<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>A new integrated approach for dye removal from wastewater by polyoxometalates functionalized membranes (Main article)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Yao, Lei; Zhang, Lizhi; Wang, Rong; Chou, Shuren; Dong, ZhiLi</td>
</tr>
<tr>
<td><strong>Date</strong></td>
<td>2015</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/38970">http://hdl.handle.net/10220/38970</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>© 2015 Elsevier B.V. This is the author created version of a work that has been peer reviewed and accepted for publication by Journal of Hazardous Materials, Elsevier B.V. It incorporates referee’s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<a href="http://dx.doi.org/10.1016/j.jhazmat.2015.09.027">http://dx.doi.org/10.1016/j.jhazmat.2015.09.027</a>].</td>
</tr>
</tbody>
</table>
A new integrated approach for dye removal from wastewater by polyoxometalates functionalized membranes

Lei Yao\textsuperscript{a,b}, Lizhi Zhang\textsuperscript{b}, Rong Wang\textsuperscript{b,*}, Shuren Chou\textsuperscript{b}, ZhiLi Dong\textsuperscript{a,*}

\textsuperscript{a} School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

\textsuperscript{b} Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore

*Corresponding authors: Rong Wang & ZhiLi Dong

Mailing address: School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore.

Tel: 65-67906727; Fax: 65-67909081.

E-mail addresses: rwang@ntu.edu.sg (R. Wang); zldong@ntu.edu.sg (Z. Dong)
Abstract

Membrane technique is a promising way for the removal of dyes from wastewater. A unique approach combining both the adsorptive and the catalytic membrane processes was proposed on the basis of a new functionalized membrane. The membrane integrating both the adsorptive and catalytic activities was developed by introducing polyoxometalates (POMs) as an ideal candidate for the membrane functionalization via a novel sol-gel method. A two-step protocol, adsorptive separation and catalytic degradation, was designed for dye removal, realizing an excellent dye rejection with easy and economic membrane regeneration through simply soaking the membrane in a limited volume of dilute oxidant solution. This approach is feasible and versatile owing to the flexible selection of distinct POMs and design of catalytic degradation routes as required. As a result, the current research provides insight into a new methodology of the membrane technique in dye removal applications.

Keywords: polyoxometalates, membrane, adsorption, catalytic degradation, dye removal
1. Introduction

The intensive industrialization throughout the world has always been followed by increasing generation of wastewater. Industrial wastewater contains hazardous and refractory organic pollutants, causing severe environmental problems. One of the typical organic pollutant species, synthetic dyes with an annual production of more than 700,000 tonnes are widely used in textile, leather, paper, paint, plastic and other industries [1]. It has been estimated that more than 10–15% of the total dyestuff was released into the environment during their synthesis and dyeing process [2], which is a serious threat to aquatic ecosystem as well as public health. The removal of dyes from wastewater is hence of great importance before discharging into the environment.

For the removal of dyes from wastewater, researchers in the past few decades have made great efforts, and various techniques such as adsorption [3-5], coagulation/flocculation [6, 7], membrane separation [8-12], catalytic oxidation [4, 13, 14], etc. have been well developed. Each of these techniques has its specific advantages. At the same time, specific disadvantages are also accompanied. For example, adsorption or coagulation/flocculation is highly efficient and flexible for dye removal from wastewater, while the high sludge production as well as the post-treatment of the toxic sludge is all the time a big issue for large-scale applications [15]. Similarly, membrane separation technique such as nanofiltration (NF) and reverse osmosis (RO) is promingly attractive for the removal of dyes from wastewater because of its production of high-quality effluent without the generation of sludge, while the major disadvantage of this technique is the low water permeability with the high energy cost. [16, 17] In addition, catalytic oxidation (e.g.,
Fenton reaction) is able to generate highly reactive radicals driving the mineralization of dyes in wastewater within a short duration, while there are great issues in terms of the recycling and recovery of catalysts from wastewater and the high cost due to the employment of a large amount of oxidants (e.g., H$_2$O$_2$) in a large volume of effluents. In order to make best use of the advantages and bypass the disadvantages, researchers in recent years have begun to focus on the development of integrated techniques for the removal of dyes from wastewater.

