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# One-step synthesis of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres and practical application in Cu(II) ion adsorption

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Polyimide(PI)@magnetite(Fe<sub>3</sub>O<sub>4</sub>) composite microspheres have been successfully synthesized from poly(amic acid) triethylamine salts (PAAS) and Fe(III) ions by a facile one-step solvothermal process. Furthermore, the formation mechanism of the PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres has been investigated. The morphology and structure of the samples were both characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and infrared spectroscopy (IR). The results obtained show that the surface of magnetite could be successfully coated with polyimide and the coating could permeate throughout the crystals via a self-assembly process. The size of the composite microspheres was found to increase upon increasing the concentration of PAAS. The thermal properties of the composite microspheres were studied via thermo gravimetric analysis (TGA) and the magnetic properties were determined by a vibrating sample magnetometer (VSM). Even though the saturation magnetization of the PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres is lower than that of pure Fe<sub>3</sub>O<sub>4</sub>, the microspheres coated with PI exhibit an increased stability. In addition, basic hydrolysis of the composite microspheres has been carried out and the Cu(II)-adsorption properties of the composite microspheres before and after hydrolysis have been investigated. In doing so, it could be determined that the adsorption capacity of hydrolyzed composite microspheres increases from 5.84 mg/g to 24.63 mg/g.

#### 1. Introduction

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is one of the best-known magnetic materials and has been extensively studied with respect to properties involving a high saturation magnetization, biocompatibility and low toxicity.<sup>1-5</sup> Due to superior performance characteristics, the material has been widely used in applications such as catalysis,<sup>6</sup> wave absorption,<sup>7,8</sup> environmental remediation,<sup>9</sup> biotechnology/biomedicine,<sup>10,11</sup> and magnetic resonance imaging<sup>12,13</sup>. However, bare magnetite microspheres prove to be highly reactive and readily oxidize in air. This generally results in a loss of magnetism and dispersibility. The development of strategies to protect bare magnetite microspheres against chemical reactions remains a crucial goal for a variety of applications. In order to isolate the magnetite core from environmental conditions, most of the protection strategies involve magnetite microspheres with a core-shell structure, e.g. bare magnetite microspheres coated with polymers,<sup>14,15</sup> silica,<sup>16,17</sup> carbon<sup>18,19</sup> and precious metals<sup>20,21</sup>. Among such examples, core-shell structures of magnetite composite microspheres represent particularly promising materials. Furthermore, coatings may stabilize the magnetite microspheres, leading to improved dispersibility and biocompatibility characteristics. Further modifications with functional molecules may also result in the formation of various other materials for diverse applications.<sup>22-24</sup>

Core-shell magnetite composite microspheres with polymer coatings exhibit specific features, including high biocompatibility and biological activity. This is why polymer-Fe<sub>3</sub>O<sub>4</sub> core-shell structures have been extensively studied in the past.<sup>25-27</sup> Wang et al. developed a core-shell nanocomposite by coating magnetic iron oxide nanoclusters with a polypyrrole (PPy) matrix functionalized with polyethylene glycol for imaging guided combinatory anticancer therapy.<sup>28</sup> Fang et al. have synthesized Fe<sub>3</sub>O<sub>4</sub>/PMMA composite microspheres via a facile mini-emulsion polymerization as a platform for multimodal protein separation.<sup>29</sup> Furthermore, magnetite core-shell particles also feature a variety of applications in adsorption processes of heavy metal ions. Yi et al. have synthesized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@1,3-calixcron microspheres in an effort to remove Pb(II) ions from.<sup>30</sup> Chang et al. have synthesized chitosan-bound magnetic nanoparticles designed for the removal of Cu(II) ions from.<sup>31</sup>

One general weakness exhibited by most polymer-coated magnetite microspheres is the relatively low intrinsic stability of the coating at higher temperature, an issue that proves to be escalated by the occurrence of possible catalytic side reactions in the metallic cores.<sup>32</sup> Among various polymers, polyimide (PI) features outstanding performance characteristics with excellent thermal stabilities, exceptional mechanical and electrical properties as well as superior chemical resistance. The material has been used in a variety of different applications.<sup>33-36</sup> Combined with increased thermal stability, coating magnetite microspheres with polyimide may also improve dispersibility. PI/metal composite films and PI/metal nanowires have been successfully prepared via an ion exchange method, demonstrated by Shang *et al.* for the preparation of a PI/CuS composite film.<sup>37</sup> Han *et al.* have prepared PI/Ag

