any residual carbon from the air or gases. Any possible carbon signals resulting from the low concentration of $\text{CdCO}_{3(s)}$ would be overwhelmed by the other two carbon sources. Figure 7.4 showed that all peaks have same binding energy positions suggesting the signals originate from the same dominant sources (i.e. adventitious carbon and carbon adhesive tape).

7.1.4 Sodium 1s Peak

Protocols for sample preparations were similar to §7.1.2, except that an additional set of samples (0.05 g/L, IS = 0.1 M, pH 3, 7 and 9) were prepared to simulate TNT before sorption. Figure 7.5 showed the high resolution scans of Na 1s peak. The XPS can be interpreted in 2 ways: (i) before sorption (Figure 7.5 top curves), we can observe an increase in areas of Na 1s peak as pH increases. This is explained by the surface charge of the TNT (Figure 4.13). At pH 7 and 9, surface of TNT is overall negatively-charged and attracts Na⁺ readily. The increase in sodium signal is due to the increase in monovalent cation, from NaNO₃, bound to the TNT surface.

Figure 7.5 Sodium 1s peak of samples before and after sorption (top and bottom spectra respectively) under different pH conditions. TNT = 0.05 g/L; IS = 0.1 M; C₀ = 10⁻⁴ M.

At pH 3 the peak is almost negligible. This could be explained by the exchange of protons with Na ions within TNT interlayer to form H-titanate at the interlayer of TNT. In comparing Na 1s before and after sorption, significant reductions in peak areas can be observed after sorption. The reduced in peak area before and after

sorption suggests that Na^+ might be partially removed from interlayers of TNT with the uptake of Cd, through the following reaction:

From the above XPS spectra, we could gain insights to the possible sorption mechanisms involved. Cadmium 3d peaks suggests cadmium uptake increased with the increased of equilibrium pH. De-convolution of $3d_{5/2}$ showed two primary peaks for pH 7 and 9, likely due to Cd-O and Cd-CO₃. From Na 1s spectra, it was found that sodium was release from TNT after sorption process.

The above conclusion can be a hypothesis at best. XPS is known to be a semi-quantitative analysis and peak fitting is largely a judgement of the user. Moreover, XPS are performed *in-vacuo*.

7.2 Introduction to X-Ray Absorption Spectroscopy (XAS)

XAS is a generic term encompassing techniques such as x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). The portion of spectrum before the absorption edge is known as XANES and the region after is EXAFS (Figure 7.6). As with §7.1, §7.2 is meant to provide an overview of XAS with EXAFS theory adequate for understanding the experimental results herein. For in-depth knowledge of its theory and applications, the recommended references are Teo and Joy (Teo and Joy 1981), Koningsberger and Prins (Koningsberger and Prins 1988) and Bunker (Bunker 2010). For detail explanations of data reduction and spectra fitting processes, one can refer to wiki websites such as xafs.org (<http://xafs.org/>) and IFEFFIT (<http://cars9.uchicago.edu/ifeffit/>).

Figure 7.6 A typical XAS spectrum. Manganese K-edge of MnO at $T = 80\text{ K}$ (adapted from (Bunker 2010)).

In order to understand XAS, we need to differentiate it from another useful x-ray spectroscopy, XPS. Both methods and utilize x-rays to probe the sample and are non-destructive. However, the information yield from these techniques and other aspects are different. Table 7.2 lists the main differences of between XAS and XPS.

Table 7.2 Comparison of XAS and XPS techniques.

	X-ray Absorption Spectroscopy (XAS)	X-ray Photoelectron Spectroscopy (XPS)
Information determined from spectrum	Local structural information (bond lengths and coordination of absorbing atom)	Qualitative and semi-quantitative surface analysis, chemical states
Nature of technique	Non-destructive (for environmental science)	Non-destructive (without surface etching)
Environment during experiment	No requirements (i.e. <i>in-situ</i> measurement is possible)	<i>In-vacuo</i> (Ultrahigh vacuum)
Depth of analysis	Dependent on absorption coefficient of the sample	1 – 5 nm from surface
Incident radiation	X-ray from synchrotron	X-ray typically from Al K α or Mg K α , (synchrotron radiation can also be used)
Radiation detected	X-ray transmitted, x-ray fluoresced or electron yield.	Electron emitted
Magnitude of energy source	Element dependent and limit by synchrotron capacity	1253.6 eV (MgK α) or 1486.6 eV (Al K α)
Energy level during experiment	Increases from (edge – 500 eV) to (edge + 1000 eV)	Constant energy
Detection limit	0.01 – 0.1 at.%(100 – 1000 ppm)	0.1 – 1 at.%(1 – 10 ppth)
Data analysis software	IFFEFIT, SIXPack	CasaXPS

7.2.1 Extended X-Ray Absorption Fine Structure (EXAFS)

As shown in Figure 7.6, the EXAFS region is defined as the oscillations from 30-50 to 1000 eV after the absorption edge. The amplification of these oscillations is relatively weaker than the edge jump. EXAFS is the result of interacting photoelectron waves. As a wave (electron) is emitted from the central atom, it may be backscattered by neighbouring atoms (Figure 7.7). These outgoing and backscattered waves, depending on its wavelength, will interfere with each other resulting in amplification and reduction of the signal to the detector (Teo and Joy 1981).

Figure 7.7 Schematic depicting (A) constructive and (B) destructive interferences between outgoing photoelectron wave from the central atom (black) and backscattered wave from a neighbouring atom (grey) (Papelis 1992). The oscillations of EXAFS spectrum is the result of these interferences.

The phenomenon, illustrated in Figure 7.7, when core electron gains sufficient energy to be ejected from the absorbing atom can be described by (Hayes 1987):

$$\lambda = \frac{h}{\sqrt{2m_e(E - E_0)}} \quad [49]$$

where λ is the wavelength of the ejected photoelectron wave, h is the Planck constant, m_e is the mass of an electron, E is the energy of the incident x-ray and E_0 is the binding energy of core electron that needs to be overcome for the electron to be excited (i.e. the position of absorption edge). The EXAFS spectrum, also known as k-space plot can be obtained by converting from energy space to k-space by (Hayes 1987):

$$k = \sqrt{0.262(E - E_0)}$$

where k is also known as the photoelectron wave vector. The k-space spectrum is characterized by sinusoidal oscillations which is the result of constructive-destructive wave interferences. From the k-space and absorption spectra, preliminary qualitative information can already be extracted (Bunker 2010):

- (i). fast oscillations (high frequency) are usually related to a long inter-atomic distances between absorbing and backscattering atoms
- (ii). complex wave patterns would suggest a sample with well-ordered structure
- (iii). rapid decay of amplitude after the absorption edge indicates the backscatters are of low atomic number (low Z).

EXAFS, also known as Kronig structure, was previously confined to theoretical studies until the seminal work by Sayers, Stern and Lytle (Sayers et al. 1971). Fourier transformation (FT) was incorporated to convert EXAFS spectra to radial space (r-space). The resulting r-space (also known as FT magnitude) is the combination of real and imaginary parts. Important data can be obtained only after additional analysis procedure. Often electron scattering paths from theoretical crystallographic database were fitted to spectra (either the FT magnitude or the real part) to acquire local structural information such as paths involved, the respective bond lengths and coordination number.

EXAFS is a powerful tool because data acquisition can be performed under various in-situ conditions. This technique also allows the sample to be in any state (i.e. solid, liquid, gaseous or aqueous state). In addition, EXAFS can be used to measure non-crystalline materials, which is often the case in environmental remediation. Hayes et al. (Hayes et al. 1987) pioneered the use of EXAFS on sorption samples. They investigated selenium complexes on goethite. Subsequently, Chisholm-Brause et al. discovered multinuclear complexes on metal oxides (Chisholm-Brause et al. 1990). EXAFS since became the technique-of-choice to elucidate sorption complexation on terrestrial soils and sorbents.

In this work, the samples consist of cadmium on sodium titanate nanotube. Cadmium is an environmentally relevant component of industrial wastewater (§1.1). This system was chosen for XAS analysis due to complement and substantiate hypothesis from the batch tests (Chapter 6). Cadmium is also a good candidate for XAS analysis as the high binding energy of Cd K-edge (26,711 eV) does not overlap with the other constituents of the system (Na K-edge at 1070.8 eV, Ti K-edge at 4,966 eV and O K-edge at 543.1 eV, (Thompson et al. 2009)). Moreover, at this energy level, incidence x-ray will not be significantly absorbed by the argon gas or Kapton tape.