Adsorptive membranes, which integrate the membrane separation and the adsorption process in one device, have drawn increasing attention for dye removal from wastewater. For example, Lin et al. prepared poly(methyl methacrylate)/Na$^+$-montmorillonite membranes for the adsorptive removal of methyl violet [18]. Chiu et al. fabricated quaternary ammonium groups functionalized glass fiber membranes for the adsorptive removal of Cibacron blue 3GA [19]. In addition, Daraei et al. employed organoclay/chitosan-coated PVDF membrane for the adsorptive removal of methylene blue and acid orange 7 [20]. Compared with the single adsorption or coagulation/flocculation process, enrichment separation of dyes from wastewater with less sludge generation can be achieved through adsorbing dyes onto fixed membranes. However, not only the membrane regeneration but also the post-treatment of the desorbed dyes was still a big headache, because a large amount of eluting solution (usually 60–80% methanol solution) was needed [18, 19] and then a new pollution source including the desorbed dyes and plenty of organic solvents emerged.
Catalytic membranes, which integrate the membrane separation and the catalytic oxidation in one device, have drawn increasing attention for dye removal from wastewater. For example, Dorraji et al. incorporated Fenton-like catalysts (nanosized Fe₂O₄) with chitosan membranes for the removal of reactive blue 19 in the presence of H₂O₂ [21]. Zhu et al. immobilized the Ti-Mn catalyst on the TiO₂ coated Al₂O₃ membrane for the catalytic degradation of reactive Red-3BS with ozone as the oxidant [22]. In addition, Kiwi et al. utilized Fe-Nafion membranes with H₂O₂ for the photodegradation of orange II [23, 24]. Compared with the single catalytic oxidation process, catalytic oxidation with easier catalyst recycling and recovery can be achieved through incorporating the catalysts with the membrane substrate. However, such a technique still cannot overcome the challenge in terms of the high cost due to the employment of a large amount of oxidants (e.g., H₂O₂ or ozone) in a large volume of effluents. Although it was reported that oxygen in air can be allowed as the green and cheap oxidant if catalytic membranes acted as an interface contactor which is favorable for accelerating the catalytic oxidation, the catalytic efficiency was limited even for those less refractory organic pollutants (such as phenol and organic acids) than dyes [25-27].

Relying on strengths to mutually offset weaknesses, the current work intends to combine both the adsorptive and catalytic membrane processes to develop a new integrated approach (adsorptive separation and catalytic degradation) for the even better removal of dyes from wastewater. The strategy for realizing this idea is to construct a membrane with both adsorptive and catalytic activities, which shall be achieved by introducing polyoxometalates (POMs) for membrane functionalization. POMs, which are unique nano-
sized metal-oxygen cluster species, have been attracting considerable attention in broad fields such as catalysis, materials, environment, medicine and biology, by virtue of their versatile nature in terms of composition, structure, size, charge distribution, solubility, acidity and redox potential [28-33]. POMs as potent catalysts have been well reported for catalytic degradation of dyes in wastewater [34-37]. On the other side, it was demonstrated by our previous work [38] that POMs possess the capability to absorb dyes from wastewater. Accordingly, POMs are becoming the ideal candidate for the construction of the desired membrane.