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nanofibers by thermally treating the silver(I)-doped PAA ultrafine fibers and loading of silver(I) ions through ion exchange reactions of the carboxylic acid groups of the PAA macromolecules with  $[Ag(NH_3)_2]^+$  cations in aqueous solution.<sup>38</sup> However, to the best of our knowledge, no reports in the literature exist to date, describing a comprehensive one-step preparation of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres. The reactions involved here include the hydrolysis of a common polyimide precursor of polyimide under basic conditions, polyamide acid, and an appropriate basic environment to result in the precipitation of Fe<sub>3</sub>O<sub>4</sub>.

In this report, we describe the development of a facile one-step solvothermal method for the preparation of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres using poly(amic acid) triethylamine salts (PAAS) and ferric chloride hexahydrate (FeCl<sub>3</sub>6H<sub>2</sub>O) as starting materials. The preparation and addition of Fe<sub>3</sub>O<sub>4</sub> particles is not required, avoiding а complicated production process. Furthermore, no additional precipitating agent needs to be added to the reaction mixture, except for triethylamine. The latter may be generated from a high-temperature thermal cyclization of PAAS. A series of material samples were prepared by varying the stoichiometry of PAAS and FeCl<sub>3</sub>·6H<sub>2</sub>O. Subsequently, the thermal and magnetic properties of the prepared samples were tested. Using an ion exchange method, we have also carried out a hydrolysis reaction of the composite microspheres. Via ion exchange of Cu(II) ions, the Cu(II)-adsorption properties of the composite microspheres before and after hydrolysis could be evaluated.

#### 2. Experimental

#### 2.1 Materials

N,N-dimethylacetamide (DMAc), ethylene glycol (EG) and triethylamine (TEA) were purchased from Tianjin Fuyu Fine Chemical Co. Ltd.; Pyromellitic dianhydride (PMDA) was purchased from Sinopharm Chemical Reagent Co. Ltd.;  $3,4^{2}$ -oxydianline ( $3,4^{2}$ -ODA) was purchased from Changzhou Sunlight Chemical Co. Ltd.; Ferric chloride hexahydrate (FeCl<sub>3</sub> 6H<sub>2</sub>O) was purchased from Tianjin Yuanli Chemical Co. Ltd.; Copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) was purchased from the Tianjin Guangfu Fine Chemical Research Institute. Potassium hydroxide (KOH) was purchased from Tianjin Dalu Chemical Reagent Factory. All reagents were of analytical grade and were used as received without further purification.

#### 2.2 Preparation of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres

#### 2.2.1 Synthesis the PAAS solution

The polyimide precursors, i.e. poly(amic acid) triethylamine salts (PAAS) were synthesized as reported previously.<sup>39</sup> 10.0 g (50 mmol) ODA and 125 ml DMAc were placed in a 250 ml three-neck round-bottom flask equipped with a mechanical stirrer. Once ODA dissolved entirely, one equivalent (10.9 g, 50 mmol) of PMDA was added and the mixture was stirred at room temperature for 4 hours. After preparation of the PAA solution, 10.1 g (0.1 mol) of TEA at a PAA-TEA (molar ratio 1:2) was added to the PAA solution at room temperature and the mixture was stirred for another 4 hours. Finally, the PAAS solution was obtained with a mass fraction of 20 wt.%.