Samples were cadmium-sorbed titanate (TNT) equilibrate under 0.001 and 0.1 M ionic strength. Handling of collected data was performed in IFEFFIT, an EXAFS data analysis freeware package. Multiple scans were averaged using Athena. Background subtraction and normalization were performed on all raw spectra. The normalized plots are converted to k-space, weighted by k^3 . Resulting EXAFS spectra (k-space plots) were Fourier transformed into R-space plots.

EXAFS analysis were performed on 2 samples equilibrate at different IS. In §6.5 batch tests data have shown that IS affected the cadmium uptake significantly. Table 7.3 shows that at IS = 0.001 M, cadmium sorbed is 73.6% or 6.61 $\mu\text{mol}/\text{m}^2$ whereas uptake at 0.1 M was lower at 51.5% or 4.62 $\mu\text{mol}/\text{m}^2$. TNT is known to have a layered structure and the sodium at the interlayer is viewed as ionically

bonded (Feist and Davies 1992; Chen et al. 2002). This bonding is in accordance with the IS dependency of result in this thesis.

Table 7.3 Solution chemistry and cadmium uptake of XAS samples. TNT = 0.05 g/L; $C_o = 10^{-4}$ M.

	Ionic strength (mol/L)	pH _{final}	Cd _{uptake}		
			(%)	(mmol/g)	(μmol/m ²)
Sample 1	0.001	4.67	73.6	1.36	6.61
Sample 2	0.1	4.68	51.5	0.952	4.62

7.2.2 Data Reduction and Fitting Protocols

Raw data collected from SSRL were analyzed using IFEFFIT, an interactive EXAFS analysis package (Newville 2001). Calibration, alignment and merging of multiple scans were performed using ATHENA (Ravel and Newville 2005; Ravel and Newville 2005), one of the programs inside IFEFFIT. E_o was determined as the position of the first peak in the 1st derivative plot (not shown). Background subtraction and normalization were performed using AUTOBK (Newville et al. 1993) by considering pre-edge, normalization and spline ranges. R_{bkg} was set at 1.0 Å, k-weight was 2, 3rd order normalization and spline clamps strong and none at high and low energy, respectively. Fourier transformation of k-space was done from 2 to 9 Å⁻¹ with Hanning window and dk value of 1.0 Å⁻¹. High-k signals were enhanced by factor of k^3 . Fitting and processing of scattering paths were executed in ARTEMIS (Ravel and Newville 2005; Ravel and Newville 2005). Embedded programs ATOMS and FEFF perform *ab initio* calculation from theoretical crystallographic files to obtain scattering paths for fitting. The fitting range for k-space and r-space were 2 – 9 Å⁻¹ and 1 – 4 Å, respectively. More details of XAS configurations and sample preparations are located in §3.4.7.

7.2.3 Empirical Analyses of EXAFS Result

Figure 7.8 illustrates the normalized x-ray absorption spectra cadmium K-edge (at 26,711 eV) of samples and standards. Data of standards, except foil, were from Farrel Lytle Database (http://ixs.iit.edu/database/data/Farrel_Lytle_data/index.html). It was found that spectra of Samples 1 and 2 had similar post-edge amplitude. As pointed out by Bunker (Bunker 2010), rapid deteriorating post-edge amplitude suggests that the surrounding atoms to be of low atomic number (low Z). This is likely to be the case for Samples 1 and 2. The possible atoms surrounding cadmium would be oxygen, nitrogen or sodium, all of which are low Z elements.

In addition, note that the intensities of white lines immediately after the edge are strong and relatively higher than spectra of CdO standard. However, XANES analysis of absorption spectra is beyond the scope of this thesis.

Figure 7.8 Stacked x-ray absorption spectra of cadmium K-edge (26,711 eV) of samples and standards. Data of standards, except foil, were from Farrel Lytle Database.

Normalized absorption spectra were converted to k-space EXAFS spectra as shown in Figure 7.9. Due to diminishing signal as k increases the ordinate were multiplied by k^3 to enhance the signal. It can be observed from Figure 7.9 that the scans for samples were considered reliable up to $9 \text{ \AA}^{-1}$. Beyond that, oscillations became irregular and would affect analysis process detrimentally. The regular oscillations ensured wide range of k-space ($k = 2 - 9 \text{ \AA}^{-1}$) can be utilized for Fourier transformation. In contrast, EXAFS of cadmium foil in Figure 7.9 showed an even more consistent spectrum. Regular oscillation can be observed from $1 - 12 \text{ \AA}^{-1}$. This is proof of the consistency of incident x-ray source and spurious high-k data of Sample 1 and 2 is due to sample per se and not the radiation.

Figure 7.9 Stacked k^3 -weighted EXAFS spectra of cadmium samples and standards. Data of standards, except foil, were from Farrel Lytle Database.

Figure 7.10 Stacked Fourier transformed magnitude of respective EXAFS spectra from Figure 7.9. Hanning window range of $k = 2 - 10 \text{ \AA}^{-1}$. Data of standards, except foil, were from Farrel Lytle Database.

As shown in Figure 7.10, Fourier transformed magnitude of standards and samples. It was found that both samples have an identical first shell peak positioned at $R = 1.6 \text{ \AA}$. The major peak is characterized by an additional shoulder at low R ($1.1 \text{ \AA}$). Peak of Sample 1, however, is more intense than Sample 2. This is because of the different in cadmium loading on TNT. As shown in Table 7.3, at $IS = 0.001 \text{ M}$, Sample 1 has higher uptake of cadmium ions than at 0.1 M IS . In addition, it can be observed from Figure 7.10 that Sample 1 has an additional minor but significant peak at $R = 2.3 \text{ \AA}$.

Without proceeding to fitting, one can have a preliminary deduction of the possible atom surrounding the cadmium atom. A possible scenario is that cadmium is surrounded by neighbouring cadmium atoms in the case of cadmium precipitate on surface of TNT. However note that in pC-pH of cadmium (Figure 6.2) that it is not plausible that cadmium precipitates at these pH conditions (i.e. $pH = ca. 4.7$). Therefore, we can eliminate the possibility of central cadmium atom surrounded by

other cadmium atoms. The nearest scattering neighbours from the central cadmium atom should be oxygen atoms.

Among the standards shown in Figure 7.10, CdO has peaks that are positioned at same distance as the peaks in both samples. It is not surprising as cadmium ions will likely be binded onto surface oxygen atoms. This form of deduction will give an indication of which scattering path to start with during the fitting process. It was noted that caution must be taken in using these values directly. It is because peaks are usually shifted ca. 0.1 – 0.5 Å toward lower R (Calvin et al. 2003). This peak shifting can be ascribed to several factors such as (Rehr and Albers 2000):

- (i). potential of central and scattering atoms
- (ii). core-hole lifetime
- (iii). multiple scattering

For both samples, the FT magnitudes have clean spectra in that no significant peaks can be detected at high R. The third or fourth scattering shells surrounding the central cadmium atoms may be absence or are of low atomic number (i.e. weak scatterer). Unlike the standards, in which majority of the central cadmium atoms are located inside the bulk of the foil/powder, these high-Z atoms act both as central atoms by themselves and simultaneous as scattering atoms to the neighbours.

7.2.4 Fitting of EXAFS Data

Using empirical deductions made from §7.2.3, input files for ARTEMIS were obtained from The Atoms.inp Archive (<http://cars9.uchicago.edu/~newville/adb/>) and Crystallography Open Database (<http://www.crystallography.net/>).

After trying different scattering paths, two paths were found to be able to describe the data collected from synchrotron radiation. Table 7.4 listed the fitted parameters of paths Cd-O and Cd-Ti.

Table 7.4 Distance and σ^2 values of paths used to fit cadmium EXAFS.

	Path	Distance (Å)	σ^2 (Å ²)
Sample 1	Cd-O	2.2604	0.0113
	Cd-Ti	3.4987	0.0275
Sample 2	Cd-O	2.2689	0.0133
	Cd-Ti	3.5145	0.0228

Paths Cd-O and Cd-Ti can be used together to fit Fouier transformed spectra (Figure 7.11 and Figure 7.12) and EXAFS k-space (Figure 7.13). It was found that that the paths fitted the data of both samples well. It was found from Figure 7.11 that both samples have peaks of nearest neighbour at $R = 1.7$ and $2.8 \text{ \AA}$. These peaks are attributed to the Cd-O path. Sample 1 has higher amplitude than Sample 2 which is due to the high cadmium loading determined from ICP analysis. The second nearest neighbour is positioned at $R = 3.5 \text{ \AA}$ which is the result of scattering path Cd-Ti. No significant difference can be observed between the FT magnitudes of both samples. This observation indicates that sorption mechanisms between 0.001 and 0.1 M ionic strength are the same. It is likely that both inner-sphere complexation and ion-exchange mechanisms are occurring concomitantly with only that Sample 1 has a higher cadmium uptake.

