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參展科別 環境工程科

作品名稱 Application of molecular templates on magnetic particles for adsorption and desorption of heavy metals

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關鍵字 Molecular Template、Magnetic Particles、Heavy Metal

About The Author

Hi, I am glad to be here for joining this contest. Thank you for giving me this opportunity to introduce myself. My name is Michael Lee. I am 18 years old now. My father is a chair professor at National Tsing Hua University and my mother is a full-time house-keeper. I also have a younger sister, who is 16 years old now.

I am in the 12th grade in Chien-Kung High School, Hsinchu. I have been there since junior high school. I am proud of being well educated in its Science Class there since it provides me a lot of opportunities to work on several hand-on science projects in the field of chemistry.

The topic that I have been working on is entitled with "magnetic molecular templates for extraction of heavy metal ions". We synthesized magnetic particles and molecular templates such that they could be combined to extract heavy metal ions in water. After one year of hard work, we won several awards, including the first place in local chemistry competition and the third place in a national contest. I am also the winner of prestigious Won-Hong contests.

I. Abstract

This study investigated the production of novel molecular templates, and analyze their adsorption effect on four heavy metal ions (Cu^{+2}, Pb^{+2}, Zn^{+2}, Mn+2), which commonly exist in Taiwan's rivers. Different operating conditions (such as competitive adsorption, pH value and other factors) were explored to compare their adsorption effect of heavy metal ions by using the synthesized template molecules. The molecular templates were found to be specific towards their target metal ions with a high adsorption effect. Then combined with the idea of magnetic particles to produce magnetic molecule templates, a maximum amount of adsorption of heavy metal ions up to 95% through the molecular template was achieved while the effect of heavy metals desorption of up to 83% could be also successfully obtained. Experimental results showed that the magnetic molecule templates did not affect the adsorption of heavy metal ions. Not only can they speed up the recovery time of adsorption but the template molecules can also be collected more efficiently. We also proposed three different applications for the developed molecular templates. The development of magnetic molecular template may provide an affordable, highly-efficient way for dealing with heavy metal pollutions.

II. Introduction

Heavy metal pollution is increasingly serious in Taiwan. Environmental background values of heavy metals indicated that river pollution has seriously exceeded the safety standard value [1-2]. Therefore, the aim of this study is to come up with innovative ideas to solve today's serious river pollution problems in Taiwan. Previous study reported that chitosan could be used for adsorption of heavy metals [3-5]. However, they did not have sufficient specificity toward heavy metals. We continued to extend this research to further explore a new technology - molecular templates [6]. This new technology can quickly adsorb heavy metals with high specificity with a relatively low cost. In addition to effective adsorption of heavy metals, desorption and re-use of the molecular templates could be achieved. In this work, we used new monomers for formation of molecular templates such that they could be further used for heavy metal ions. Figure 1 shows a schematic view of a magnetic molecular template. During the formation of the template, specific heavy metal ions were used. After depleting the ions, a specific binding site ("vacancy") was formed. Therefore, it could be used for collection of heavy metal ions with high specificity. Furthermore, it could be magnetically collected if it was coated on the surface of a magnetic particle. Also combined with the concept of magnetic particles, the recovery of heavy metal ions can be more effective on magnetic molecular templates since they could be collected magnetically. For three different applications

including wastewater treatment plant, river heavy metal removal and household drinking water, we also proposed three devices integrated with magnetic molecular templates.
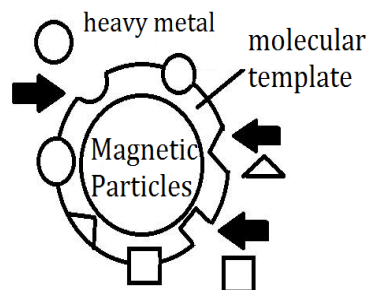

Figure 1： A schematic view of a magnetic molecular template. During the formation of the template, specific heavy metal ions were used. After depleting the ions, a specific binding site ("vacancy") was formed. Therefore, it could be used for collection of heavy metal ions with high specificity. Furthermore, it could be magnetically collected if it was coated on the surface of a magnetic particle.

III. Objectives

Use of heavy metal ions in the formation of the molecular templates creates specific vacancies ("holes") that can adsorb specific metal ions that exist in polluted rivers. While combining the concept of magnetic particles, the magnetic molecular templates which represent molecular templates with specificity towards metal ions surface-coated on magnetic particles, could be used to quickly and efficiently recover heavy metal ions in solutions. Then by using special operating conditions after desorption heavy metal ions, one can desorb the metal ions such that molecular templates could be re-used. The purpose of this study is therefore to implement this innovation and to explore the formation of molecular templates and heavy metal adsorption, desorption of heavy metals and magnetic molecular templates (Fig. 1) adsorption and recovery. Finally, this study proposed the ideas of three applications, including household drinking water and industrial wastewater removal of heavy metals.

Th objectives of the study are as follows.

(1) investigate the adsorption effect of the synthesized molecular templates, especially under the condition with the same amount of molecular templats for heavy metal ions under different concentations.

(2) explore the adsorption effect of the synthesized molecular templates, especially under the condition with the same concentation of heavy metal ions for molecular templates under different concentations.

(3) investigate the adsorption effect of "blank template" (without any vacancy) for a particular solution of heavy metal ions.

(4) investigate the competitive adsorption effects for the mixed metal ion solution.

(5) explore the desorption effect of the synthesized molecular templates.

(6) explore the specificity of molecular templates.

IV. Experimental

Facilities, equipment and reagents used in this study are listed as follows.

|	
(1) Manganese nitrate, 99 %	(18) Electronic balance (AND Inc.,GF300)
(2) Zincnitrate, 99 %	(19) 50 ml Beaker x5
(3) Zinc nitrate, 99 %	(20) Distillation flask
(4) Copper nitrate, 99 %	(21) Fume Hood
(5) Trimethylol propane triacrylate, 99%	(22) Mortar
(6) Soxhlet extractor (Fig. 2)	(23) Filter (mesh 400，mesh 200)
(7) Glutaraldehyde, 99%	(24) 500 ml Beaker x5
(8) Azobisisobutyronitrile (AIBN), 99 %	(25) 200 ml Beaker x5
(9) Ethanol, 95 %	(26) 150 ml Beaker x5
(10) Sulfuric acid, 1 N	(27) Atomic absorption spectrophotometer (Jas. C. D V-730) (Fig. 4)
(11) Nitrogen, 99 %	
(12) Industrial caustic soda, 45%	
(13) Sodium hydroxide, 6 M	
(14) Ferric chloride solution ($FeCl_3 \cdot 6H_2O$), 97 %	
(15) Ferrous chloride solution ($FeCl_2 \cdot 4H_2O$), 97 %	
(16) Oven (Fig. 3)	
(17) pH meter	

Figure 2：Soxhlet extractor

Figure 3：Oven
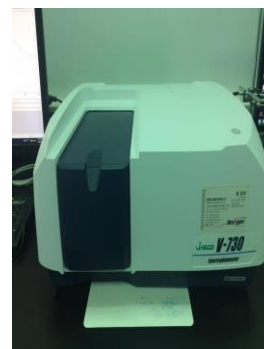
Figure 4：Atomic absorption spectrophotometer

V. Methods

V.1 Principle

Before polymerization of monomers and the target molecule (or ion) to form a specific bonding, synthesis can be made by polymerizing the target molecule (or ion) derivatives, followed by addition of a crosslinking agent molecules which could bond to each other to make linked into a network structure to form cellular macromolecules. The bonding between polymer and the target molecule (or ion) can be easily broken chemically, after removal of the target molecule (or ion) such that a specific vacancy of the target molecule (or ion) could be formed. With this approach, the synthesized molecular template will exhibit high affinity and high specificity since the formation of vacancies is specific to the target molecule (or ion). Since the template is formed at a molecular level, it is commonly called "molecular template". In this study, we adopt the similar concept to form a template for heavy metal ions.

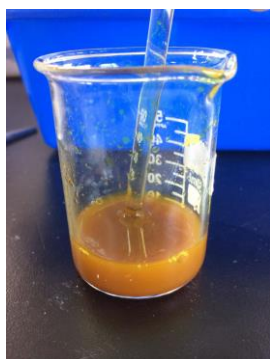## V.2 Methods

(a) Synthesis of magnetic particles

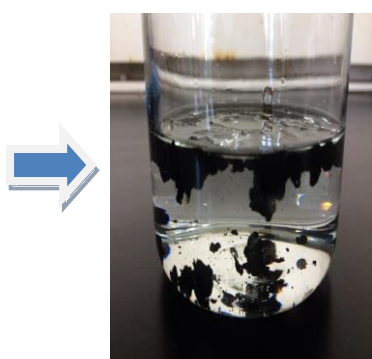Figure 5: Ferric chloride and ferrous chloride solution were dissolved in hydrochloric acid.

Figure 6: NaOH solution was added in the mixed solution of ferric chloride and ferrous chloride to form iron-oxide magnetic particles.

Figure 7: After precipitation, magnetic particles were collected.