The  $Fe_3O_4$  microspheres were obtained through a solvothermal method<sup>40</sup> using mixed solvents and triethylamine as a precipitant. The PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres were prepared as follows: PAAS solution was added to the mixed solvents DMAc and EG and stirred to obtain a homogeneous solution. The varving reaction amounts of PAAS, DMAc and EG are shown in Table 1. Afterwards, 10 mL of a solution consisting of ferric chloride dissolved in ethylene glycol equaling 0.5 mol/L was added to this solution and was stirred for 1 hour. The resulting mixture was then transferred into a 100 ml teflon-lined autoclave for thermal treatment at 200 °C for 8 hours. The products were extracted using a permanent magnet, were rinsed with deionized water and acetone three times and then dried in a vacuum oven at 75 °C for 6 hours. According to the mass of the PAAS solution added (10.0 g, 15.0 g, 20.0 g and 25.0 g), the obtained PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres were marked as PI@Fe<sub>3</sub>O<sub>4</sub>-1, PI@Fe<sub>3</sub>O<sub>4</sub>-2, PI@Fe<sub>3</sub>O<sub>4</sub>-3 and PI@Fe<sub>3</sub>O<sub>4</sub>-4, respectively.

Table 1. Reaction parameter of PAAS, DMAc and EG

Sample	Amount of PAAS solution (g)	DMAc (ml)	EG (ml)	Concentration of mixed solution (wt%)
PI@Fe <sub>3</sub> O <sub>4</sub> -1	10	25	25	3
PI@Fe <sub>3</sub> O <sub>4</sub> -2	15	20	25	4.5
PI@Fe <sub>3</sub> O <sub>4</sub> -3	20	15	25	6.1
PI@Fe <sub>3</sub> O <sub>4</sub> -4	25	10	25	7.7

#### 2.3 Adsorption test

The resulting samples of  $PI@Fe_3O_4-1$  and  $PI@Fe_3O_4-4$  were subjected to hydrolysis using a KOH solution of 4 mol/L for 1 hour. The hydrolyzed samples were coined PI@Fe<sub>3</sub>O<sub>4</sub>-1H and PI@Fe<sub>3</sub>O<sub>4</sub>-4H, respectively. Assessment of the Cu(II)-adsorption of the bare Fe<sub>3</sub>O<sub>4</sub> samples and PI/Fe<sub>3</sub>O<sub>4</sub> composite microspheres (hydrolyzed/not hydrolyzed) was performed. The solution of Cu(II) ions was prepared by dissolving an appropriate quantity of CuSO<sub>4</sub>·5H<sub>2</sub>O in distilled water to result in a final concentration 50 mg/L. 10 mg samples were added to 50 ml of Cu(II) solution and the mixture was ultrasonicated for 1 hour. The samples were then removed from the solution using a permanent magnet. After the extraction, the concentrations of Cu(II) ions in the supernatant were directly determined using an atomic absorption spectrometer..

#### 2.4 Characterization

Scanning electron microscopy (SEM) images were obtained with a Quanta 200 microscope using an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained out on a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. X-ray diffraction (XRD) analysis was performed using a Y500 diffractometer by use of a CuK $\alpha$ source, with 0.02° step and a scan range between 10° and 80°. IR spectra (IR) were recorded on a Bruker Equinox 55 Fourier transform IR spectrometer. The samples were ground, mixed with

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KBr and then pressed into pellets. The scanning range was set at 400-4000 cm<sup>-1</sup>. Thermogravimetric analyses (TGA) were performed using a Pyris 6 TGA operated in an air atmosphere at a heating rate of 10 °C/min. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) at room temperature. The Cu(II) concentration was determined using a TAS-986 (Beijing Pgeneral Company, Beijing, China) flame atomic absorption spectrometer (FAAS) in an air-acetylene flame, using a copper hollow cathode lamp at a wavelength of 324.7 nm.

#### 3. Results and Discussion

#### 3.1 Mechanism of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres

A possible mechanism for the synthesis of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres is illustrated in Scheme 1. At first, a polyimide precursor (PAAS) was synthesized, exhibiting good stability. PAAS was dissolved in a mixed solvent consisting of DMAC and EG and FeCl<sub>3</sub>·6H<sub>2</sub>O in ethylene glycol was added dropwise. Due to the presence of a large number of carbonyl groups in the PAAS main chain, it is believed that iron(III) ions first coordinate to the side chains of PAAS via complexation effects. In the teflon-lined autoclave and with rising temperature, triethylamine gets removed from the PAAS main chain and dissipates in solution, resulting in a pH increase. Iron(III) oxide precipitates under such weakly basic conditions and ethylene glycol serves as a reductant to support the formation of Fe<sub>3</sub>O<sub>4</sub> instead of Fe<sub>2</sub>O<sub>3</sub> at high temperature. Meanwhile, the formed intermediate PAA is being transformed from PAAS and imidizes immediately upon precipitation on the surface of the nanocrystal grains to form the final composite microsphere constructs.