Figure 7.11 Fourier transform magnitude data and fits for Sample 1 and 2. Fitting range was $R = 1 - 4 \text{ \AA}$.

Figure 7.12 Real part of the Fourier transform magnitude data and fits for Sample 1 and 2. Fitting range was $R = 1 - 4 \text{ \AA}$.

Figure 7.13 k^3 -weighted EXAFS spectra data and fits of Sample 1 and 2. Fitting range was $k = 2 - 9 \text{ \AA}^{-1}$.

7.3 Conclusion

XPS confirmed the decreased of surface sodium for samples after equilibration. This indicated that sodium was released during the uptake of cadmium and ion-exchanging mechanism was involved in the sorption process. XAS analyses illustrated that the experimental data can be fitted by considering the scattering paths of Cd-O and Cd-Ti.

Chapter 8 Modelling Cadmium Complexes on Titanate Nanotube

8.1 Introduction to Modelling Programmes

In this work, computer softwares were used to perform speciation calculations and parameter optimizations. PHREEQC is a computer program written by Parkhurst and Appelo (Parkhurst and Appelo 1999) using C programming language. A detailed description of the program can be found in its user manual (Parkhurst and Appelo 1999). In general, the program can perform a wide range of low-temperature geochemical calculations such as:

- (i). speciation and saturation-index calculations
- (ii). reversible batch-reaction and one-dimensional (1D) transportation that involves aqueous, solid, gas, solid-solution, surface complexation and ion-exchange equilibria and other geochemistry-related problems.

PhreePlot (Kinniburgh and Cooper 2009) has an embedded version of PHREEQC which functions similarly to its stand-alone counterpart. PhreePlot complements PHREEQC by providing added flexibility in performing repetitive geochemical calculations (such as calculating sorption uptake at different pH). In addition, PhreePlot has an optimization function which can be used to fit models to data. Often in surface complexation models, some parameters (sites density, binding constants, etc.) cannot be accurately obtained from experiments.

8.2 Protocol for Parameter Optimization

CDMUSIC is a combination of charge allocation function and consideration of sorption sites based on crystallography of mineral surface (§3.5). In comparison with other surface complexation models CDMUSIC is able to describe sorption at different ionic strength and able to achieve a better fit with its charge distribution

function (Villalobos et al. 2001; Appelo et al. 2002). In this modelling, a series of reactions (Table 8.1) were invoked to describe the experimental data.

Table 8.1 Equilibrium constants used in CDMUSIC model

Reaction	Chemical Equations ^a		Log K	z ₀	z ₁
1	$\equiv\text{Ti}_2\text{O}^{0.667-} + \text{H}^+ \leftrightarrow \equiv\text{Ti}_2\text{OH}^{0.333+}$	K ₁	5.14	1 ^f	0 ^f
2	$\equiv\text{TiOH}^{0.333-} + \text{H}^+ \leftrightarrow \equiv\text{TiOH}_2^{0.667+}$	K ₂	5.70	1 ^f	0 ^f
3	$\equiv\text{TiOH}^{0.333-} + \text{Na}^+ \leftrightarrow \equiv\text{TiOHNa}^{0.667+}$	K _C	2.21	0 ^f	1 ^f
4	$\equiv\text{TiOH}^{0.333-} + \text{H}^+ + \text{NO}_3^- \leftrightarrow \equiv\text{TiOH}_2\text{NO}_3^{0.333-}$	K _A	6.60	1 ^f	-1 ^f
5	$\equiv\text{Ti}_2\text{O}^{0.667-} + \text{Na}^+ \leftrightarrow \equiv\text{Ti}_2\text{ONa}^{0.333+}$	K _C	2.21	0 ^f	1 ^f
6	$\equiv\text{Ti}_2\text{O}^{0.667-} + \text{H}^+ + \text{NO}_3^- \leftrightarrow \equiv\text{Ti}_2\text{OHNO}_3^{0.667-}$	K _A	6.60	1 ^f	-1 ^f
7	$2\equiv\text{TiOH}^{0.333-} + \text{Cd}^{2+} \leftrightarrow (\equiv\text{TiOH})_2\text{Cd}^{1.334+}$	K _{Cd}	9.1	0.3	1.7
8	$\text{NaX} + \text{H}^+ \leftrightarrow \text{Na}^+ + \text{HX}$		1.4	-	-
9	$2\text{NaX} + \text{Cd}^{2+} \leftrightarrow 2\text{Na}^+ + \text{CdX}_2$	K _{XCd}	-2	-	-

^aSite densities of singly coordinate sites ($\equiv\text{TiOH}^{0.333-}$) = doubly coordinate sites ($\equiv\text{Ti}_2\text{O}^{0.667-}$) = 2.88 nm⁻¹

^bBoth capacitances of inner (C₁) and outer (C₂) Stern layer are 0.9 F/m²

^cIn the chemical equations ion-exchange site ($\equiv\text{Ti}_3\text{O}_7^{2-}$) is denoted by X. Cation exchange capacity is calculated to be 6.629 meq/g

^dSurface area from BET measurement is 206 m²/g

^fFixed parameters

Using the above equations, a two-step fitting approach was used to determine equilibrium constants. Figure 8.1 shows the flowchart of the parameter optimization process. Firstly, a titration model is set up to determine affinity constants for protons and electrolyte (i.e. Reactions 1-6, 8 of Table 8.1). Results from fitting titration data (Figure 8.2) were input into a second file which involves fitting of sorption edges data to obtain parameters of Reactions 7 and 9.

Figure 8.1 Flowchart illustrating a two-step process to obtaining equilibrium constants using PhreePlot.

Figure 8.2 CDMUSIC modelling of titration data from Figure 4.13. TNT = 12.5 g/L;
 $V = 20$ mL.

8.3 Result and Discussions

Both singly and doubly coordinated functional groups are responsible for the acid-base behavior of the nanotubes whereas the triply coordinated group is inert within the pH range of interest and will not be considered in this work (Hiemstra et al. 1989; Bourikas et al. 2001). For sorption of cadmium ions only singly coordinated oxygen is involved.

The presence of outer-sphere complexation at the surface is not possible because, as explained in §6.5, cadmium is a soft acid and tends to bond strongly to metal oxides (Posselt and Weber 1971; Hayes 1987; Papelis 1992). Addition of outer-sphere reaction (Equation 50) did not achieve a better fit than that of inner-sphere reaction alone.

In the initial fitting of the experimental data, each cadmium ion was assumed to binding to a single hydroxyl group:

The resulting fits, based on assumption that cadmium ion forms monodentate inner-sphere complex, are presented in Figure 8.3 and Figure 8.4. It was found that the experimental data were poorly fitted especially at low pH. The fit at low ionic strength appears accurate but Equation 51 was unable to describe sorption behaviour at higher ionic strengths.

Figure 8.3 CDMUSIC modelling of Figure 6.5 based on monodentate inner-sphere complex. IS = 0.1 M; $C_0 = 10^{-5}$ M.

Figure 8.4 CDMUSIC modelling of Figure 6.7 based on monodentate inner-sphere complex. TNT = 0.005 g/L; $C_0 = 10^{-5}$ M.

Equation 51 was replaced by using the second assumption that a single cadmium ion is binded to two hydroxyl groups (i.e. bidentate inner-sphere complex):

Figure 8.5 and Figure 8.6 showed the fits using Equation 52. It was observed that the cadmium complex form on TNT is better described as bidentate instead of monodentate inner-sphere. This is in accordance with previous literature on cadmium sorption by metal oxide (Venema et al. 1996). Bidentate cadium complex not only fitted the data well, the modelling also considred the effect of ionic strength on cadmium uptake, in that, increase concentration of NaNO₃ reduced the cadmium uptake (Figure 8.6). Otavite precipitation was simulated as well to indicate that the cadmium removed was due to sorption rather than precipitation.

In general better fit was achieved when both surface adsorption and ion-exchange of cadmium ion (Table 8.1 Reaction 7 and 9) was considered simultaneously.

Figure 8.5 CDMUSIC modelling of Figure 6.5 based on bidentate inner-sphere complex. IS = 0.1 M; C₀ = 10⁻⁵ M.

Figure 8.6 CDMUSIC modelling of Figure 6.7 based on bidentate inner-sphere complex. TNT = 0.005 g/L; $C_0 = 10^{-5}$ M.

8.4 Conclusion

From the results of this work, sorption of cadmium onto TNT involved two mechanisms. Firstly cadmium ions can be adsorbed onto hydroxyl groups at titanate nanotube surface forming inner-sphere complex with the OH groups. Secondly the heavy metal can be sorbed by ion-exchange at the interlayer. An uptake of a single cadmium ion results in the release of two monovalent ions into the solution.