Figure 8: Magnetic particles after using a mortar to mash them.

The detail procedure for formation of magnetic particles is described as follows. Briefly, different concentrations of $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were prepared to synthesize magnetic particles. After optimization of these reactants, we chose fixed concentrations for formation of the magnetic particles. Note that a fixed concentration of HCl and NaOH was used in this work.

1. $FeCl_2 \cdot 4H_2O$ (24 mM, 2.50 g) and $FeCl_3 \cdot 6H_2O$ (12 mM, 1.50 g) were first dissolved in HCl (2 N, 12.00 ml) (Fig. 5).
2. After they were completely dissolved, 3.00 ml of the solution was mixed with NaOH (20%, 50.00 ml) to form an oxidation reaction of the magnetic particles (Fig. 6).
3. After washing with distilled water for 3 times to remove the residual NaOH (Fig. 7),

then a mortar was used to mash them such that the magnetic particles could be formed (Fig. 8).

(b) Formation of molecular templates

The detail procedure for formation of magnetic particles is described as follows. Briefly, we formed molecular templates with specific vacancies for heavy metal ions.

1. Four heavy metal ion solutions (manganese nitrate, 2.0 M, 1.79 g; lead nitrate, 2.0 M, 3.31 g; zinc nitrate, 2.0 M, 1.89 g; copper nitrate, 2.0 M, 1.88 g) were first dissolved in ethanol (75%, 3.00 ml), respectively.

2. Monomer (trimethylol propane triacrylate, 2.0 M, 3.00 ml) was mixed with these metal ion solutions

3. An initiator (AIBN, 2.0 M, 3.00 g) was added. Mixed solution was stirred completely. Note that nitrogen was added to prevent oxidation during the process.

4. Then they were placed in an oven at 60^0C for 24 hours for polymerization (Fig. 9). Then the Soxhlet extractor was used to extract heavy metals from the polymers to form holes having the specificity toward specific metal ions (Fig. 10). Finally a mortar was used to ground them into powders.

5. Finally, filters (mesh 200 and mesh 400) were used to filter particles with sizes in the range of 37-74 μm and particles less than 37 μm for the subsequent experiments (Figure 11) [7] [8].

Figure 9: Copper polymers before the extraction of copper ions to form the molecular template.

Figure 10: Soxhlet extractor was used to extract heavy metals from the polymers to form holes having the specificity toward copper ions.

Figure 11: Copper molecular template after air dry, and then through grinding and filtering processes. After these processes, molecular templates with high affinity and high specificity could be formed.

Similarly, by adding different metal ions in the polymerization process and using the same extraction, grinding and filtering processes, the other three molecular templates could be formed.

(c) Formation of blank molecular template

The detail procedure for formation of blank molecular template (Figure 12) is described as follows. Briefly, no metal ions were added in the process of polymerization. Therefore, there was no vacancy for metal ions formed.

1. Monomer (trimethylol propane triacrylate, 2.0 M, 3.00 ml) was dissolved in ethanol (75%, 3.00 ml).

2. An initiator (AIBN, 2.0 M, 3.00 g) was added. Mixed solution was completely stirred. Note that nitrogen was used to prevent oxidation.

3. Then they were placed in an oven at 60^0C for 24 hours for polymerization. Then the Soxhlet extractor was used. Finally a mortar was used to ground them into powders.

4. Finally, filters (mesh 200 and mesh 400) were used to filter particles with sizes in the range of 37-74 μm and particles less than 37 μm for the subsequent experiments (Figures 13.14).
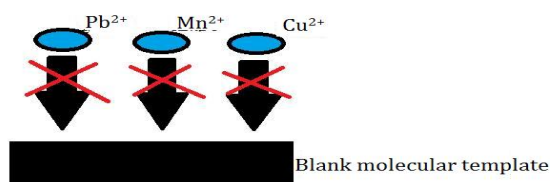

Figure12: Schematic illustration of blank molecule template. Blank templates without vacancies could not adsorb heavy metal ions.
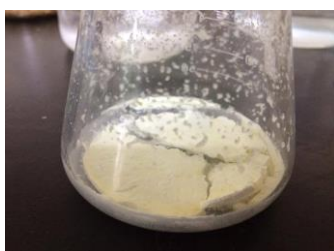

Figure 13: Photograph of blank molecular template after the polymerization.

Figure 14: Photograph of blank molecule template powder after extraction, grinding and filtering processes.

(d) Formation of magnetic molecular templates

The detail procedure for formation of magnetic molecular templates is described as follows.

1. Four heavy metal ion solutions (manganese nitrate, 2M, 1.79 g; zinc nitrate, 2M, 3.31 g; zinc nitrate, 2M, 1.89 g; copper nitrate, 2M, 1.88 g) were dissolved in ethanol (75%, 3.00 ml).

2. Magnetic particles (1.00 g) were added to the solution.

3. Monomer (trimethylol propane triacrylate, 2.0 M, 3.00 ml) was added in ethanol (75%, 3.00 ml).

4. An initiator (AIBN, 2.0 M, 3.00 g) was mixed and stirred completely. Note that nitrogen was used to prevent oxidation.

5. Then they were placed in an oven at 60^0C for 24 hours for polymerization (Fig. 15). Then the Soxhlet extractor was used. Finally a mortar was used to ground them into powders (Fig. 16).

6. Finally, filters (mesh 200 and mesh 400) were used to filter particles with sizes in the range of 37-74 μm and particles less than 37 μm for the subsequent experiments (Fig. 17).
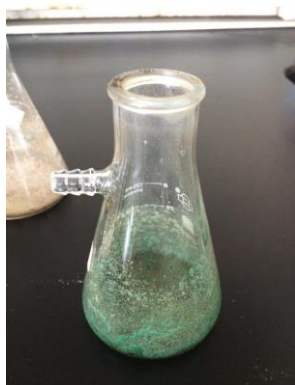

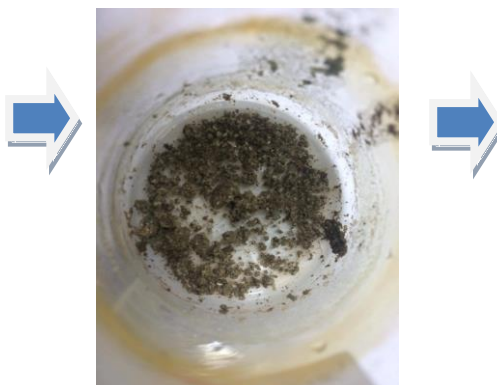Figure15: Polymeric molecular magnetic copper template completed.

Figure 16: Molecular Template magnetic copper powder extracted completion.
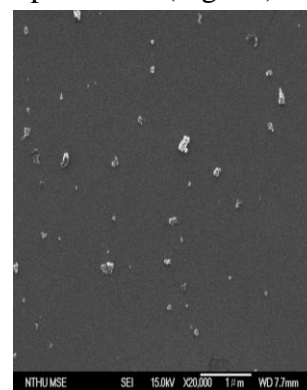

Figure 17: SEM of the formed magnetic molecular templates.

(e) Adsorption effect of molecular templates

The detail procedure for investigating the adsorption effect of molecular templates is described as follows. Briefly, different concentrations of heavy metal ions were first used to explore the adsorption effect of molecular templates while the weight of molecular templates was fixed.

1. Four different kinds of molecular templates (copper, 0.0030 g; manganese 0.0072 g; zinc 0.0024 g; zinc, 2.7450 g) were used to test their adsorption effect on specific ions.

2. Copper nitrate solutions with concentrations of 0.0013 M, 0.0085 M and 0.0157 M in a volume of 100 ml were prepared for adsorption tests. Similarly, manganese nitrate solutions with concentrations of 0.0001 M, 0.0011M and 0.0036 M in a volume of 100 ml were prepared for adsorption tests; Zinc nitrate solutions with concentrations of 0.0007 M, 0.0067 M and 0.0127 M in a volume 100 ml were prepared for adsorption tests; Lead nitrate solution with concentrations of 0.00001 M, 0.00015 M and 0.00050 M in a volume of 100 ml were prepared for adsorption tests.

3. The molecular templates were then tested with different concentrations of heavy metal ions in solution at room temperature for 24 hours.

4. After the adsorption, the molecular templates were removed and the sample solution remaining heavy metal ions were further tested to measure its adsorption effect.

(f) Explore the adsorption effects of molecular templates at different weights

The detail procedure for investigating the adsorption effects of molecular templates at different weights is described as follows.

1. Four concentrations of heavy metal ion solutions (Cu, 0.0157 M; Mn, 0.0036 M; Zn, 0.0127 M; Pb, 0.00050 M) were prepared.

2. Four kinds of molecular templates in three different templates weights (copper, 0.0015 g, 0.0030 g, 0.0060 g; manganese, 0.0035 g, 0.0070 g, 0.0140 g; zinc, 0.0012 g, 0.0024 g, 0.0050 g; Pb, 0.09 g, 0.18 g, 0.36 g) were prepared.

3. The molecular templates with different weights were then tested with different concentrations of heavy metal ions in solution at room temperature for 24 hours.