2. Experimental

2.1. Materials and chemicals

A commercially available polymer, polyetherimide (PEI, Ultem® 1000, General Electric Plastics), was selected as the polymeric material for membrane fabrication, where a sol-gel precursor, aluminum-tri-sec-butoxide (ASB, Sigma-Aldrich), was used as the additive. N-methyl-2-pyrrolidone (NMP, >99.5%, Merck) was used as a solvent for dope preparation. Polyethylene glycol (PEG, Sigma-Aldrich) was used as a pore-former during the membrane fabrication. (3-aminopropyl)trimethoxysilane (APTMS, Sigma-Aldrich) was used as a coupling agent for POMs incorporation with the membrane. \( \text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}] \) (PVMo) was selected as a model of POMs and synthesized according to the literature [32]. Reactive black 5 (RB5, Sigma-Aldrich) was selected as a model dye. OXONE® (monopersulfate compound, \( 2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4 \), Sigma-Aldrich) was used as an oxidant for catalytic degradation.
2.2. Membrane fabrication route

The proposed membrane fabrication route is shown in Fig. 1.

![Proposed route for fabrication of the POMs functionalized membrane (POMs-M).](image)

**Fig. 1.** Proposed route for fabrication of the POMs functionalized membrane (POMs-M).

The alumina/PEI hollow fiber membrane was fabricated by a dry-jet wet spinning technique. The dope solution was prepared by dissolving the pre-dried PEI pellets in NMP solvent with stirring at 60 °C for 3 days. Then the ASB and PEG were added and stirred under the same temperature. The final homogenous dope solution was cooled down to room temperature, degassed under vacuum and extruded with bore fluid through a spinneret into the tap water with a certain air gap. The detailed spinning conditions are listed in Table 1. After the spinning, the resultant alumina/PEI hollow fibers were stored in a water bath for at least 3 days to remove residual solvents.

Table 1
Dry-jet wet spinning conditions.

<table>
<thead>
<tr>
<th>Spinning parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinneret o.d./i.d. (mm)</td>
<td>2.0/1.0</td>
</tr>
<tr>
<td>Dope composition (ASB/PEG/PEI/NMP) (wt.%)</td>
<td>5.0 / 0.75 / 20 / 74.25</td>
</tr>
<tr>
<td>Dope flow rate (g/min)</td>
<td>6</td>
</tr>
<tr>
<td>Bore fluid (NMP/water) (wt.%)</td>
<td>50/50</td>
</tr>
<tr>
<td>Bore fluid flow rate (g/min)</td>
<td>4</td>
</tr>
<tr>
<td>Take-up speed</td>
<td>Free falling</td>
</tr>
<tr>
<td>External coagulant</td>
<td>Tap water</td>
</tr>
<tr>
<td>Air gap distance (cm)</td>
<td>20</td>
</tr>
<tr>
<td>Spinning temperature (°C)</td>
<td>23</td>
</tr>
</tbody>
</table>

The POMs functionalization process involved the amination of the as-spun alumina/PEI hollow fiber membrane by APTMS followed by the incorporation of POMs via electrostatic interactions. First, the alumina/PEI hollow fiber membrane was immersed into the APTMS (2.0 wt.%) solution (IPA/H₂O, wt. 1:1) at 60 °C for 2 h. Second, the membrane was rinsed by water and then immersed into an aqueous solution of POMs (PVMo, 2.0 wt.%) at room temperature for 24 h. Finally, the resultant membrane (POMs-M) was rinsed by water again and freeze-dried for the following characterization and testing.

2.3. Membrane characterization

Membrane morphologies were investigated by a field emission scanning electron microscope (FESEM, JEOL JSM-7600F) (operating at 5 kV) equipped with an energy dispersive X-ray (EDX) spectrometer (operating at 20 kV). Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra were recorded by IR Presitige-21 FTIR (Shimadzu). The dimension of hollow fiber membranes was measured by a Keyence VHX 500F Digital Microscope. Pure water permeability (PWP) was measured by a lab-scaled cross-flow filtration set-up. DI water was circulated through the hollow fiber membrane module under a constant pressure of 1.0 bar. After stabilizing the
system for at least 1 h to eliminate the influence of membrane compaction, samples were taken. Molecular weight cut-off (MWCO), defined as the molecular weight at 90% rejection, was measured through the gel permeation chromatography (GPC) on a Polymer Laboratories-GPC 50 Plus system. An aqueous solution of dextran (2000 ppm) with molecular weight ranging from 6 to 500 kDa was circulated through the hollow fiber membrane module. Then the feed and permeate solutions were taken to determine the dextran molecular weight distribution. Membrane porosity was determined by gravimetric methods. Membrane surface dynamic contact angle was measured using a tensiometer (DCAT11 Dataphysics, Germany). Mechanical strength of hollow fiber membranes was examined using Zwick 0.5 kN Universal testing machine at room temperature.