Chapter 9 Conclusions and Recommendations

9.1 Conclusions

Nanotubes were synthesized via alkali hydrothermal process. From diffraction patterns, the nanotubes were determined to be crystalline with the phase sodium titanate (JCPDF 72-0148). TEM micrographs and BJH pore-size distribution showed that TNT has mesopores (2 – 3 nm). In addition, the one-dimensional nanomaterial has high surface area of 206 m²/g. Acid-base titration data showed TNT was amphoteric with positive (negative) charge at acidic (basic) condition. In addition, the absence of a point of zero salt effect was the result of permanent charge being present inside TNT.

Seven divalent cations (calcium, nickel, copper, zinc, strontium, cadmium and lead) were used to test the sorption capacities and selectivity of TNT. It was found that lead and cadmium were strongly binded to TNT. At pH 3 the sorption capacities were 1.27 and 0.39 mmol/g, correspondingly. The capacities in descending order was lead >> cadmium > copper > zinc > calcium > strontium > nickel. The Kurbatov plot of each cations, with the exception of nickel, showed the highest curve being post-transition lead followed by transition cations (cadmium, copper and zinc) and finally alkaline earth cations (calcium and strontium). Cation uptakes were correlated with the intrinsic parameters of cations. In the linear regression analyses, it was found sorption capacity was able to correlate well with hydrolysis constants, electronegativity and hardness with 95% confidence limits. Throughout the empirical analyses, nickel showed abnormality in that its sorption capacity was lower than calcium and strontium. Linear regression analyses also failed when taking nickel into consideration. It is suggested that nickel forms a different surface complex on TNT than other transition cations.

In the study of effects of solution composition on cadmium uptake by TNT, it was found that TNT can achieve a high uptake of cadmium at 1.1 mmol/g at pH 7. With

the increase of TNT concentration the sorption edge was left shifted. Higher TNT increases the sorption efficiency for a given pH. This is due to the increase in availability of sites for cadmium binding. At low ionic strength (0.001 – 0.01 M), the sorption of cadmium were not significantly affected. This is because cadmium was binded as an inner-sphere. Ionic strength, however, did have an effect on cadmium uptake at high concentration. This suggests two mechanisms were involved in cadmium uptake, mainly, inner-sphere complexation and ion-exchange. As shown from sorption isotherm, TNT showed high selectivity of cadmium over nickel in a ternary system study. The preferred selectivity indicates that TNT can be a good sorbent for the recovery of cadmium from cadmium-nickel co-exisiting wastewater (such as battery manufacturing industry).

In comparing Na 1s spectra of samples before and after sorption, it was found the latter had lower intensity. The observation was consistent for samples equilibrate at pH 3, 7 and 9. This can be attributed to a combination of followings (i) exchange of sodium with protons for samples equilibrated at pH 3 (ii) exchange of sodium with cadmium when the latter uptake is significant (iii) presence of higher sodium content due to electrostatic attraction of sodium electrolyte at pH 9. Studies of cadmium absorption K-edge showed that samples equilibrate at 0.001 and 0.1 M had similar Fourier transformed magnitude except for the intensities of the peaks. The similarities mean that local environment surrounding cadmium was the same. Fitting of spectra showed that scattering paths Cd-O and Cd-Ti fitted the spectra.

Titration and sorption data from batch test were fitted to theoretical surface complexation modelling. Charge distribution multisite ion complexation (CDMUSIC) model took into the consideration of crystallographic details on the surface oxygens. Using PhreePlot, it was found that both sets of data can be satisfactorily described by considering the interlayer sites and weak and strong surface sites. In addition, cadmium uptake can be simulated when the program considered both inner-sphere complexation at surface and ion-exchange at the interlayer (Figure 9.1).

Figure 9.1 Cadmium ions are sorbed onto lattice sodium titanate nanotube via (i) surface complexation on the surface hydroxyl and (ii) ion-exchange at the inter-layers.

The sodium nanotube showed to be a potential industrial sorbent for the removal heavy metals from wastewater, in particular the recovery of cadmium and possibly lead. Further studies relating to other aspects should be studied prior to conducting a pilot-plant study.

9.2 Recommendations for Future Research

This thesis work involved primarily with investigation of cations sorption on TNT at pseudo-equilibrium state. Future works to complement this thesis should include:

- (i). Mass transfer dynamics and mechanisms of cations on TNT. Specifically, effects of solution composition on sorption and desorption kinetics.
- (ii). Reusability of TNT. Data explaining (a) regeneration of the sorbent (using various regenerants such as chelating agents, acids and bases)

and (b) the cyclical effect of regeneration on sorption efficiencies, should be useful for feasibility study of TNT as an industrial wastewater sorbent.

- (iii) Operation of TNT in practical manner. Application of sorbent could be in form of (i) suspension in a batch reactor (ii) enclosed columns or other means which are suitable for repeated operations. In addition, comparisons should be made against current industrial sorbents to assess the commercial viability of TNT.
- (iv). XAS analysis of TNT at various solution chemistry. Booking of beam time requires the submission of proposal half a year in advance. Due to overwhelming demand, the resulting allocated slots are often limited. The use of XAS could contribute significantly to the understanding of sorption mechanisms of Cd-TNT.
- (v). Anomaly of nickel cation. Despite nickel being a transition metal, its sorption behaviour was unusually similar to alkaline earth cations. Further studies, in particular using XAS, could be performed to understand how nickel cation is attached onto the surface of sorbent at equilibrium.
- (vi). Effects of humic acid on the uptake of divalent cations. As humic acid is a macromolecule, there is more than one site available for cation bonding. Complementary spectroscopic technique would be nuclear magnetic resonance (NMR).
- (vii). For effects of competing cations, there are insufficient data points in current study to conduct a proper fit-iteration process. It is recommended a full-scale study into this area to be conducted to facilitate the modelling study.

Appendix A The Gouy-Chapman Theory

In order to understand the relationship between potential and charge at the diffuse layer, this appendix will give a brief description of the Gouy-Chapman Theory and the derivation of its equation (Sposito 1984; Lyklema 1995; Stumm and Morgan 1996):

$$\sigma_d = -0.1174\sqrt{I} \sinh \frac{ze\psi_d}{2kT}$$

or in another form:

$$\sigma_d = -(8cRT\epsilon\epsilon_0)^{\frac{1}{2}} \sinh\left(\frac{zF\psi(x)}{2RT}\right)$$

which forms the basis of surface complexation models. The theory is based on principles of Poisson law and its hypotheses are (Sposito 1984; Stumm 1992; Lyklema 1995):

- (i). the charged species are point ions and the only mode of interaction is via Coulombic forces
- (ii). the surface is a uniform infinitely large plane of charge and distance x is measured from the head of diffuse layer.
- (iii). the solvent, water, is a structureless continuum which affects the equation through its dielectric constant
- (iv). the inner potential, $\psi(x)$, is proportional to the sorption energy, $W(x)$, needed to bring ion, i , from infinity to distance x . The relationship between $\psi(x)$ and $W(x)$ is given by:

$$W_i(x) = z_i F \psi(x) \quad [A. 1]$$

As mentioned above, the Poisson equation for the case of an infinitely large plane is:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{q(x)}{\epsilon\epsilon_0} \quad [\text{A. 2}]$$

where q is space charge density, ϵ_0 is the permittivity of free space (8.85×10^{-12} C/Vm), and ϵ is the relative dielectric constant (78.5 for water at 25 °C)

The space charge density is dependent on the local electrolyte concentrations. Using Boltzmann law, we can relate the local electrolyte concentrations to the bulk concentrations. Hence:

$$q(x) = F \sum_j c_j z_j \exp\left(\frac{-z_j F \psi(x)}{RT}\right) \quad [\text{A. 3}]$$

where F is Faraday constant (96 485 C/mol), z_j is the charge of electrolyte ion, c_j is bulk concentration of the electrolyte ion, and RT is universal gas constant (8.314 J/K.mol) and temperature (K), respectively.