4. After the adsorption, the molecular templates were removed and the sample solution remaining heavy metal ions were further tested to measure its adsorption effect.

(g) Competitive adsorption of molecules templates under various metal ions

The detail procedure for investigating competitive adsorption of molecules templates under various metal ions is described as follows. Briefly, adsorption effect of the molecular templates was tested when more than one ion existed.

1. Copper nitrate solutions with concentrations of 0.0013 M, 0.0085 M and 0.0157 M were prepared; Similarly, manganese nitrate solutions with concentrations of 0.0001 M, 0.0011M and 0.0036 M were prepared; Zinc nitrate solutions with concentrations of 0.0007 M and 0.0127 M were prepared; Lead nitrate solution with concentrations of 0.00001 M, 0.00015 M and 0.00050 M were prepared.

2. Totally 16 experiments with different combinations of multiple ions were performed for competitive tests. The molecular template was mixed with a solution of two or even more metal ions for testing their adsorption toward its corresponding target ion at room temperature for 24 hours.

3. After the adsorption, the molecular templates were removed and the sample solution remaining heavy metal ions were further tested to measure its adsorption effect.

(h) Explore the desorption effect of molecular templates

The detail procedure for investigating desorption effect of molecular templates is described as follows. Briefly, we would like to explore if the developed molecular templates could be re-used after desorption.

1. Molecular templates after adsorption of metal ions were first dissolved in deionized water and then hydrochloric acid (pH 4 to pH 6) was added. The desorption was performed at room temperature for 24 hours.

2. After the desorption, sample solution remaining heavy metal ions were tested to measure its desorption effect.

VI. Results and discussion

VI.1 Calibration curve

(a) The calibration curve for copper ions was first made by using atomic absorption spectrophotometer (AA, Jas. C. D., V-730). Figure 18 shows the relationship between the absorbance values and copper ions with different concentrations (at the main absorbance wavelength). Note that it covers the dynamic ranges occurring in the polluted rivers. The concentrations of copper ion solutions were 0.0013 M, 0.0031 M, 0.0085 M and 0.0157 M, respectively. Note that the copper absorption occurs at 324.5 nm.
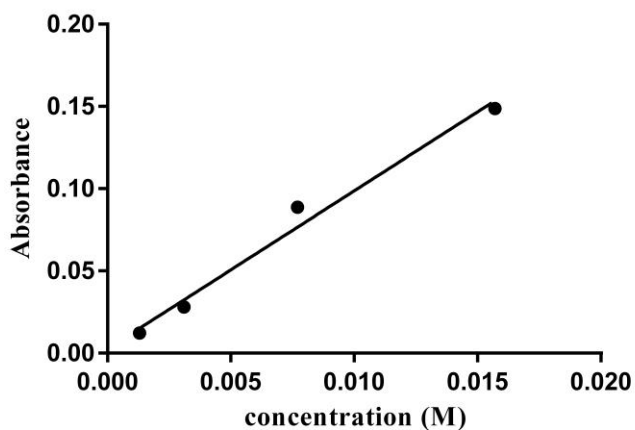

Figure 18: The calibration line for copper ions by using atomic absorption spectrophotometer (at a wavelength of 324.5 nm).

(b) The calibration curve for manganese ions was also made by using atomic absorption spectrophotometer. Figure 19 shows the relationship between the absorbance values and manganese ions with different concentrations (at the main absorbance wavelength). Note that it covers the dynamic ranges occurring in the polluted rivers. The concentrations of manganese ion solutions were 0.0001 M, 0.0006M, 0.0011 M, 0.0025M and 0.0036 M, respectively. Note that the copper absorption occurs at 279.5 nm.
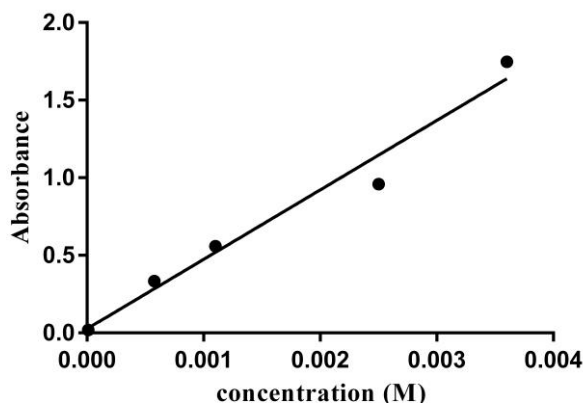

Figure 19: The calibration line for manganese ions by using (at a wavelength of 279.5 nm).

(c) Similarly, the calibration curve for zinc ions was also made by using atomic absorption spectrophotometer. Figure 20 shows the relationship between the absorbance values and zinc ions with different concentrations (at the main absorbance wavelength). Note that it covers the dynamic ranges occurring in the polluted rivers. The concentrations of zinc ion solutions were 0.0007 M, 0.0024 M, 0.0043 M, 0.0067 M and 0.0127 M, respectively. Note that the zinc absorption occurs at 213.9 nm.

Figure 20: The calibration line for zinc ions by using (at a wavelength of 213.9 nm).

(d) The calibration curve for zinc ions was also made by using atomic absorption spectrophotometer. Figure 21 shows the relationship between the absorbance values and zinc ions with different concentrations (at the main absorbance wavelength). Note that it covers the dynamic ranges occurring in the polluted rivers. The concentrations of zinc ion solutions were 0.00001 M, 0.00015 M, 0.00033 M and 0.00050 M, respectively. Note that the zinc absorption occurs at 283.3 nm.
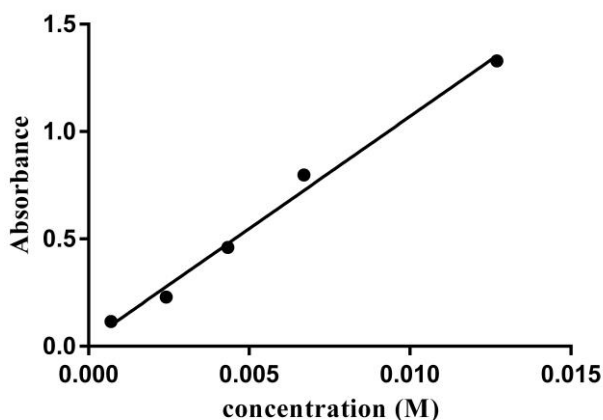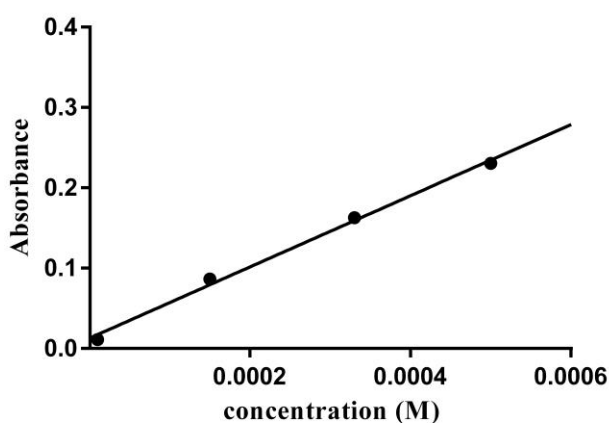

Figure 21: The calibration line for zinc ions by using (at a wavelength of 283.3 nm).

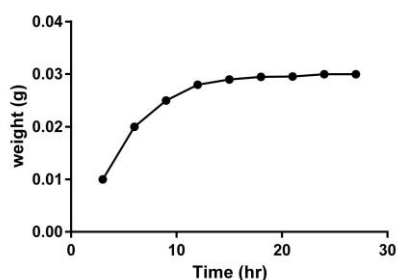## VI.2   Polymerization of molecular templates

Figure 22: Polymerization of copper molecular templates.
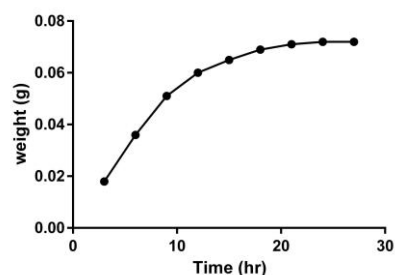

Figure 23: Polymerization of manganese molecular templates.
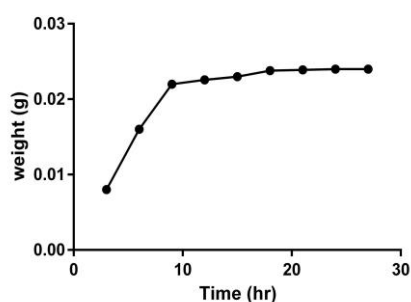
Figure 24: Polymerization of lead molecular templates.
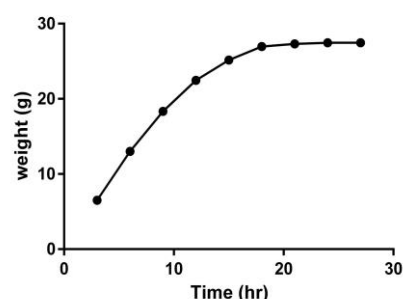
Figure 25: Polymerization of zinc molecular templates.