2.4. Dye removal protocol

The proposed two-step protocol for dye removal is shown in Fig. 2. First, the feed solution (RB5, 20 ppm) was pumped through the shell side of the membrane module under a constant pressure of 0.5 bar, while the permeate solution was collected from the lumen side. The dye rejection (adsorptive separation) was monitored by UV-vis spectroscopy (UV-1800, Shimadzu) analysis. Then, the used membranes were soaked in an aqueous solution of OXONE (0.28 wt.%) at 45 °C for 6 h. The dye removal from POMs-M (catalytic degradation) was monitored by UV-vis diffuse reflectance spectroscopy (DRS, UV-2501PC) and Raman spectroscopy (Renishaw) analyses.
3. Results and discussion

3.1. Membrane characterization

Morphologies of the prepared POMs-M were examined by FESEM coupled with EDX, as shown in Fig. 3. From the cross-section images, it was observed that the POMs-M principally exhibited a sponge-like structure. Generally speaking, a sponge-like structure plays a negative role in mass transfer due to its higher resistance than a finger-like structure [39]; nevertheless, this structure is favorable in the current work, because it may help for the dye adsorption in consideration of the longer retention time of wastewater in the membrane. In comparison with the initial alumina/PEI hollow fiber substrate, the pore size of the POMs-M tended to reduce, which can be observed especially from images of both the outer and the inner surfaces, presenting a preliminary evidence for the successful incorporation of POMs with the membrane. Further evidence was offered by EDX analysis.
(Fig. 4), which confirmed the successful incorporation of POMs (PVMo) with the membrane substrate on both surfaces as well as the membrane interior.

**Fig. 3.** FESEM images of (a)–(d) the POMs-M and (e)–(g) the alumina/PEI membrane: (a) cross-section, (b) and (e) outer surface, (c) and (f) interior sponge-like structure, (d) and (g) inner surface.
Fig. 4. EDX spectrum of the POMs-M with inset of atomic contents of Molybdeum (A mass fraction tendency rather than accurate contents was provided by EDX analysis).

The prepared POMs-M was further comparatively examined by ATR-FTIR analysis (Fig. 5). For the alumina/PEI substrate, the broad peak around 3290 cm\(^{-1}\) and the strong peak at 1035 cm\(^{-1}\) should be attributed to the stretching vibration and the deformation vibration of alfol groups (Al–OH), respectively [40]. After the APTMS treatment, both peaks decreased accordingly due to the depletion of Al–OH groups by the condensation with APTMS. This result is in agreement with the reaction proposed in Fig. 1. Finally, with the incorporation of POMs, sharp and strong peaks at 946 and 779 cm\(^{-1}\) (marked by dashed blue lines) emerged and should be attributed to the characteristic vibrations of the M–O and M–Oe–M (M = Mo or V, Oe: edge-sharing oxygen) groups of the PVMo Keggin structure [41].