For the case of 1:1 symmetrical electrolyte, $z_{\text{cation}} = +1$ and $z_{\text{anion}} = -1$, $c_{\text{cation}} = c_{\text{anion}} = c$, and the space charge density becomes:

$$q(x) = F \left[c \exp\left(\frac{-zF\psi(x)}{RT}\right) - c \exp\left(\frac{zF\psi(x)}{RT}\right) \right] \quad [\text{A. 4}]$$

Given that $(e^x - e^{-x}) = 2 \sinh x$ and substituting Equation [A.4] into Equation [A.2]:

$$\frac{d^2\psi(x)}{dx^2} = \frac{2cF}{\epsilon\epsilon_0} \sinh\left(\frac{zF\psi(x)}{RT}\right) \quad [\text{A. 5}]$$

For convenience, we can introduce the reciprocal of Debye length into Equation [A.5], given that reciprocal Debye length is:

$$\kappa = \left(\frac{F^2 \sum_j c_j z_j^2}{\varepsilon \varepsilon_0 RT} \right)^{\frac{1}{2}} \quad [\text{A. 6}]$$

For the case of 1;1 symmetrical electrolyte, Equation [A.6] becomes:

$$\kappa = \left(\frac{2cF^2}{\varepsilon \varepsilon_0 RT} \right)^{\frac{1}{2}} \quad [\text{A. 7}]$$

By substituting [A.7] into [A.5]:

$$\frac{d^2 \psi(x)}{dx^2} \frac{F}{RT} = \kappa^2 \sinh \left(\frac{zF\psi(x)}{RT} \right) \quad [\text{A. 8}]$$

To facilitate ease of integration, let $y = \frac{zF\psi(x)}{RT}$ and the Poisson-Boltzmann equation of [A.8] becomes:

$$\frac{d^2 y}{dx^2} = \kappa^2 \sinh y \quad [\text{A. 9}]$$

In order to integrate [A.9], a mathematical identity is needed:

$$2 \frac{d^2 y}{dx^2} dy = d \left(\frac{dy}{dx} \right)^2 \quad [\text{A. 10}]$$

Substituting [A.9] into left hand side of [A.10] and integrating both sides

$$2\kappa^2 \int \sinh y dy = \int d \left(\frac{dy}{dx} \right)^2 \quad [\text{A. 11}]$$

$$2\kappa^2 (\cosh y + \text{const.}) = \left(\frac{dy}{dx} \right)^2 \quad [\text{A. 12}]$$

Applying boundary conditions of the diffuse layer, $\frac{dy}{dx} = 0; y = 0$, the integral constant in [A.12] is -1. Hence:

$$2\kappa^2 (\cosh y - 1) = \left(\frac{dy}{dx} \right)^2 \quad [\text{A. 13}]$$

Given the trigonometric identity, $1 + 2 \sinh^2 \left(\frac{x}{2} \right) = \cosh x$, [A.14] becomes:

$$\left(\frac{dy}{dx} \right)^2 = 4\kappa^2 \sinh^2 \left(\frac{y}{2} \right) \quad [\text{A. 14}]$$

$$\frac{dy}{dx} = 2\kappa \sinh \left(\frac{y}{2} \right) \quad [\text{A. 15}]$$

Substituting the definitions of reciprocal Debye length [A.7] and $y = \frac{zF\psi(x)}{RT}$ back into [A.15] we get:

$$\frac{d\psi(x)}{dx} = - \left(\frac{8cRT}{\epsilon\epsilon_0} \right)^{\frac{1}{2}} \sinh \left(\frac{zF\psi(x)}{2RT} \right) \quad [\text{A. 16}]$$

Due to the relationship of the potential, ψ , behaving inversely to the distance, x , a negative sign is needed (Lyklema 1995). Using Gaussian law we can relate electric field strength, $\frac{d\psi(x)}{dx}$, to the charge at the diffuse layer:

$$\frac{d\psi(x)}{dx} = \frac{\sigma_d}{\epsilon\epsilon_0} \quad [\text{A. 17}]$$

Substitute [A.16] into [A.17] :

$$\frac{\sigma_d}{\varepsilon\varepsilon_0} = -\left(\frac{8cRT}{\varepsilon\varepsilon_0}\right)^{\frac{1}{2}} \sinh\left(\frac{zF\psi(x)}{2RT}\right) \quad [\text{A. 18}]$$

$$\sigma_d = -(8cRT\varepsilon\varepsilon_0)^{\frac{1}{2}} \sinh\left(\frac{zF\psi(x)}{2RT}\right) \quad [\text{A. 19}]$$

Appendix B Sensitivity of Measurement

Reproducibility of ICP measurement was determined by doing 50 replicates of a single cadmium solution (2×10^{-6} M). The corrected intensities of 50 replicates are given below:

Corrected Intensity				
28196.0	28791.6	28988.3	28741.6	28981.0
28530.8	28928.7	28925.1	28989.6	29003.1
28633.8	28755.6	28915.0	28950.7	28928.3
28706.3	28807.9	28899.7	28952.6	28880.1
28799.0	28758.9	28966.8	28753.2	28710.9
28824.5	28926.6	28848.3	28886.7	28768.1
28764.8	28798.5	29042.0	28819.7	28747.0
28744.0	28812.6	28920.3	28625.0	28792.4
28677.4	28712.1	28877.1	29013.1	28591.1
28933.9	28694.9	29002.6	28859.7	28623.2

Mean corrected intensity of 50 replicates is 28,816.2
Standard deviation of 50 replicates is 152.15.

Appendix C Experimental Data

Figure 4.13

IS = 0.001 M		IS = 0.01 M		IS = 0.1 M	
pH	Q (mol/g)	pH	Q (mol/g)	pH	Q (mol/g)
4.25	1.4500E-03	4.06	1.4400E-03	3.60	1.1700E-03
5.26	9.7930E-04	4.96	9.7820E-04	4.62	7.3412E-04
6.45	4.9499E-04	5.97	4.9484E-04	5.15	4.9363E-04
7.24	2.4878E-04	6.65	2.4872E-04	5.77	2.4842E-04
7.86	1.2483E-04	7.04	1.2469E-04	6.14	1.2455E-04
9.27	-1.2096E-04	8.33	-1.2426E-04	6.90	-1.2470E-04
9.74	-2.3776E-04	8.92	-2.4709E-04	7.28	-2.4872E-04
10.20	-3.4050E-04	9.40	-3.6717E-04	8.40	-3.7170E-04
		9.88	-4.7986E-04	8.97	-4.9316E-04

Figure 5.1

Pb		Cu		Zn	
C _e	q	C _e	q	C _e	q
(mmol/L)	(mmol/g)	(mmol/L)	(mmol/g)	(mmol/L)	(mmol/g)
4.202E-04	4.190E-01	2.630E-03	9.587E-02	1.171E-02	4.599E-02
1.332E-03	7.913E-01	7.567E-03	1.541E-01	2.315E-02	7.043E-02
7.904E-03	1.050E+00	1.253E-02	1.878E-01	3.909E-02	9.057E-02
2.074E-02	1.180E+00	1.993E-02	2.165E-01	5.121E-02	8.546E-02
1.433E-01	1.410E+00	5.768E-02	3.105E-01	1.234E-01	1.498E-01

Ca		Sr		Ni	
C _e	q	C _e	q	C _e	q
(mmol/L)	(mmol/g)	(mmol/L)	(mmol/g)	(mmol/L)	(mmol/g)
3.220E-03	3.931E-03	5.325E-03	1.249E-02	5.496E-03	1.189E-03
7.324E-03	1.410E-02	1.694E-02	2.151E-02	1.101E-02	3.733E-03
1.141E-02	2.564E-02	2.700E-02	3.349E-02	1.655E-02	4.223E-03
3.735E-02	4.100E-02	3.969E-02	3.635E-02	2.202E-02	7.213E-03
		1.028E-01	4.263E-02	5.486E-02	1.016E-02

Figure 5.2

Pb	Cu	Zn
----	----	----

pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed
10.12	99.506	10.06	99.654	10.09	97.196
9.67	99.652	9.60	99.859	9.62	98.239
7.87	99.512	7.50	91.156	8.37	78.924
5.36	89.877	5.70	40.059	5.85	31.748
5.17	87.995	5.46	35.968	5.54	26.421
4.39	77.722	4.46	21.943	4.49	10.547
4.01	71.414	4.02	19.428	4.02	10.280
Ca		Sr		Ni	
pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed
10.05	45.519	10.06	27.282	10.05	97.197
9.67	36.018	9.68	24.187	9.66	83.025
8.76	22.612	8.67	16.730	8.72	27.089
7.33	17.898	7.30	10.539	8.06	16.279
6.79	15.492	6.66	7.784	7.49	14.116
6.40	14.805	6.40	7.170	7.05	10.353
4.08	0.000	4.08	0.000	6.79	7.983
				6.69	6.050
				6.42	6.279

Figure 6.9

1:1				1:0.1			
Cd		Pb		Cd		Pb	
pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed
6.61	12.859	6.61	92.938	9.58	89.096	9.58	91.852
6.4	9.443	6.4	89.033	8.22	75.449	8.22	94.434
5.82	8.843	5.82	83.196	6.84	58.227	6.84	93.750
4.44	5.947	4.44	65.917	6.03	47.818	6.03	90.667
4.22	6.720	4.22	63.511	4.41	32.228	4.41	91.186
3.99	5.976	3.99	59.556	3.95	27.126	3.95	93.982
3.69	6.303	3.69	56.387	3.69	22.153	3.69	92.076