Figures 22-25 show the template weights during polymerization. It is clearly seen that when the polymerization reached plateau after a certain period of time. The reaction increased until 24 hr. Therefore, we chose this time for all four templates to complete the polymerization.

VI.3   Adsorption effect of blank molecular templates

Table 1: Adsorption for blank molecular templates

Ion original concentration	Ion concentration after adsorption	Adsorption (%)
Cu^{2+} 0.0157 M	0.0157 M	0.00%
Mn^{2+} 0.0036 M	0.0036 M	0.00%
Pb^{2+} 0.00050 M	0.00050 M	0.00%
Zn^{2+} 0.0127 M	0.0127 M	0.00%

In order to explore the absorption effect of the blank molecular templates, we used blank templates to see if they could adsorb any metal ion. Since we did not include copper, zinc, manganese, zinc ions during the polymerization of the molecular templates, no specific vacancies for metal ions could be formed. Thus it is expected that no adsorption will occur. Table 1 lists adsorption rates for blank molecular templates for four different ion solutions. As

expected, for four heavy metal ions, no absorption was measured since no specific vacancy was generated in the bland molecular templates. It demonstrates that non-specific adsorption of the blank polymer toward heavy metal ions could be neglected.

VI.4   Specific adsorption of the molecular templates

To further explore the specific adsorption of molecular templates, we tested four kinds of molecular templates to measure their adsorption on their non-target metal ions. For example, for exploring the adsorption zinc molecular template toward Cu^{2+}, Mn^{2+} and Pb^{2+}, we measured the original ion concentration and the ion concentration after adsorption. The results were listed in Table 2. It was experimentally found that less than 1% adsorption (Tables 2-5) was made for non-specific adsorption toward their non-target metal ions. It therefore proves the non-specific adsorption of the specific molecular templates.

Table 2: Adsorption of zinc molecular template toward Cu^{2+}, Mn^{2+} and Pb^{2+}

Ion original concentration	Ion concentration after adsorption	Adsorption (%)
Cu^{2+} 0.007 M	0.00027 M	0.03%
Mn^{2+} 0.0008 M	0.000031 M	0.03%
Pb^{2+} 0.0011 M	0.00004 M	0.04%

Table 3: Adsorption of lead molecular template toward Cu^{2+}, Mn^{2+} and Zn^{2+}

Ion original concentration	Ion concentration after adsorption	Adsorption rate (%)
Cu^{2+} 0.007 M	0.00077 M	1.00%
Mn^{2+} 0.0008 M	0.00004 M	0.05%
Zn^{2+} 0.0055 M	0.00003 M	0.01%

Table 4: Adsorption of copper molecular template toward Zn^{2+}, Mn^{2+}, Pb^{2+}

Ion original concentration	Ion concentration after adsorption	Adsorption (%)
Zn^{2+} 0.0055 M	0.0004 M	0.07%
Mn^{2+} 0.0008 M	0.00006 M	0.08%
Pb^{2+} 0.0011 M	0.0001 M	0.09%

Table 5: Adsorption of manganese molecular template toward Cu^{2+}, Zn^{2+} and Pb^{2}

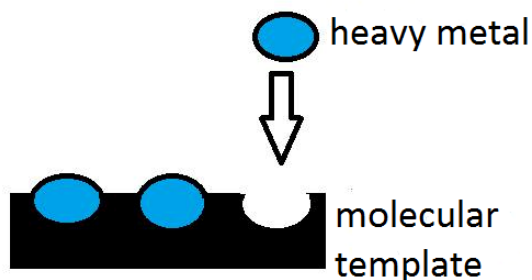| Ion original concentration	Ion concentration after adsorption	Adsorption (%)
Cu^{2+} 0.007 M	0.00057 M	0.08%
Zn^{2+} 0.0055 M	0.00017 M	0.03%
Pb^{2+} 0.0011 M	0.00008 M	0.07%

Figure 26 Schematic illustration of molecular templates. Because heavy metal ions were added during polymerization, the formed molecular template is capable of absorbing specific heavy metal ions.

VI.5   Adsorption effect of molecular templates toward target heavy metal ions

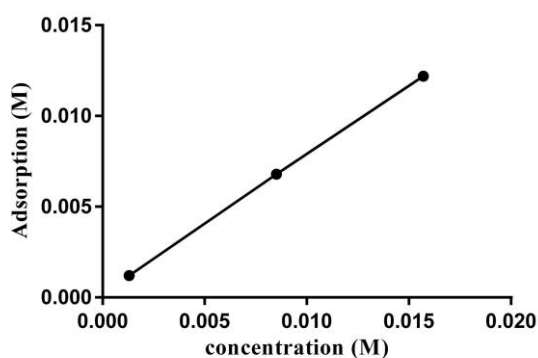(a) Adsorption effect of copper molecular template

Fig. 27 The relationship between the copper ion adsorption and concentration of copper ions. Note that a fixed amount of copper molecular templates were used.

Fig. 28 The relationship between the copper ion adsorption and weight of the copper molecular templates. Note that a fixed concentration of copper ions was used.

Adsorption effect of copper molecular template was first explored. Note that a fixed amount of copper molecular template (0.003 g) was used for this experiment. Figure 27 shows the relationship between the copper ion adsorption and concentration of copper ions. Because a fixed amount of molecular templates were used, the heavy metal ions absorbed by the templates increased linearly first and gradually approached saturation if higher concentrations were used (not shown here). When the concentration of copper ion solution was 0.0013 M, the adsorption of copper ions reached 0.0012 M, indicating absorption of 92%. Similarly, when the concentration of copper ion solution was 0.0085 M, the adsorption of coppers was 0.0068 M, representing absorption of 80%. At a high concentration of 0.0157 M, the adsorption of copper ions was 0.0122 M with absorption of 78% (Figure 27). Note that three repeated experiments were performed.
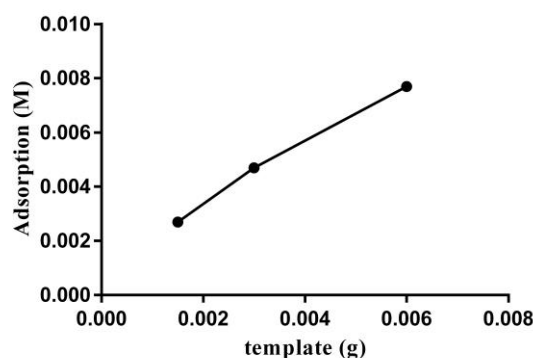
In addition, the relationship between the copper ion adsorption and the weight of the copper molecular templates at a fixed concentration of copper ions (0.0157 M) was further investigated. As expected, the more molecular templates we added, the more adsorption was observed (Figure

28).

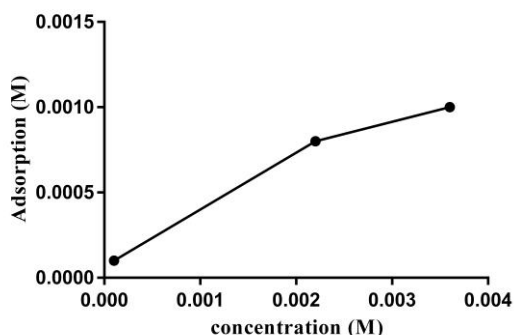(b) Adsorption effect of manganese molecular template

Figure 29 The relationship between the manganese adsorption and concentration of manganese ions. Note that a fixed amount of manganese molecular templates were used.

Figure 30 The relationship between the manganese adsorption and weight of the manganese molecular templates. Note that a fixed concentration of manganese ions was used.

Adsorption effect of manganese molecular template was also explored. Note that a fixed amount of manganese molecular template (0.0072 g) was used for this experiment. Figure 29 shows the relationship between the manganese ion adsorption and concentration of manganese ions. Because a fixed amount of molecular templates were used, the heavy metal ions absorbed by the templates increased linearly first and gradually approached saturation. When the concentration of manganese ion solution was 0.0001 M, the adsorption of manganese ions reached 0.000095 M, indicating absorption of 95%. Similarly, when the concentration of manganese ion solution was 0.0011 M, the adsorption of manganese was 0.00097 M, representing absorption of 88%. At a high concentration of 0.0036 M, the adsorption of manganese ions was 0.00288 M with absorption of 80% (Figure 29). Note that three repeated experiments were performed.

In addition, the relationship between the manganese ion adsorption and the weight of the manganese molecular templates at a fixed concentration of manganese ions (0.0036 M) was further investigated. As expected, the more molecular templates we added, the more adsorption was observed (Figure 30).