Scheme 1. Illustrative formation processes of PI@Fe<sub>3</sub>O<sub>4</sub> composites microspheres.

#### 3.2 Structure and morphology characterization

Figure 1 shows the IR spectra of pure  $Fe_3O_4$  and  $PI@Fe_3O_4-3$  composite microspheres. In the spectrum of pure  $Fe_3O_4$  (cf. Figure 1a), an intense absorption band at 591 cm<sup>-1</sup> can be observed. This signal can be assigned to a characteristic band of the Fe-O group, characteristic for the presence of  $Fe_3O_4$ .<sup>41</sup> Figure 1b shows a strong peak at 1713 cm<sup>-1</sup> that can be ascribed to the symmetrical stretching vibration of C=O. The bands at 1776, 1360 and 721 cm<sup>-1</sup> can be assigned to the vibrational frequencies of the C=O asymmetrical stretching, the C-N stretching and the C-N bending, respectively. This finding indicates that the imidization reaction of the polyimide is complete. Typical peaks of  $Fe_3O_4$  at 591cm<sup>-1</sup> can also be found in Figure 1b. The spectral changes between Figure 1a and Figure 1b provide evidence for a successful coating reaction of  $Fe_3O_4$  microspheres with PI.

Figure 2 shows the different XRD patterns of Fe<sub>3</sub>O<sub>4</sub> and PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres. Sharp and intense peaks can be observed in the spectrum of pure Fe<sub>3</sub>O<sub>4</sub> with  $2\theta = 30.12^{\circ}$ ,  $35.48^{\circ}$ ,  $43.12^{\circ}$ ,  $57.02^{\circ}$  and  $62.62^{\circ}$ , matching the characteristic signals for magnetite (JCPDS, No. 19-0629) and corresponding to the indices (220), (311), (400), (511) and (440), respectively.<sup>42</sup> Furthermore, five characteristic peaks in curve of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres can be observed. However, the diffraction peak intensity is weaker and broader, indicating the presence of an amorphous species (i.e. PI) coated on the surface of Fe<sub>3</sub>O<sub>4</sub>. With an increasing amount of PAAS, the crystal parameters of the composite microspheres become less ideal. PI@Fe<sub>3</sub>O<sub>4</sub>-3 and PI@Fe<sub>3</sub>O<sub>4</sub>. This finding may be due to the crystal-like arrangement of the PI structure induced by the Fe<sub>3</sub>O<sub>4</sub> crystals.



Figure 1. IR spectra of (a) pure  $Fe_3O_4$  and (b)  $PI@Fe_3O_4-3$  composite microspheres.



Figure 2. XRD patterns of (a) pure  $Fe_3O_4$ , (b)  $PI@Fe_3O_{4}-1$  composite microspheres, (c)  $PI@Fe_3O_4-2$  composite microspheres, (d)  $PI@Fe_3O_4-3$  composite microspheres and (e)  $PI@Fe_3O_4-4$  composite microspheres.

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To gain a visual understanding of the morphology of the composites, studies involving scanning electron microscopy (SEM) were performed. The corresponding SEM images are shown in Figure 3. By comparing the images of pure Fe<sub>3</sub>O<sub>4</sub> microspheres (cf. Figure 3a) to the images of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres, a rough surface and larger diameter of the composite microspheres can be observed, most notably due to the polyimide coated surface of the Fe<sub>3</sub>O<sub>4</sub> microspheres and formation of the core-shell magnetite polymers.43 Moreover, the concentration of the mixed solution affects the size of the PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres. By inspection of the SEM images it can be determined that the particle size of Fe<sub>3</sub>O<sub>4</sub>, PI@Fe<sub>3</sub>O<sub>4</sub>-1, PI@Fe<sub>3</sub>O<sub>4</sub>-2, PI@Fe<sub>3</sub>O<sub>4</sub>-3 and PI@Fe<sub>3</sub>O<sub>4</sub>-4 microspheres is approximately 200 nm, 300 nm, 500 nm, 1 µm and 1 µm, respectively. These results obtained provide evidence for the notion that composite microspheres maintain their relative size with a solution concentration of more than 6.1 wt.%.