Figure 6.10

1:1				1:5			
Cd		Zn		Cd		Zn	
pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed

6.71	47.117	6.71	17.246	8.06	39.468	8.06	51.815
6.33	46.050	6.33	14.930	7.32	44.212	7.32	11.797
5.97	41.767	5.97	10.064	6.68	44.075	6.68	6.677
4.43	28.426	4.43	3.820	6.09	41.018	6.09	5.447
4.23	27.988	4.23	3.775	4.41	30.203	4.41	2.793
4.02	24.534	4.02	2.343	4.02	27.406	4.02	2.558
3.7	20.992	3.7	1.369	3.68	23.379	3.68	1.832

Figure 6.11

1:1				1:5			
Cd		Cu		Cd		Cu	
pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed
6.26	33.469	6.26	42.989	6.46	25.912	6.46	74.817
6.17	34.680	6.17	33.843	6.34	19.458	6.34	26.445
5.92	32.318	5.92	23.759	6.21	21.675	6.21	17.965
4.49	25.997	4.49	7.340	5.80	24.200	5.80	10.703
4.24	23.930	4.24	7.067	4.40	24.115	4.40	4.060
4.00	21.727	4.00	6.447	4.00	22.081	4.00	5.011
3.71	18.841	3.71	4.991	3.69	19.907	3.69	3.552

Figure 6.12

1:1				1:5			
Cd		Ni		Cd		Ni	
pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed
6.43	59.090	6.43	4.061	8.9	79.836	8.9	40.212
6.21	52.153	6.21	3.423	7.45	67.582	7.45	5.406
5.95	48.361	5.95	2.594	6.69	57.487	6.69	3.608
4.39	32.901	4.39	2.153	6	47.684	6	2.395
4.22	29.982	4.22	1.555	4.43	31.269	4.43	0.791
3.99	26.893	3.99	0.863	4.02	28.384	4.02	0.726
3.67	22.245	3.67	0.000	3.69	23.738	3.69	0.480

Figure 6.13

1:1				1:5			
Cd		Ca		Cd		Ca	
pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed
6.73	60.045	6.73	4.392	9.5	82.535	9.5	2.526

6.3	52.419	6.3	4.239	8.04	67.547	8.04	1.957
5.93	47.225	5.93	3.467	6.73	54.160	6.73	1.974
4.39	31.314	4.39	0.000	5.96	44.744	5.96	1.690
4.19	31.338	4.19	0.336	4.44	29.884	4.44	0.935
3.97	27.668	3.97	0.000	4.04	26.456	4.04	0.924
3.67	24.436	3.67	0.000	3.73	24.592	3.73	0.130

Figure 6.14

1:1				1:5			
Cd		Sr		Cd		Sr	
pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed
6.44	57.431	6.44	3.049	9.48	86.581	9.48	4.427
6.2	53.162	6.2	2.811	8.08	72.997	8.08	3.072
5.9	48.596	5.9	1.876	6.91	60.230	6.91	3.518
4.4	32.639	4.4	2.134	6.04	50.168	6.04	2.835
4.24	30.391	4.24	1.563	4.45	33.918	4.45	2.193
3.98	28.151	3.98	1.634	4.02	29.671	4.02	1.653
3.7	24.354	3.7	0.993	3.72	25.050	3.72	1.026

Figure 5.10, Figure 5.11 and Figure 5.9

pH 3				pH 4.8			
Time (h)	Cd (μM)	Na (μM)	Ti (μM)	Time (h)	Cd (μM)	Na (μM)	Ti (μM)
1416	3.9692	6.3098	0.1425	1416	0.0152	3.6100	0.0539
1248	3.8515	6.3915	0.1425	1248	0.0110	3.5518	0.0443
1104	3.7321	6.2578	0.1465	1104	0.0129	3.5518	0.0455
912	3.5892	6.3395	0.1533	912	0.0138	3.5736	0.0453
744	3.4471	6.2578	0.1606	744	0.0222	3.5701	0.0519
648	3.3862	6.3123	0.1573	648	0.0141	3.6100	0.0466
552	3.2789	6.3238	0.1607	552	0.0147	3.5518	0.0461
360	3.0042	6.2977	0.1717	360	0.0151	3.5736	0.0457
312	2.9638	6.3217	0.1867	312	0.0133	3.5684	0.0468
264	2.8543	6.2502	0.1631	264	0.0143	3.5915	0.0493
216	2.7971	6.3493	0.1818	216	0.0144	3.6075	0.0482
168	2.7340	6.3395	0.1880	168	0.0140	3.5874	0.0462
120	2.5083	6.2578	0.1804	120	0.0157	3.5971	0.0462
96	2.4170	6.4434	0.1809	96	0.0155	3.5951	0.0486
72	2.3809	6.4099	0.1868	72	0.0163	3.5842	0.0481

48	2.2475	6.4926	0.1911	48	0.0150	3.5629	0.0480
24	2.0614	6.4335	0.1898	24	0.0160	3.5391	0.0478
12	1.9028	6.4373	0.1792	12	0.0156	3.5311	0.0461
10	1.9337	6.4572	0.1814	10	0.0152	3.5491	0.0474
8	1.9297	6.4448	0.1868	8	0.0167	3.5095	0.0486
6	1.9396	6.4741	0.1855	6	0.0188	3.5333	0.0478
5	1.9226	6.3711	0.1787	5	0.0174	3.5463	0.0489
4	1.9278	6.4396	0.1751	4	0.0180	3.5146	0.0466
3	1.9280	6.3904	0.1681	3	0.0190	3.5229	0.0479
2	1.9821	6.4160	0.1596	2	0.0187	3.4778	0.0490
1	2.1369	6.3511	0.1436	1	0.0243	3.5489	0.0508
0.833	2.2085	6.3098	0.1408	0.833	0.0220	3.5323	0.0493
0.667	2.2808	6.3915	0.1370	0.667	0.0214	3.5298	0.0477
0.500	2.4748	6.3449	0.1323	0.500	0.0269	3.5019	0.0664
0.333	2.7545	6.2713	0.1284	0.333	0.0285	3.5309	0.0469
0.167	3.4760	6.3968	0.1268	0.167	0.0370	3.5145	0.0484
0	10.0000	0.0000	0.1408	0	10.0000	0.0000	0.0664

Figure 6.4

pH 3		pH 4		pH 7	
C _e	q	C _e	q	C _e	q
(mmol/L)	(mmol/g)	(mmol/L)	(mmol/g)	(mmol/L)	(mmol/g)
1.372E-05	1.464E-02	7.129E-06	1.477E-02	4.843E-05	3.397E-02
6.975E-04	8.407E-02	4.493E-04	8.904E-02	4.885E-05	8.316E-02
8.813E-04	1.443E-01	1.016E-04	1.598E-01	5.386E-06	1.988E-01
5.654E-03	2.483E-01	8.763E-04	3.439E-01	4.015E-03	8.987E-01
2.348E-02	3.232E-01	1.104E-02	5.722E-01	3.284E-02	1.071E+00
6.759E-02	4.135E-01	5.319E-02	7.016E-01	3.610E-01	1.039E+00
1.638E-01	4.955E-01	1.445E-01	8.811E-01	1.292E-01	1.024E+00
4.198E-01	4.910E-01	4.018E-01	8.509E-01	8.337E-01	1.075E+00
8.602E-01	4.810E-01	8.414E-01	8.574E-01	4.313E+00	1.102E+00
4.589E+00	1.304E+00	4.432E+00	1.811E+00		

Figure 6.5

TNT = 0.005 g/L		TNT = 0.02 g/L		TNT = 0.05 g/L		TNT = 0.5 g/L	
pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed	pH _{final}	%sorbed
6.63	75.3	3.13	33.5	3.31	78.9	3.18	100

6.54	71.3	3.68	53.9	3.88	93.6	3.6	99.7
6.35	69.3	4.04	60.8	4.25	97.9	4.56	99.9
5.93	62.5	4.48	76.1	4.87	99.7	5.61	100
5.53	56.4	5.15	91.4	5.78	99.7	6.85	99.9
5.3	52.9	5.38	92.3	5.9	100	7.3	100
5.31	51.8	5.48	92.3	6.16	100		
5.08	49.5	6.39	99.8	6.22	100		
4.38	36.9	6.75	99.9	6.74	100		
3.98	29.6						
3.68	23.7						
3.35	16.3						
3.08	12.4						