(c) Adsorption effect of zinc molecular template

Figure 31 The relationship between the zinc adsorption and concentration of zinc ions. Note that a fixed amount of zinc molecular templates were used.
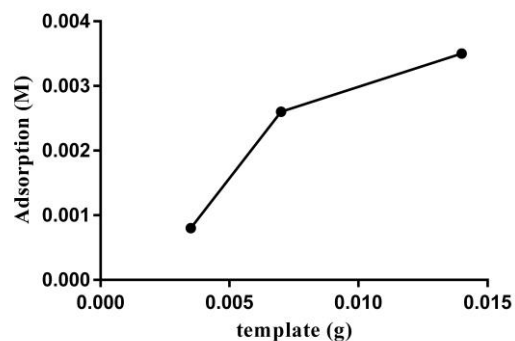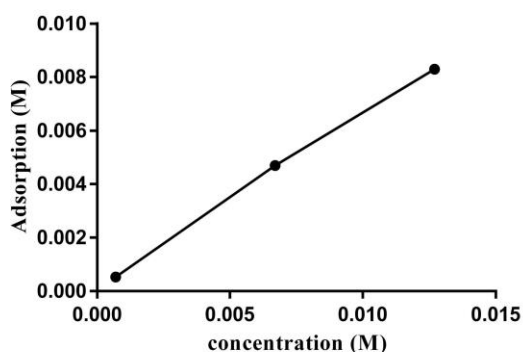
Figure 32 The relationship between the zinc adsorption and weight of the zinc molecular templates. Note that a fixed concentration of zinc ions was used.

Adsorption effect of zinc molecular template was also explored. Note that a fixed amount of zinc molecular template (0.0024 g) was used for this experiment. Figure 31 shows the relationship between the zinc ion adsorption and concentration of zinc ions. Because a fixed amount of molecular templates were used, the heavy metal ions absorbed by the templates increased linearly first and gradually approached saturation if higher concentrations were used (not shown here). When the concentration of zinc ion solution was 0.0007 M, the adsorption of zinc ions reached 0.00053 M, indicating absorption of 75%. Similarly, when the concentration of zinc ion solution was 0.0067 M, the adsorption of zincs was 0.0047 M, representing absorption of 70%. At a high concentration of 0.0127 M, the adsorption of zinc ions was 0.0083 M with absorption of 53% (Figure 31). Note that three repeated experiments were performed.

In addition, the relationship between the zinc ion adsorption and the weight of the zinc molecular templates at a fixed concentration of zinc ions (0.0127 M) was further investigated. As expected, the more molecular templates we added, the more adsorption was observed (Figure 32).

(d)   Adsorption effect of lead molecular template

Figure 33 The relationship between the lead adsorption and concentration of lead ions. Note that a fixed amount of lead molecular templates were used.
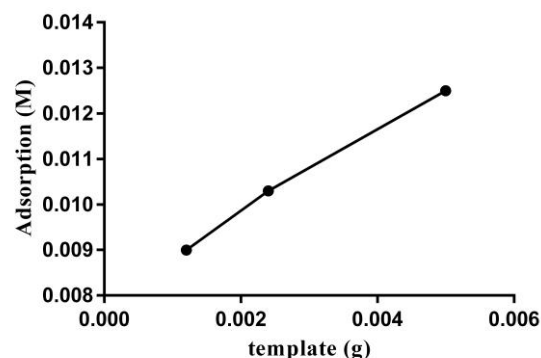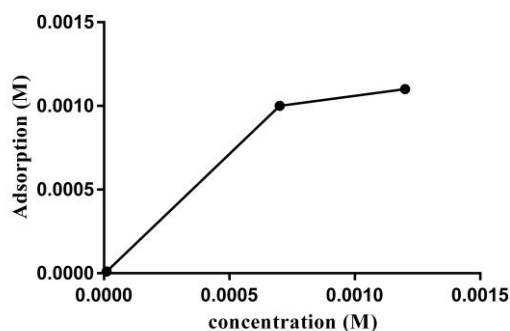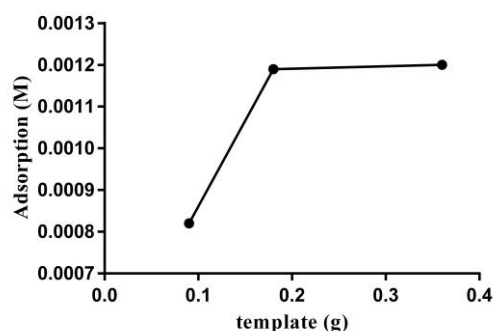
Figure 34 The relationship between the lead adsorption and weight of the lead molecular templates. Note that a fixed concentration of lead ions was used.

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Adsorption effect of lead molecular template was also explored. Note that a fixed amount of lead molecular template (0.027 g) was used for this experiment. Figure 33 shows the relationship between the lead ion adsorption and concentration of lead ions. Because a fixed amount of molecular templates were used, the heavy metal ions absorbed by the templates increased linearly first and gradually approached saturation if higher concentrations were used   When the concentration of lead ion solution was 0.00001 M, the adsorption of lead ions reached 0.0000095 M, indicating an absorption of 95%. Similarly, when the concentration of lead ion solution was 0.00015 M, the adsorption of lead was 0.00012 M, representing adsorption of 80%. At a high concentration of 0.00050 M, the adsorption of lead ions was 0.00039 M with absorption of 77% (Figure 33). Note that three repeated experiments were performed.

In addition, the relationship between the lead ion adsorption and the weight of the lead molecular templates at a fixed concentration of lead ions (0.00050 M) was further investigated. As expected, the more molecular templates we added, the more adsorption was observed (Figure 34).

VI. 6 Competitive adsorption effect of molecular templates

(a) Competitive adsorption of copper and manganese ions
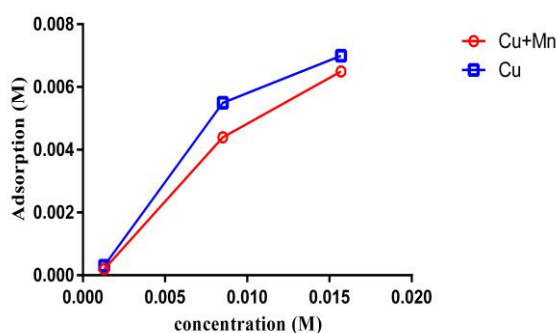
Figure 35   Competitive adsorption of copper and manganese ions for copper molecular templates.
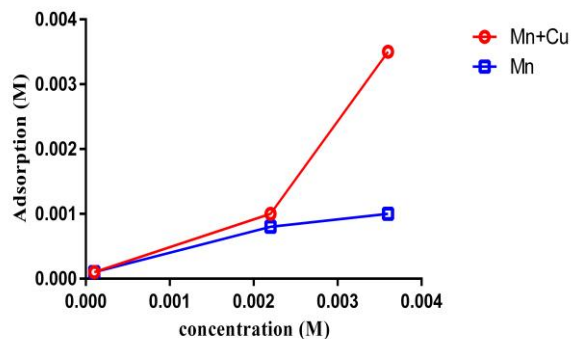
Figure 36 Competitive adsorption of copper and manganese ions for manganese molecular templates. M of copper and manganese.

The competitive adsorption of copper and manganese ions compared to single heavy metal ions (copper and manganese ions) by using the corresponding molecular template (copper or manganese molecular template) was further investigated since multiple metal ions may exist in rivers. As shown in Figure 35, the adsorption of copper molecular template toward copper may drop about 20-30% when compared with the case of copper ions only if manganese ions exist. Surprisingly, under the competitive adsorption, adsorption of manganese molecular template toward manganese would not be affected. In fact, the amount of adsorption of manganese molecular template increased if the copper ions exist (Figure 36). It could be explained by the fact that the hydrated manganese ions are bigger than hydrated copper ions .Therefore,

manganese could occupy the specific vacancies of copper molecular templates. Adsorption of manganese molecular templates thus increased. It then resulted in the decrease of absorption for the copper molecular templates and the increase of absorption for the manganese molecular templates. Similar trends have been observed for the other competitive tests. The following tables summarized the results.

(b) Competitive adsorption of copper and lead ions

Table 6 Comparison of competitive adsorption of copper and lead ions

〔Cu^{2+}〕	Concentration of Cu^{2+} in absorption of single heavy metal ion	Concentration of Cu^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0013 M	0.0012 M	0.0010 M	-16 %
0.0085 M	0.0068 M	0.0045 M	-24 %
0.0157	0.0122 M	0.0055 M	-43 %

〔Pb^{2+}〕	Concentration of Pb^{2+} in absorption of single heavy metal ion	Concentration of Pb^{2+} in competitive adsorption	Increasing/decreasing percentage
0.00001 M	0.0000095 M	0.00001 M	+0.05 %
0.00015 M	0.00012 M	0.00014 M	+13 %
0.00050 M	0.00039 M	0.00044 M	+10 %

The competitive adsorption of copper and lead ions compared to single heavy metal ions (copper ions and lead ions) by using the corresponding molecular template (copper or lead molecular template) was investigated. As shown in Table 6, the adsorption of copper molecular template toward copper may drop about 16-43% when compared with the case of copper ions only if lead ions exist. Similarly, under the competitive adsorption, the amount of adsorption of lead molecular template increased if the copper ions exist (Table 6). It could be explained by the fact that the hydrated lead ions are bigger than hydrated copper ions. Therefore, lead ions could occupy the specific vacancies of copper molecular templates. Adsorption of lead molecular templates thus increased. It then resulted in the decrease of absorption for the copper molecular templates and the increase of absorption for the manganese molecular templates.