Figure 3. SEM images of (a) bare  $Fe_3O_4$  microspheres, (b)  $PI@Fe_3O_4-1$  composite microspheres, (c)  $PI@Fe_3O_4-2$  composite microspheres, (d)  $PI@Fe_3O_4-3$  composite microsphere and (e)  $PI@Fe_3O_4-4$  composite microspheres.

The transmission electron microscopy (TEM) images of  $PI/Fe_3O_4$  composite microspheres are shown in Figure 4. The internal dark core was coated with an external light shell. From this finding it can be determined that the  $Fe_3O_4$  particles have been successfully coated with PI. The dark core consists of abundant nanocrystal grains.<sup>44</sup> PI coats not only on the surface of the microspheres, but also permeates each nanocrystal grain. With increasing PAAS content, the shell thickness of the composite microspheres increases proportionately. Furthermore, the interface of the two phases is most likely not due to a mutual penetration of PI and  $Fe_3O_4$ .

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Figure 4. TEM images of (a) bare  $Fe_3O_4$  microspheres, (b)  $PI@Fe_3O_4-1$  composite microspheres, (c)  $PI@Fe_3O_4-2$  composite microspheres, (d)  $PI@Fe_3O_4-3$  composite microspheres and (e)  $PI@Fe_3O_4-4$  composite microspheres.



**Figure 5.** Photographic image of a suspension consisting of (a) pure Fe<sub>3</sub>O<sub>4</sub>, (b) PI@Fe<sub>3</sub>O<sub>4</sub>-1 composite microspheres, (c) PI@Fe<sub>3</sub>O<sub>4</sub>-2 composite microspheres, (d) PI@Fe<sub>3</sub>O<sub>4</sub>-3 composite microspheres and (e) PI@Fe<sub>3</sub>O<sub>4</sub>-4 composite microspheres.

The obtained samples appear as black brown powders. Figure 5 depicts a photographic image of the samples suspended in distilled water. The color of the suspension changes from black to brown, and

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finally turns to yellow due to a reduced proportion of  $Fe_3O_4$  in the composite microspheres and an increased proportion of PI. Therefore, the color of the suspensions gradually changes to the color of pure PI resins, particularly true in the case of  $PI@Fe_3O_4-4$ .

#### 3.3 Thermal stabilities and magnetic properties

Thermogravimetric analysis (TGA) measurements were carried out with Fe<sub>3</sub>O<sub>4</sub> microspheres and PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres in air. The corresponding TGA curves are shown in Figure 6. Due to the oxidization of magnetite in air, the material weight increases accordingly between 230 and 300 °C in the curve of pure Fe<sub>3</sub>O<sub>4</sub>. However, this phenomenon cannot be observed in the case of PI@Fe3O4 composite microspheres, indicating that the polyimide coating is able to protect the magnetite core from oxidation. However, compared to the TGA curve of pure PI, a lower decomposition temperature can be observed in the TGA curve of the PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres. Presumably, this finding is due to a catalytic-decomposition reaction of the magnetite core with PI. However, all sample decomposition temperatures are found to be above 300 °C, demonstrating that PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres exhibit excellent thermal stabilities compared to other polymer matrices coated on Fe<sub>3</sub>O<sub>4</sub>.<sup>45</sup>Moreover, the decomposition temperatures increase with raising the PI content. The weight percentage quality is not decreased exceeding 600 °C in air, indicating that PI completely decomposed at or around 600 °C. The weight loss of  $PI@Fe_3O_4-1$ ,  $PI@Fe_3O_4-2$ ,  $PI@Fe_3O_4-3$  and PI@Fe<sub>3</sub>O<sub>4</sub>-4 is found to be 20.05 wt.%, 39.52 wt.%, 72.00 wt.% and 81.40 wt.%, respectively. This indicates that the mass fraction of magnetic particles in the composite microspheres is 79.95 wt%, 60.48 wt.%, 38.00 wt.%, 18.60 wt.%, respectively. Hence, a linear relationship with the percentage of the added FeCl<sub>3</sub> 6H<sub>2</sub>O glycol solution can be determined.