Figure 6.6

TNT = 0.005 g/L		TNT = 0.02 g/L		TNT = 0.05 g/L		TNT = 0.5 g/L	
pH _{initial}	pH _{final}	pH _{initial}	pH _{final}	pH _{initial}	pH _{final}	pH _{initial}	pH _{final}
8.24	6.63	3.31	3.13	3.32	3.31	3.09	3.18
7.3	6.54	3.8	3.68	3.97	3.88	3.45	3.6
6.95	6.35	4.14	4.04	4.3	4.25	4.35	4.56
6.39	5.93	4.68	4.48	5.01	4.87	5.66	5.61
5.98	5.53	5.8	5.15	5.96	5.78	6.88	6.85
5.78	5.3	5.95	5.38	6.2	5.9	7.79	7.3
5.74	5.31	6.08	5.48	6.31	6.16		
5.39	5.08	6.22	6.39	6.31	6.22		
4.42	4.38	8.16	6.75	7.16	6.74		
3.98	3.98						
3.67	3.68						
3.36	3.35						
3.04	3.08						

Figure 6.7

IS = 0.001 M	
pH _{final}	%sorbed
8.37	98.9
6.77	96.9
6.62	95.2
6.51	93.2

IS = 0.01 M	
pH _{final}	%sorbed
8.45	98.8
6.85	92.5
6.59	88.1
6.33	84.4

Figure 6.8

IS = 0.001 M	
pH _{initial}	pH _{final}
9.22	8.37
8.23	6.77
7.19	6.62
7.11	6.51

IS = 0.01 M	
pH _{initial}	pH _{final}
9.26	8.45
8.61	6.85
7.96	6.59
7.4	6.33

6.09	86.1	6.05	82.1	6.5	6.09	7.05	6.05
5.73	79.7	5.61	69.1	6.37	5.73	6.33	5.61
5.47	75.4	5.38	65.7	6.21	5.47	6.05	5.38
5.45	75.2	5.37	65.5	6.15	5.45	6.02	5.37
5.22	70.4	5.16	61.9	5.77	5.22	5.57	5.16
4.47	50.1	4.49	43.5	4.54	4.47	4.46	4.49
4.06	37.2	4.1	35.4	4.08	4.06	4.02	4.1
3.75	28.1	3.82	27.6	3.74	3.75	3.69	3.82
3.45	20	3.52	22.3	3.47	3.45	3.4	3.52
3.18	10.7	3.22	18.5	3.17	3.18	3.1	3.22

Appendix D PhreePlot Files

```
# Predominance diagram for the Cd2+-CO2-H2O

SPECIATION
# database          minteq.v4.dat
  jobTitle          "Predominance diagram for the Cd2+-CO2-H2O"
  calculationType    ht1
  calculationMethod  1
  mainSpecies        Cd
  xmin              4.0
  xmax              11.0
  ymin              -9.0
  ymax              -1.0
  resolution        200

PLOT
  xtitle            pH
  ytitle            "log P<sub>CO2</sub> (atm)"
  pxmajor           1
  pymajor           1

CHEMISTRY

include 'ht1.inc'

SOLUTION 1
  temp  25
  pH    1.8
  units mol/kgw
# Na    1e-1
# N(+5) 1e-1 charge
  Cd    1e-5
END

USE solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+ -<x_axis> NaOH 1
```

```
-force_equality true
CO2(g) <y_axis> 1
-force_equality true

Otavite      0 0
Cd(OH)2(a)   0 0

END
```

Model cadmium speciation

SPECIATION

```
# database                minteq.v4.dat
  calculationType          custom
  calculationMethod        1
  xmin                     3.0
  xmax                     10
  resolution               101
```

PLOT

```
  plotTitle               "Cd solubility vs pH<br>(plotting relevant
species)"
  xtitle                  pH
  ytitle                  "log [C] (mol/kgw)"
  pymin                   -10.0
  pymax                   -3.0
  lineWidth               0.4
  customXcolumn           pH
  lines                   Cd<sub>T</sub> Cd+2 CdOH+ CdNO3+ CdCO3 \
                          CdHCO3+ Cd(CO3)2-2 Otavite NaCO3- NaHCO3 \
                          CO3-2 HCO3- CO2
```

CHEMISTRY

TITLE Model cadmium speciation

SELECTED_OUTPUT

```
  reset false
  high_precision true
```

PHASES

```
  Fix_H+
  H+ = H+
  log_k 0.0
```

SOLUTION 1

```
  temp    25
  pH      2.8
```

```

units      mol/kgw
density    1
Cd         1e-5      # 1e-4
Na         0.1       # 0.01 and 0.001
N(5)       0.1 charge # 0.01 and 0.001

USER_PUNCH
headings pH  Cd<sub>T</sub> Cd+2 CdOH+ CdNO3+ CdCO3 CdHCO3+ \
Cd(CO3)2-2 Otavite NaCO3- NaHCO3 CO3-2 HCO3- CO2
-start
10 totel = SYS("Cd",n,n$,t$,c)
20 punch -la("H+"), log10(tot("Cd")), lm("Cd+2"), lm("CdOH+"),\
lm("CdNO3+"), lm("CdCO3"), lm("CdHCO3+"), lm("Cd(CO3)2-2"),\
log10(equi("Otavite")), lm("NaCO3-"), lm("NaHCO3"), lm("CO3-2"),\
lm("HCO3-"), lm("CO2")
END

USE solution 1

EQUILIBRIUM_PHASES
O2(g) -0.677 0.1
CO2(g) -3.5 1
Fix_H+ -<x_axis> NaOH 10
-force_equality true

Otavite 0 0
Cd(OH)2 0 0

END

```

```
# Fit acid/base titration data

SPECIATION
# database                                minteq.v4.dat
  calculationType                         fit
  calculationMethod                       1
  numericTags                             <mass> = 0.25 \
                                           <V0> = 0.02 \
                                           <areapergram> = 206 \
                                           <Xeq> = 6.629e-3*<mass>
                                           <acid> = 0.25 \
                                           <base> = 0.25

FIT
  dataFile                               "titration.dat"
  fitMethod                              nlls
  dependentVariableColumnObs             pHobs
  dependentVariableColumnCalc            pHcalc
  fitFiniteDiffStepSize                  1.0E-5
  fitConvergenceCriterion                 1.0E-9
  fitMaxStepSize                         1.0
  fitWeightingMethod                     0
  numberOfFitParameters                  6
  fitParameterNames                      "K12" "K21" "Kc" "Ka" "Kxh"
  fitLogParameters                       0 0 0 0 0
  fitAdjustableParameters                0 0 0 0 1
  fitParameterValues                     5.70 5.14 2.21 6.6 1.07
  fitlowerparametervalues                 -100 -100 -100 -100 -100
  fitupperparametervalues                 100 100 100 100 100

PLOT
  plotTitle                             "Fit Acid/Base Titration Data"
  xoffset                                60
  pxmin                                  3
  pxmax                                  11
  pymin                                  3
  pymax                                  11
  xtitle                                pH<sub>observed</sub>
  ytitle                                pH<sub>calculated</sub>
```

```

customXcolumn      pHobs
points             pHcalc
labels             "NaNO3 = 0.001M" "NaNO3 = 0.01M" "NaNO3 =
0.1M"
legendTextSize     1.9
pointSize          3.0
labelSize          0
post               id
extraSymbolsLines  extraSymbolsLinesFit.dat
extraText          extraTextFit.dat

```

CHEMISTRY

TITLE Fit Acid/Base Titration Data

PHASES

```

Fix_H+
H+ = H+
log_k 0.