(c) Competitive adsorption of copper and zinc ions

Table 7 Comparison of competitive adsorption of copper and zinc ions

〔Cu^{2+}〕	Concentration of Cu^{2+} in absorption of single heavy metal ion	Concentration of Cu^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0013 M	0.0012 M	0.0003 M	-70 %
0.0085 M	0.0068 M	0.0040 M	-33 %
0.0157	0.0122 M	0.0065 M	-37 %

〔Zn^{2+}〕	Concentration of Zn^{2+} in absorption of Single heavy metal ion	Concentration of Zn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0007 M	0.00053 M	0.0006 M	+7 %
0.0067 M	0.0047 M	0.0057 M	+5 %
0.0127 M	0.0083 M	0.00112 M	+10 %

The competitive adsorption of copper and zinc ions compared to single heavy metal ions (copper ions and zinc ions) by using the corresponding molecular template (copper or zinc molecular template) was investigated. As shown in Table 7, the adsorption of copper molecular template toward copper may drop dramatically (about 37-70%) when compared with the case of copper ions only if zinc ions exist. Similarly, under the competitive adsorption, the amount of adsorption of zinc molecular template increased (about 5-10%) if the copper ions exist (Table 7). It could be explained by the fact that the hydrated zinc ions are bigger than hydrated copper ions. Therefore, zinc ions could occupy the specific vacancies of copper molecular templates. Adsorption of zinc molecular templates thus increased. It then resulted in the decrease of absorption for the copper molecular templates and the increase of absorption for the zinc molecular templates.

(d) Competitive adsorption of manganese and zinc ions

Table 8 Comparison of competitive adsorption of manganese and zinc ions

〔Mn^{2+}〕	Concentration of Mn^{2+} in absorption of single heavy metal ion	Concentration of Mn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0001 M	0.000095 M	0.0001 M	+0.05 %
0.0011 M	0.00097 M	0.0011 M	+12 %
0.0036 M	0.00288 M	0.0030 M	+3 %

〔Zn^{2+}〕	Concentration of Zn^{2+}	Concentration of Zn^{2+}	Increasing/decreasing

	in absorption of Single heavy metal ion	in competitive adsorption	percentage
0.0007 M	0.00053 M	0.0001 M	-64 %
0.0067 M	0.0047 M	0.0030 M	-22 %
0.0127 M	0.0083 M	0.0050 M	-14 %

The competitive adsorption of zinc and manganese ions compared to single heavy metal ions (zinc ions and manganese ions) by using the corresponding molecular template (zinc or manganese molecular template) was investigated. As shown in Table 8, the adsorption of zinc molecular template toward zinc may drop dramatically (about 14-64%) when compared with the case of zinc ions only if manganese ions exist. Similarly, under the competitive adsorption, the amount of adsorption of manganese molecular template increased (up to 12%) if the zinc ions exist (Table 8). It could be explained by the fact that the hydrated manganese ions are bigger than hydrated zinc ions. Therefore, manganese ions could occupy the specific vacancies of zinc molecular templates. Adsorption of manganese molecular templates thus increased. It then resulted in the decrease of absorption for the zinc molecular templates and the increase of absorption for the manganese molecular templates.

(e) Competitive adsorption of manganese and lead ions

Table 9 Comparison of competitive adsorption of manganese and lead ions

〔Mn^{2+}〕	Concentration of Mn^{2+} in absorption of single heavy metal ion	Concentration of Mn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0001 M	0.000095 M	0.0001 M	+0.05 %
0.0011 M	0.00097 M	0.0011 M	+12 %
0.0036 M	0.00288 M	0.0032 M	+9 %

〔Pb^{2+}〕	Concentration of Pb^{2+} in absorption of single heavy metal ion	Concentration of Pb^{2+} in competitive adsorption	Increasing/decreasing percentage
0.00001 M	0.0000095 M	0 M	-95 %
0.00015 M	0.00012 M	0.00010 M	-23 %
0.00050 M	0.00039 M	0.00011 M	-56 %

The competitive adsorption of lead and manganese ions compared to single heavy metal ions (lead ions and manganese ions) by using the corresponding molecular template (lead or manganese molecular template) was investigated. As shown in Table 9, the adsorption of lead molecular template toward lead may drop dramatically (about 23-95%) when compared with the case of lead ions only if manganese ions exist. Similarly, under the competitive adsorption, the amount of adsorption of manganese molecular template increased (up to 12%) if the lead ions exist (Table 9). It could be explained by the fact that the hydrated manganese ions are bigger than hydrated lead ions. Therefore, manganese ions could occupy the specific vacancies of lead molecular templates. Adsorption of manganese molecular templates thus increased. It then resulted in the decrease of absorption for the lead molecular templates and the increase of absorption for the manganese molecular templates.

(f)   Competitive adsorption of zinc and lead ions

Table 10 Comparison of competitive adsorption of zinc and lead ions

〔 Zn^{2+} 〕	Concentration of Zn^{2+} in absorption of single heavy metal ion	Concentration of Zn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0007 M	0.00053 M	0.0007 M	+12 %
0.0067 M	0.0047 M	0.0057 M	+15 %
0.0127 M	0.0083 M	0.0098 M	+24 %

〔 Pb^{2+} 〕	Concentration of Pb^{2+} in absorption of single heavy metal ion	Concentration of Pb^{2+} in competitive adsorption	Increasing/decreasing percentage
0.00001 M	0.0000095 M	0.0000093 M	-0.02 %
0.00015 M	0.00012 M	0.00009 M	-20 %
0.00050 M	0.00039 M	0.00010 M	-58 %

The competitive adsorption of lead and zinc ions compared to single heavy metal ions (lead ions and zinc ions) by using the corresponding molecular template (lead or zinc molecular template) was investigated. As shown in Table 10, the adsorption of lead molecular template toward lead may drop dramatically (up to 58%) when compared with the case of lead ions only if zinc ions exist. Similarly, under the competitive adsorption, the amount of adsorption of zinc molecular template increased (about 12-24%) if the lead ions exist (Table 10). It could be explained by the fact that the hydrated zinc ions are bigger than hydrated lead ions. Therefore, zinc ions could occupy the specific vacancies of lead molecular templates. Adsorption of zinc molecular templates thus increased. It then resulted in the decrease of absorption for the lead molecular templates and the increase of absorption for the zinc molecular templates.

(g) Competitive adsorption of copper, manganese and zinc ions

Table 11 Comparison of competitive adsorption of copper, manganese and zinc ions

〔Cu^{2+}〕	Concentration of Cu^{2+} in absorption of single heavy metal ion	Concentration of Cu^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0013 M	0.0012 M	0.0002 M	-77 %
0.0085 M	0.0068 M	0.0030 M	-45 %
0.0157	0.0122 M	0.0055 M	-45 %

〔Zn^{2+}〕	Concentration of Zn^{2+} in absorption of single heavy metal ion	Concentration of Zn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0007 M	0.00053 M	0.0007 M	+12 %
0.0067 M	0.0047 M	0.0050 M	+5 %
0.0127 M	0.0083 M	0.0097 M	+23 %

〔Mn^{2+}〕	Concentration of Mn^{2+} in absorption of single heavy metal ion	Concentration of Mn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0001 M	0.000095 M	0.0001 M	+0.05 %
0.0011 M	0.00097 M	0.0010 M	+2 %
0.0036 M	0.00288 M	0.0035 M	+17 %

The competitive adsorption of copper, manganese and zinc ions compared to single heavy metal ions (copper, manganese and zinc ions) by using the corresponding molecular template (copper, manganese or zinc molecular template) was explored. As shown in Table 11, the adsorption of copper molecular template toward lead may drop dramatically (about 45-77%) when compared with the case of copper ions only if the other two ions exist. As expected, under the competitive adsorption, the amount of adsorption of zinc molecular template increased (about 12-24%) if the other ions exist (Table 11). Similarly, under the competitive adsorption, the amount of adsorption of manganese molecular template increased (up to 17%) if the other ions exist (Table 11). It could be explained by the fact that the hydrated manganese ions and hydrated

zinc ions are bigger than hydrated copper ions. Therefore, manganese and zinc ions could occupy the specific vacancies of copper molecular templates. Adsorption of zinc and manganese molecular templates thus increased. It also resulted in the decrease of absorption for the copper molecular templates.