Fig. 5. FTIR spectra of (a) the original alumina/PEI membrane, (b) the alumina/PEI membrane after APTMS treatment and (c) the POMs-M.
Characteristics of the prepared POMs-M in terms of dimension, PWP, MWCO, porosity, surface dynamic contact angle and mechanical strength, in comparison with the initial alumina/PEI hollow fiber substrate, are listed in Table 2. The alumina/PEI substrate fell into the ultrafiltration (UF) category with the MWCO of 283 kDa. Its dynamic contact angle was as low as 50° and its tensile modulus was as high as 258 MPa, exhibiting better hydrophilicity and mechanical strength than pure PEI hollow fiber membranes (~80° and ~140 MPa, respectively) [42]. The enhanced hydrophilicity and mechanical strength of the alumina/PEI substrate should benefit from its inorganic/organic hybrid feature. After the POMs incorporation, the resultant PWP, MWCO and porosity all decreased, demonstrating that the pore size of the alumina/PEI substrate was reduced with the POMs incorporation. This result is consistent with the above morphological observations. On the other hand, the POMs-M still stayed in the ultrafiltration (UF) category with the MWCO of 120 kDa. Its hydrophilicity, as well as mechanical strength, was further enhanced after the incorporation of POMs.

Table 2

Comparison of the POMs-M with the alumina/PEI membrane.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>POMs-M</th>
<th>alumina/PEI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber o.d./i.d. (mm)</td>
<td>1.44/1.00</td>
<td>1.44/1.00</td>
</tr>
<tr>
<td>PWP (L/m² h bar)</td>
<td>19.0</td>
<td>81.9</td>
</tr>
<tr>
<td>MWCO (kDa)</td>
<td>120</td>
<td>283</td>
</tr>
<tr>
<td>Contact angle (°)</td>
<td>36.9</td>
<td>50.0</td>
</tr>
<tr>
<td>Porosity</td>
<td>72</td>
<td>76</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>339</td>
<td>258</td>
</tr>
</tbody>
</table>

3.2. Dye removal performance
The POMs-M was made into a lab-scale module to perform the proposed dye removal testing shown in Fig. 2. At the first stage, a cross-flow filtration was carried out under a constant pressure of 0.5 bar. The permeation performance in terms of dye rejection and water permeability is summarized in Table 3. Compared with the reported polysulfone-polyamide nanofiltration membrane for the removal of RB5 [17], the POMs-M exhibited much (three orders of magnitude) higher water permeability with 100% dye rejection. The excellent dye rejection should result from the adsorption effect of the POMs-M, since the POMs-M was not able to exclude RB5 molecules in consideration of its MWCO of 120 kDa. In order to further confirm the adsorption effect, an experiment was conducted by directly adding the POMs-M into RB5 aqueous solution, where the influence of membrane filtration was eliminated. The experimental result demonstrated the adsorption behaviour of the POMs-M towards RB5, as shown in Fig. 6b. In this case, the adsorption rate was much lower than the cross-flow filtration, which may be attributed to the insufficient contact between the dye molecules with the membrane interior structures. It is noticed that the selection of feed pressure which determines water flux is crucial in the membrane filtration process because the dye rejection (adsorption) may decline with the considerable increase of the water flux. The feed pressure of 0.5 bar applied in the current work not only realized energy-efficient low-pressure driven filtration, but also attained desirable dye adsorption activity. It should be pointed out that the operating time of the POMs-M at the first stage should not exceed 3 h in order to maintain the 100% dye rejection, which was determined by the performance as a function of time (see Fig. 6a).

Table 3

Dye rejection and water permeability of the POMs-M and another reported membrane [17].
<table>
<thead>
<tr>
<th>Membrane</th>
<th>Dye</th>
<th>Rejection (%)</th>
<th>Pressure (bar)</th>
<th>Water permeability (L/m²·h·bar)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>POMs-M</td>
<td>RB5</td>
<td>100</td>
<td>0.5</td>
<td>19</td>
<td>Current work</td>
</tr>
<tr>
<td>Polysulfone-polyamide membrane</td>
<td>RB5</td>
<td>60–97</td>
<td>1.7</td>
<td>0.0059–0.0206</td>
<td>[17]</td>
</tr>
</tbody>
</table>

![Graph](image)

**Fig. 6.** (a) Dye rejection and water permeability of the POMs-M (dye 20 ppm, 7 fibers sealed in the membrane module with a length of 19 cm, inlet pressure 0.5 bar, T = 25 °C). (b) UV-vis spectra of the RB5 solution before and after the adsorption (24 h) with the POMs-M without stirring. The inset photographs are the corresponding dye solutions with POMs-M (ca. dye/POMs-M/water = 0.006:1:150 (wt.)).