```

SURFACE_MASTER_SPECIES

```

Tit_unia  Tit_uniaOH-0.333
Tit_bi    Tit_biO-0.667

```

SURFACE_SPECIES

Singly Coordinated Oxygen

```

Tit_uniaOH-0.333 = Tit_uniaOH-0.333
-cd_music 0 0 0 0 0
log_k 0

```

```

Tit_uniaOH-0.333 + H+ = Tit_uniaOH2+0.667
-cd_music 1 0 0 0 0
log_k <K12>

```

```

Tit_uniaOH-0.333 + Na+ = Tit_uniaOHNa+0.667

```

```
-cd_music 0 1 0 0 0
log_k <Kc>

Tit_uniaOH-0.333 + H+ + NO3- = Tit_uniaOH2NO3-0.333
-cd_music 1 -1 0 0 0
log_k <Ka>

# Doubly Coordinated Oxygen

Tit_biO-0.667 = Tit_biO-0.667
-cd_music 0 0 0 0 0
log_k 0

Tit_biO-0.667 + H+ = Tit_biOH+0.333
-cd_music 1 0 0 0 0
log_k <K21>

Tit_biO-0.667 + Na+ = Tit_biONa+0.333
-cd_music 0 1 0 0 0
log_k <Kc>

Tit_biO-0.667 + H+ + NO3- = Tit_biOHNO3-0.667
-cd_music 1 -1 0 0 0
log_k <Ka>

EXCHANGE_MASTER_SPECIES
X X-

EXCHANGE_SPECIES
X- = X-
log_k 0

H+ + X- = HX
log_k <Kxh>

Na+ + X- = NaX
log_k 0

SURFACE 1
```

```
-cd_music
-sites_units density
Tit_unia0-0.691      2.88 206 <mass>
Tit_bi0-0.629      2.88
-cap      0.9  0.9
-equil 1

EXCHANGE 1
X- <Xeq>
-equil 1

SELECTED_OUTPUT
high_precision true
reset false

USER_PUNCH
headings pHcalc vh2o I charge0 charge1 charge2
-start
10 vh2o = TOT("water")
20  punch  -LA("H+"),  vh2o,  MU,  EDL("charge","Tit"),
EDL("charge1","Tit"), EDL("charge2","Tit")
-end

# 1. first simulation
# equilibrate surface at initial pH and I and save

SOLUTION 1
units mol/kgw
water  <V0>
pH      <pH0>          # from data file
Na      <IS>           # background electrolyte
N(+5)   <IS>  charge   # from data file

EQUILIBRIUM_PHASES
O2(g) -0.67          # to prevent N2 -> NH4+

SAVE solution 2
SAVE exchange 2
SAVE surface 2
```


END

2. second simulation

add alkali

titrate one step

USE solution 2

USE exchange 2

USE surface 2

REACTION 1

NaOH <base>

H2O 55.5

<vol_base>

EQUILIBRIUM_PHASES

O2(g) -0.67 # to prevent N2 -> NH4+

SAVE solution 3

SAVE exchange 3

SAVE surface 3

END

3. third simulation

add acid

titrate one step

USE solution 3

USE exchange 3

USE surface 3

REACTION 2

HNO3 <acid>

H2O 55.5

<vol_acid> # L

EQUILIBRIUM_PHASES

O2(g) -0.67 # to prevent N2 -> NH4+

END

```
# Fit sorption edge data

SPECIATION
  database           wateq4f.dat
  calculationType    fit
  calculationMethod   1
  numericTags        <mass> = <dose>*0.05*<sites> \
                     <Xeq> = 6.629e-3*<dose>*0.05 \
                     <K12> = 5.7 \
                     <K21> = 5.14 \
                     <Kc> = 2.21 \
                     <Ka> = 3.6 \
                     <Kxh> = 1.4 \
                     <z1> = 2-<z0>

FIT
  dataFile           "ExptData2.dat"
  fitMethod          nlls
  dependentVariableColumnObs pcsorbobs
  dependentVariableColumnCalc pcsorb
  fitFiniteDiffStepSize 1.0E-5
  fitConvergenceCriterion 1.0E-9
  fitMaxStepSize      1.0
  fitWeightingMethod   0
  fitParameterNames    KxCd K1Cd z0 sites
  fitLogParameters     0 0 0 0
  fitAdjustableParameters 0 0 1 0
  fitParameterValues    -2 9.1 0.3 10
  fitlowerparametervalues -100 -100 -100 -100
  fitupperparametervalues 100 100 100 100

PLOT
  plotTitle          "Fit Sorption Edge Data"
  xoffset            60
  xtitle             pH<sub>observed</sub>
  ytitle             Cd<sub>solution</sub> " mol/L"
  pxmin              3
  pxmax              9
  pxmajor            1
```

```

customXcolumn      pHobs
points             pcsorbobs
lines              pcsorb
legendTextSize     1.9
pointSize          3.0
labelSize          0
lineColor          red
post               id
extraText          extraTextCdTitanate0.dat
    
```

CHEMISTRY

TITLE Fit sorption edge data

PHASES

```

Fix_H+
H+ = H+
log_k 0
    
```

SURFACE_MASTER_SPECIES

```

Tit_unia      Tit_uniaOH-0.333
Tit_bi        Tit_biO-0.667
    
```

SURFACE_SPECIES

Singly Coordinated Oxygen

```

Tit_uniaOH-0.333 = Tit_uniaOH-0.333
-cd_music 0 0 0 0 0
log_k 0
    
```

```

Tit_uniaOH-0.333 + H+ = Tit_uniaOH2+0.667
-cd_music 1 0 0 0 0
log_k <K12>      # 5.70
    
```

```

Tit_uniaOH-0.333 + Na+ = Tit_uniaOHNa+0.667
-cd_music 0 1 0 0 0
log_k <Kc>      # 2.21
    
```

```

Tit_uniaOH-0.333 + H+ + NO3- = Tit_uniaOH2NO3-0.333
-cd_music 1 -1 0 0 0
log_k <Ka>      # 6.6

# Doubly Coordinated Oxygen

Tit_biO-0.667 = Tit_biO-0.667
-cd_music 0 0 0 0 0
log_k 0

Tit_biO-0.667 + H+ = Tit_biOH+0.333
-cd_music 1 0 0 0 0
log_k <K21>      # 5.14

Tit_biO-0.667 + Na+ = Tit_biONa+0.333
-cd_music 0 1 0 0 0
log_k <Kc>      # 2.21

Tit_biO-0.667 + H+ + NO3- = Tit_biOHNO3-0.667
-cd_music 1 -1 0 0 0
log_k <Ka>      # 6.6

# Cd+2 bidentate inner-sphere

2Tit_uniaOH-0.333 + Cd+2 = (Tit_uniaOH)2Cd+1.334
-cd_music <z0> <z1> 0 0 0
log_k <K1Cd>

# Cd+2 monodentate inner-sphere

# Tit_uniaOH-0.333 + Cd+2 = (Tit_uniaOH)Cd+1.667
# -cd_music <z0> <z1> 0 0 0
# log_k <K1Cd>

EXCHANGE_MASTER_SPECIES
X    X-

EXCHANGE_SPECIES

```

```
X- = X-
log_k 0

H+ + X- = HX
log_k <Kxh>    # 1.4

Na+ + X- = NaX
log_k 0

Cd+2 + 2X- = CdX2
log_k <KxCd>

SURFACE 1
-cd_music
-sites_units density
Tit_uniaOH-0.333      2.88 206 <mass>
Tit_biO-0.667        2.88
-cap    0.9  0.9
-equil 1

EXCHANGE 1
X- <Xeq>
-equil 1

SELECTED_OUTPUT
high_precision true
reset false

USER_PUNCH
headings pHcalc vh2o MOLCd SYSCd TOTCd pcsorb
-start
10 vh2o = TOT("water")
20 MOLCd = MOL("Cd+2")
30 SYSCd = SYS("Cd")/vh2o
40 TOTCd = TOT("Cd")
45 pcsorb = (1 - TOTCd/SYSCd) * 100
50 punch -LA("H+"), vh2o, MOLCd, SYSCd, TOTCd, pcsorb
-end
```

```
# 1. first simulation
# equilibrate surface at initial pH and I and save

SOLUTION 1
  units mol/kgw
  water      0.05
  pH         <pH0>          # from data file
  Na         <IS>           # background electrolyte
  N(+5)      <IS> charge    # from data file
  Cd         0

EQUILIBRIUM_PHASES
  O2(g)      -0.67          # to prevent N2 -> NH4+
  CO2(g)     -3.5

SAVE solution 2
SAVE exchange 2
SAVE surface 2

END

# 2. second simulation
# add alkali
# titrate one step

USE solution 2
USE exchange 2
USE surface 2

REACTION 1
  NaOH       <conc_base>
  H2O        55.5
  <vol_base>          # L

EQUILIBRIUM_PHASES
  O2(g)      -0.67          # to prevent N2 -> NH4+
  CO2(g)     -3.5

SAVE solution 3
```

SAVE exchange 3

SAVE surface 3

END

3. third simulation

add acid

titrate one step

USE solution 3

USE exchange 3

USE surface 3

REACTION 2

HNO3 <conc_acid>

H2O 55.5

<vol_acid> # L

EQUILIBRIUM_PHASES

O2(g) -0.67 # to prevent N2 -> NH4+

CO2(g) -3.5

SAVE solution 4

SAVE exchange 4

SAVE surface 4

END

4. fourth simulation

add cadmium

USE solution 4

USE exchange 4

USE surface 4

REACTION 3

Cd <Cdstock>

H2O 55.5

1e-4 # L

EQUILIBRIUM_PHASES

O2(g) -0.67 # to prevent N2 -> NH4+

CO2(g) -3.5

Fix_H+ -<pHobs> NaOH

-force_equality true

Otavite 0 0

END

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