(h) Competitive adsorption of manganese, zinc and lead ions

Table 12 Comparison of competitive adsorption of manganese, zinc, lead ions

〔Mn^{2+}〕	Concentration of Mn^{2+} in absorption of single heavy metal ion	Concentration of Mn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0001 M	0.000095 M	0.0001 M	+0.05 %
0.0011 M	0.00097 M	0.0011 M	+12 %
0.0036 M	0.00288 M	0.0031 M	+6 %

〔Zn^{2+}〕	Concentration of Zn^{2+} in absorption of single heavy metal ion	Concentration of Zn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0007 M	0.00053 M	0.0006 M	+8 %
0.0067 M	0.0047 M	0.0054 M	+11 %
0.0127 M	0.0083 M	0.0115 M	+38 %

〔Pb^{2+}〕	Concentration of Pb^{2+} in absorption of single heavy metal ion	Concentration of Pb^{2+} in competitive adsorption	Increasing/decreasing percentage
0.00001 M	0.0000095 M	0.00001 M	+0.05 %
0.00015 M	0.00012 M	0.00008 M	-27 %
0.00050 M	0.00039 M	0.00010 M	-58 %

The competitive adsorption of manganese, zinc, lead ions compared to single heavy metal ions (manganese, zinc, lead ions) by using the corresponding molecular template (manganese, zinc, or lead molecular template) was explored. As shown in Table 12, the adsorption of lead molecular template toward lead may drop dramatically (up to 58%) when compared with the case of lead ions only if the other two ions exist. As expected, under the competitive adsorption, the amount of adsorption of manganese molecular template increased (up to 12%) if the other ions exist (Table 12). Similarly, under the competitive adsorption, the amount of adsorption of zinc molecular template increased (up to 38%) if the other ions exist (Table 12). It could be explained by the fact that the hydrated manganese ions and hydrated zinc ions are bigger than hydrated lead ions. Therefore, manganese and zinc ions could occupy the specific vacancies of lead molecular templates. Adsorption of zinc and manganese molecular templates thus increased.

It also resulted in the decrease of absorption for the lead molecular templates.

(i) Competitive adsorption of copper, zinc and lead ions

Table 13 Comparison of competitive adsorption of copper, zinc, lead ions

〔Cu^{2+}〕	Concentration of Cu^{2+} in absorption of single heavy metal ion	Concentration of Cu^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0013 M	0.0012 M	0.0003 M	-69 %
0.0085 M	0.0068 M	0.0044 M	-28 %
0.0157 M	0.0122 M	0.0065 M	-37 %

〔Zn^{2+}〕	Concentration of Zn^{2+} in absorption of single heavy metal ion	Concentration of Zn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0007 M	0.00057 M	0.0007 M	+12 %
0.0067 M	0.0047 M	0.0057 M	+15 %
0.0127 M	0.0083 M	0.0117 M	+39 %

〔Pb^{2+}〕	Concentration of Pb^{2+} in absorption of single heavy metal ion	Concentration of Pb^{2+} in competitive adsorption	Increasing/decreasing percentage
0.00001 M	0.0000095 M	0.00000 M	-0.05 %
0.00015 M	0.00012 M	0.00013 M	+7 %
0.00050 M	0.00039 M	0.00042 M	+6 %

The competitive adsorption of copper, zinc and lead ions compared to single heavy metal ions (copper, zinc and lead ions) by using the corresponding molecular template (copper, zinc or lead molecular template) was explored. As shown in Table 13, the adsorption of copper molecular template toward copper ions may drop dramatically (28-69%) when compared with the case of copper ions only if the other two ions exist. As expected, under the competitive adsorption, the amount of adsorption of zinc molecular template increased (12-39%) if the other ions exist (Table 13). Similarly, under the competitive adsorption, the amount of adsorption of lead molecular template increased (up to 7%) if the other ions exist (Table 13). It could be explained by the fact that the hydrated lead ions and hydrated zinc ions are bigger than hydrated copper ions. Therefore, lead and zinc ions could occupy the specific vacancies of copper molecular templates. Adsorption of zinc and lead molecular templates thus increased. It also

resulted in the decrease of absorption for the copper molecular templates.

(j)   Competitive adsorption of copper, manganese and lead ions

Table 14 Comparison of competitive adsorption of copper, manganese, lead ions

〔Cu^{2+}〕	Concentration of Cu^{2+} in absorption of single heavy metal ion	Concentration of Cu^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0013 M	0.0012 M	0.0002 M	-77 %
0.0085 M	0.0068 M	0.0053 M	-17 %
0.0157 M	0.0122 M	0.0060 M	-40 %

〔Mn^{2+}〕	Concentration of Mn^{2+} in absorption of single heavy metal ion	Concentration of Mn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0001 M	0.000095 M	0.0001 M	+0.05 %
0.0011 M	0.00097 M	0.0011 M	+12 %
0.0036 M	0.00288 M	0.0035 M	+17 %

〔Pb^{2+}〕	Concentration of Pb^{2+} in absorption of single heavy metal ion	Concentration of Pb^{2+} in competitive adsorption	Increasing/decreasing percentage
0.00001 M	0.0000095 M	0.00001 M	+0.05 %
0.00015 M	0.00012 M	0.00014 M	+13 %
0.00050 M	0.00039 M	0.00045 M	+12 %

The competitive adsorption of copper, manganese and lead ions compared to single heavy metal ions (copper, manganese and lead) by using the corresponding molecular template (copper, manganese or lead molecular template) was explored. As shown in Table 14, the adsorption of copper molecular template toward copper ions may drop dramatically (17-77%) when compared with the case of copper ions only if the other two ions exist. As expected, under the competitive adsorption, the amount of adsorption of manganese molecular template increased (up to 17%) if the other ions exist (Table 14). Similarly, under the competitive adsorption, the amount of adsorption of lead molecular template increased (up to 13%) if the other ions exist (Table 14). It could be explained by the fact that the hydrated manganese ions and hydrated lead ions are bigger than hydrated copper ions. Therefore, manganese and lead ions could occupy the specific vacancies of copper molecular templates. Adsorption of manganese and lead molecular templates

thus increased. It also resulted in the decrease of absorption for the copper molecular templates.

(k) Competitive adsorption of copper, manganese, zinc, and lead ions

Table 15 Comparison of competitive adsorption of copper, manganese, zinc, lead ions

〔Cu^{2+}〕	Concentration of Cu^{2+} in absorption of single heavy metal ion	Concentration of Cu^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0013 M	0.0012 M	0.0003 M	-77 %
0.0085 M	0.0068 M	0.0041 M	-20 %
0.0157 M	0.0122 M	0.0050 M	-47 %

〔Mn^{2+}〕	Concentration of Mn^{2+} in absorption of single heavy metal ion	Concentration of Mn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0001 M	0.000095 M	0.0001 M	+0.05 %
0.0011 M	0.00097 M	0.0010 M	+3 %
0.0036 M	0.00288 M	0.0035 M	+17 %

〔Zn^{2+}〕	Concentration of Zn^{2+} in absorption of single heavy metal ion	Concentration of Zn^{2+} in competitive adsorption	Increasing/decreasing percentage
0.0007 M	0.00057 M	0.0007 M	+12 %
0.0067 M	0.0047 M	0.0050 M	+5 %
0.0127 M	0.0083 M	0.0115 M	+13 %

〔Pb^{2+}〕	Concentration of Pb^{2+} in absorption of Single heavy metal ion	Concentration of Pb^{2+} in competitive adsorption	Increasing/decreasing percentage
0.00001 M	0.0000095 M	0.00000 M	-0.05 %
0.00015 M	0.00012 M	0.00012 M	+0 %
0.00050 M	0.00039 M	0.00039 M	+0 %

The competitive adsorption of copper, manganese, zinc, and lead ions compared to single heavy metal ions (copper, manganese, zinc, and lead) by using the corresponding molecular template (copper, manganese, zinc, or lead molecular template) was explored. As shown in Table 15, the adsorption of copper molecular template toward copper ions may drop dramatically (20-77%) when compared with the case of copper ions only if the other three ions exist. As

expected, under the competitive adsorption, the amount of adsorption of manganese molecular template increased (up to 17%) if the other three ions exist (Table 15). Similarly, under the competitive adsorption, the amount of adsorption of zinc molecular template increased (up to 13%) if the other three ions exist (Table 15). However, the amount of adsorption of lead molecular template did not change significantly if the other three ions exist. It could be explained by the fact that the hydrated manganese ions and hydrated zinc ions are bigger than hydrated copper ions. Therefore, manganese and zinc ions could occupy the specific vacancies of copper molecular templates. Adsorption of manganese and zinc molecular templates thus increased. It also resulted in the decrease of absorption for the copper molecular templates.

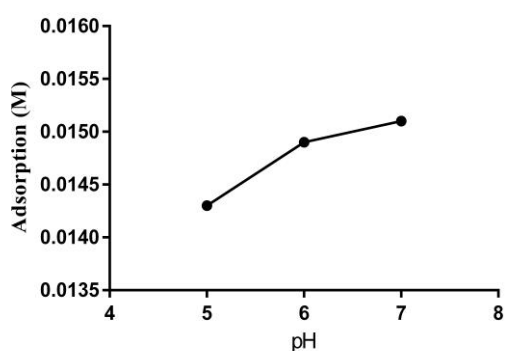**VI.7 Adsorption effect of molecular templates in different pH values**

Figure 37 Measurement of copper ion adsorption in different pH values.
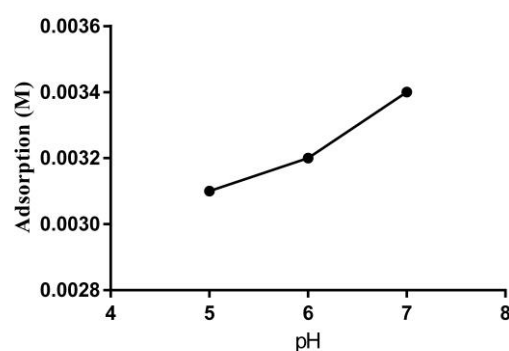

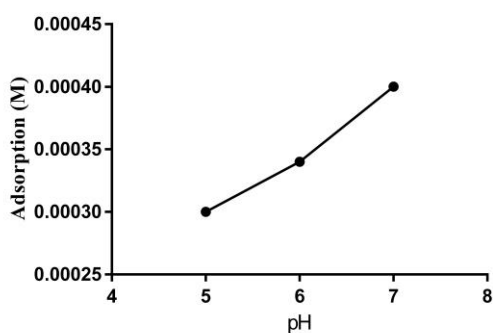Figure 38 Measurement manganese ion adsorption in different pH values.