After the first stage, the membrane module was subsequently treated with dilute OXONE solution. Besides the decoloration of the membrane from dark blue back to the original
light-yellow as an indicator, UV-vis DRS and Raman spectroscopic analyses presented evidence for the disappearance of RB5 after membrane regeneration. As shown in Fig. 7, after the treatment with OXONE, both the UV-vis absorption (~600 cm$^{-1}$) and the Raman scattering [43] peaks of RB5 disappeared with the observation of similar curves to the original membrane. The OXONE solution remained colorless (see Fig. 7d) during the treatment of POMs-M. These results implied that RB5 was degraded instead of desorbed at the current stage and the POMs-M was regenerated. The regenerated POMs-M can proceed with the next adsorptive separation and catalytic degradation cycle, and the dye removal performance as the aforementioned can be well repeated (please see the error bars in Figure 6a representing the standard deviation for six repetition cycles). The role of POMs as catalyst was further clarified through comparing the dye oxidation solely by OXONE (Fig. 7c). In contrast to the full decoloration of the POMs-M (Fig. 7d), the RB5 aqueous solution with OXONE just turned into dark purple. The corresponding UV-vis absorption peak blue-shifted and deceased to 55.2%, indicating that 44.8% RB5 was oxidized to intermediates with a shorter absorption wavelength. These results demonstrate that POMs from POMs-M catalyzed the degradation of RB5 in the presence of OXONE. The possible catalytic mechanism of PVMo can be illustrated as follows [44, 45]:

$$\text{Red} + [\text{PV}_{2}^{V}\text{Mo}_{10}]^{5-} \rightarrow \text{Ox}_{1} + [\text{PV}^{IV}_{V}\text{Mo}_{10}]^{6-}$$

$$[\text{PV}^{IV}_{V}\text{Mo}_{10}]^{6-} + \text{HSO}_{5}^{-} \rightarrow [\text{PV}_{2}^{V}\text{Mo}_{10}]^{5-} + \text{SO}_{4}^{2-} + \text{HO} \cdot$$

$$\text{Ox}_{1} + \text{HO} \cdot \rightarrow \text{Ox}_{2} + \text{H}_{2}\text{O}$$

where Red is dye as reductant, Ox$_1$ and Ox$_2$ as its oxidized form. Oxidation is expected to occur via electron transfer from dye molecules to the POMs, where the role of OXONE is to re-oxidize the reduced POMs with the production of HO$^-$ for further dye oxidation. The
reversible transformation between $V^{5+}$ and $V^{4+}$ may account for the redox property of 
POMs in the catalytic oxidation process. This two-step approach could not only economize 
the usage of oxidants through repeatedly using the post-treatment solution instead of 
directly adding oxidants into the whole water body, but also avoid the secondary pollution 
from the possible incomplete minerization of dyes and addition of oxidants.

![Fig. 7](image)

**Fig. 7.** (a) UV-vis DRS spectra and (b) Raman spectra of the original, dye-removal tested, and 
regenerated POMs-M. Photographs of (c) the RB5 aqueous solution and (d) the dyed POMs-M 
before and after treatment with OXONE under the same conditions (0.28 wt.%, 45 °C, 6 h).
3.3. Extensions