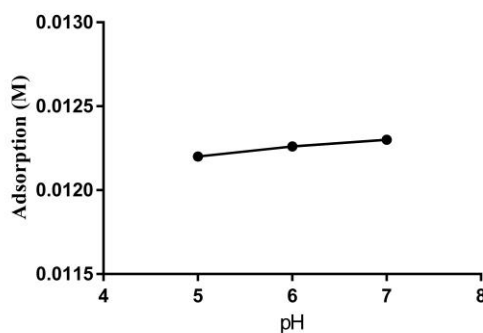Figure 39 Measurement lead ion adsorption in different pH values.

Figure 40 measurement of zinc ion adsorption in different pH values.

Absorption effect of molecular templates in different pH values was further explored. According to the literature, when the pH value of the heavy metal solution is above 7, absorption effect drops remarkably. Therefore, only pH values ranging from 5 to 7 were tested. As shown in Figures 37-40, four kinds of molecular templates could absorb heavy metal ions more easily in a neutral solution. However, the absorption capability drops if the pH value decreases. Therefore, all the absorption tests in this work were performed at pH 7.

VI.8 Desorption effect of molecular templates

Table 16 Desorption effort of copper, zinc, manganese and lead molecular templates

〔Cu^{+2}〕	Original concentration	Concentration after desorption	Desorption (%)	〔Mn^{+2}〕	Original concentration	Concentration after desorption	Desorption (%)
pH 4.0	0.0157 M	0.0100 M	64%	pH 4.0	0.0036 M	0.0030 M	83%
pH 4.5	0.0157 M	0.0075 M	48%	pH 4.5	0.0036 M	0.0027 M	75%
pH 5.0	0.0157 M	0.0065 M	42%	pH 5.0	0.0036 M	0.0022 M	61%

〔Zn^{+2}〕	Original concentration	Concentration of desorption	Desorption (%)	〔Pb^{+2}〕	Original concentration	Concentration after desorption	Desorption (%)
pH4.0	0.0127 M	0.0076 M	60%	pH 4.0	0.00050 M	0.00030 M	60%
pH4.5	0.0127 M	0.003 M	24%	pH 4.5	0.00050 M	0.00027 M	54%
pH5.0	0.0127 M	0.002 M	16%	pH 5.0	0.00050 M	0.00022 M	44%

Desorption effect of four molecular templates was explored such that they could re-used if necessary. Table 16 lists the rests for these experiments of desorption. Note that four heavy metal ions were tested at the highest concentration (Cu, 0.0157 M; Mn, 0.0036 M; Zn, 0.0127 M; Pb, 0.0005 M) for 24 hours. As shown in this table, desorption efficiencies for copper templates are 42%, 48% and 64% for pH 5, pH 4.5 and pH 4, respectively. For manganese templates, desorption efficiencies are 61%, 75% and 83% for pH 5, pH 4.5 and pH 4, respectively. Similarly, for zinc templates, desorption efficiencies are 16%, 24% and 60% for pH 5, pH 4.5 and pH 4, respectively. For lead templates, desorption efficiencies are 44%, 54% and 60% for pH 5, pH 4.5 and pH 4, respectively. It indicates that desorption efficiency is better when tested in the lower pH value. The best desorption efficiency can be as high as 83%. Note that similar results have been reported in literature that acidic solution could be used to desorb the adsorbed molecules [13].

VI.9 Adsorption effect of magnetic molecular templates

Table 17 Adsorption of four kinds of magnetic molecular templates

$[Cu^{+2}]$ Original concentration	Concentration after adsorption using original templates	Concentration after adsorption using magnetic templates	difference (%)	$[Mn^{+2}]$ Original concentration	Concentration after adsorption using templates	Concentration after adsorption using magnetic templates	difference (%)
0.0013 M	0.0012 M	0.00012M	0%	0.0001 M	0.000095 M	0.000095 M	0%
0.0085 M	0.0068 M	0.0068 M	0%	0.0011 M	0.00097 M	0.00097 M	0 %
0.0157 M	0.0122 M	0.00122 M	0%	0.0036 M	0.00288 M	0.00288 M	0 %

$[Zn^{+2}]$ Original concentration	Concentration after adsorption using templates	Concentration after adsorption using magnetic templates	Difference (%)age	$[Pb^{+2}]$ Original concentration	Concentration after adsorption using templates	Concentration after adsorption using magnetic templates	difference (%)
0.0007 M	0.00057 M	0.00057 M	0 %	0.00001 M	0.0000095 M	0.0000095 M	0 %
0.0067 M	0.0047 M	0.0047 M	0 %	0.00015 M	0.00012 M	0.00012 M	0 %
0.0127 M	0.0083 M	0.082 M	-0.04 %	0.00050 M	0.00039 M	0.00039 M	0 %

As mentioned previously, we coated molecular templates on the surface of magnetic particles such that they could be collected with easy by applying external magnetic forces. It is crucial to explore the adsorption effect of magnetic molecular templates in order to test whether the magnetic particles affect the adsorption, Table 17 lists the concentration of ions using original and magnetic molecular templates. It can be clearly seen that heavy metal ion absorption of the magnetic templates are the same as the original templates. It is then concluded that magnetic particles does not affect the adsorption. Thus, we can take magnetic molecular templates to adsorb heavy metal ions and then apply magnetic forces to collect these particles . Then acidic solution could be used to desorb the ions such that they could be reused.

VII. Conclusions

1. It was experimentally found that blank molecular templates did not absorb heavy metal ions since no specific vacancy for ions were formed during polymerization process.

2.Four kinds of molecular templates were found to possess high specificity toward their target ions.

3. The adsorption of copper, manganese, zinc and lead molecular templates could be as high as 92%, 95 %, 75 % and 95 %, respectively.

4. Significant competitive adsorption were observed while multiple ions exist, which could be explained by the activities of the ions.

5. Desorption efficiencies for copper, manganese, zinc and lead were found to be 64%, 83%, 60% and 60% at pH 4.

6. A new concept using magnetic particles to form magnetic molecular templates was realized. The ion adsorption capability of these magnetic molecular templates did not degrade.

VIII. Future Prospective

Three applications for household water, industrial wastewater and teabag filters were proposed by using the developed molecular templates. As shown in Figures 41-43, we can put the molecular templates into a faucet or a tea bag for absorbing the specific heavy metal ions rapidly. In a faucet, when the adsorption of molecular templates turn into saturation, it can be replaced rapidly, and desorb it later such that it could be reused again. In industrial water tubes, according to the specific heavy metal in rivers, the molecular templates can even absorb these metal ions effectively. When the molecular templates are packaged as a tea bag, they could also absorb heavy metal ions (especially lead).
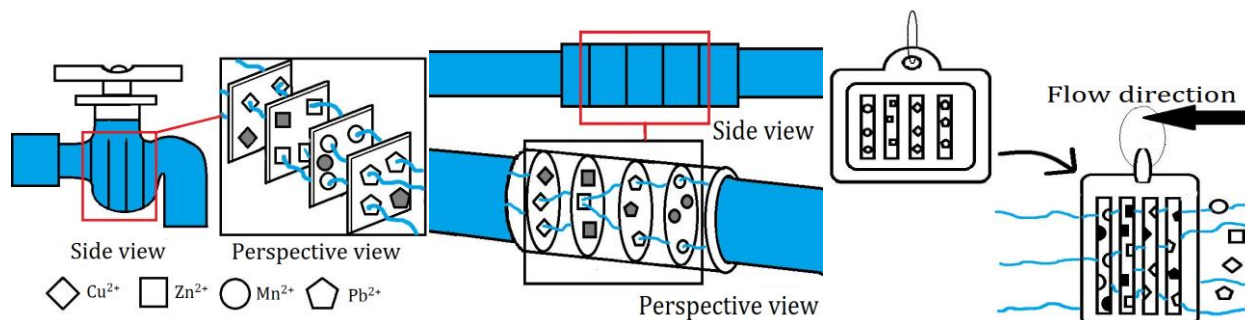

Figure 41 Molecular templates could be installed in In a faucet.

Figure 42 Molecular templates could be installed in industrial water tubes.

Figure 43 Molecular templates could be installed in a tea bag.

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