Bountiful and flexible selections of POMs might further help to design distinctive catalytic degradation pathways. For example, a transition metal mono-substituted Keggin-type \([\text{PW}_{11}\text{O}_{39}\text{Fe}({\text{H}_2\text{O}})]^{4-}\) (PWFe), which may work as a catalyst in Fenton-like reactions [46, 47], can also be incorporated with the membrane (POMs-M-2). \(\text{H}_2\text{O}_2\) which is not able to oxidize the RB5 alone (see Fig. 8a) [48] was used as oxidant instead of OXONE. Through incorporating PWFe, the blue color on POMs-M-2 totally faded to the original color of the membrane suggesting PWFe as catalyst was highly effective in the \textit{in-situ} oxidation of RB5 in the presence of \(\text{H}_2\text{O}_2\). Since the oxidation process in the current work was carried out in the controllable post-treatment solution instead of in the large volume of dye effluent, the selection of oxidation conditions (e.g., oxidants, \(\text{pH}\) or temperature) could be flexible. As a result, a wise selection of POMs with tailored catalytic degradation strategy may yield further improvements in practical applications. Interestingly, besides the adsorption towards anionic dye (see Fig. 6b), POMs-M also exhibited adsorption activity towards cationic dye (methylene blue (MB) as a dye model) (see Fig. 8b). Compared to RB5, similar dye rejection for MB by POMs-M (100% dye rejection in 1 h and 97.6% in 3 h) can also be obtained through the membrane cross-flow filtration under the same testing conditions. Since the adsorption mechanism of dyes on POMs-M is complicated (such as electrostatic interaction, hydrophobic interaction and hydrogen bonding), it is estimated that the adsorption ability of anionic dye can be partially explained by the protonated amino groups from the membrane while the electronegative POMs would also interact with cationic dyes accounting for the cationic dye adsorption.
Fig. 8. (a) Photographs of the degradation of RB5 by H₂O₂ without POMs (upper image) and with POMs-M-2 (lower image) (0.84 wt.% H₂O₂, pH = 3, 45 °C, 6 h). (b) Photographs of MB solution before and after the adsorption with POMs-M (ca. MB/POMs-M/water = 0.006:1:300 (wt.), room temperature without stirring for 48 h).

4. Conclusions

In order to make best use of the advantages and bypass the disadvantages of the membrane technique for the removal of dyes from wastewater, a unique approach, adsorptive separation and catalytic degradation, for dye removal was proposed using a polyoxometalates (POMs) functionalized hollow fiber membrane (POMs-M). The POMs-M was fabricated through a novel sol-gel method involving the fabrication of an alumina containing polyetherimide (PEI) hollow fiber membrane followed by the generation of amine-functionalized substrate with (3-aminopropyl)trimethoxysilane for the incorporation of POMs. Compared with conventional pure PEI membrane, greatly enhanced mechanical strength with sponge-like structure was attained. Then, a two-step protocol, adsorptive
separation followed by catalytic degradation, was designed so as to overcome the disadvantages of traditional adsorptive membranes and catalytic membranes. At the first stage, dyes can be separated through the membrane cross-flow filtration with almost 100% dye rejection and desirable water permeability. Then, the membrane with enriched dyes can be treated with limited volume of the post-treatment solution containing dilute oxidant to realize membrane regeneration. *In-situ* catalytic degradation of dye RB5, which is usually resistant to the oxidation of mild oxidants alone, was easily attained with a limited volume of dilute oxidant solution and POMs on/in the membrane as catalysts. The catalytic degradation process can be further designed and tailored through modifying various POMs with distinct catalytic activities and functionalities onto the membrane. Since the fabrication route developed in the current work is a general procedure, other polymeric materials can also be used instead of PEI. Consequently, the current research not only renders a versatile way for the construction of POMs functionalized membranes but provides a new approach for the removal of dyes from wastewater.

**Acknowledgements**

We would like to thank the financial support from Singapore Membrane Technology Centre (SMTC), Nanyang Technological University and NTU AcRF grant (RG76/12). We are also grateful to Singapore Economic Development Board for funding SMTC. The electron microscopy was performed at the Facility for Analysis, Characterization, Testing and Simulation (FACTS) in Nanyang Technological University, Singapore.
References