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Figure 7. VSM curves of (a) pure  $Fe_3O_4$ , (b)  $PI@Fe_3O_4-1$  composite microspheres, (c)  $PI@Fe_3O_4-2$  composite microspheres, (d)  $PI@Fe_3O_4-3$  composite microspheres and (e)  $PI@Fe_3O_4-4$  composite microspheres.



Figure 8. Photographic image of  $PI@Fe_3O_4-3$  composite microspheres before (a) and after (b) applied magnetic field.

A magnetic field was applied to a powdered sample of bare Fe<sub>3</sub>O<sub>4</sub> as well as a sample of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres and the magnetization response was studied using a vibrating sample magnetometer (VSM). The corresponding results are shown in Figure 7. It can be determined from inspection of the VSM curve that the saturation magnetization of thePI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres is lower than that of pure Fe<sub>3</sub>O<sub>4</sub> (77.71 emu/g). This phenomenon can be attributed to the non-magnetic polyimide coated on the Fe<sub>3</sub>O<sub>4</sub> surface as well as the incomplete crystallization caused by the polyimide permeated throughout the crystals. The saturation magnetization decreases gradually, increasing the polyimide content, with a saturation magnetization of PI@Fe<sub>3</sub>O<sub>4</sub>-1, PI@Fe<sub>3</sub>O<sub>4</sub>-2, PI@Fe<sub>3</sub>O<sub>4</sub>-3 and PI@Fe<sub>3</sub>O<sub>4</sub>-4 determined to be 47.29 emu/g, 34.72 emu/g, 24.98 emu/g and 11.93 emu/g, respectively. Although the presence of polyimide reduces the magnetic properties of the samples to a certain extent, Fe<sub>3</sub>O<sub>4</sub> coated with PI improves the overall stability, due to the formation of a high-performance polymer shell with excellent thermal stability and superior chemical resistance. The coercivity of PI/Fe<sub>3</sub>O<sub>4</sub>composite microspheres decreases compared to the coercivity exhibited by pure Fe<sub>3</sub>O<sub>4</sub>. The magnetic properties of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres can be manipulated using a simple permanent magnet. A sample was dispersed in distilled water and the appearance of a PI@Fe<sub>3</sub>O<sub>4</sub>-3 composite microsphere solution before (vial a) and after (vial b) a magnetic field was applied is shown in the images depicted in Figure 8.

#### 3.4 Adsorption of Cu(II)

In order to determine the copper(II) ion concentration in solution before and after adsorption, atomic emission spectrometry was used. The adsorption capacity was calculated by using an equation previously discussed in the literature.<sup>46</sup> The results obtained are listed in Table 2. It can be determined that the adsorption capacity of the composite microspheres PI@Fe<sub>3</sub>O<sub>4</sub>-1 and PI@Fe<sub>3</sub>O<sub>4</sub>-4 is very similar. The adsorption capacity of the composite microspheres was found to be 5.81 mg/g and 5.26 mg/g lower than that of pure Fe<sub>3</sub>O<sub>4</sub> microspheres (i.e. 10.56 mg/g). The latter finding may be due to a specific surface area decrease upon increasing the particle size of the polyimide coated composite microspheres. However, after hydrolysis, the composite microspheres PI@Fe<sub>3</sub>O<sub>4</sub>-1H and PI@Fe<sub>3</sub>O<sub>4</sub>-4H exhibit a higher adsorption capacity of 24.63 and 24.44 mg/g, respectively. A possible underlying mechanism of this observation is the formation of potassium carboxylates on the surface of the composite microspheres. After placing the microspheres in a solution containing Cu(II) ions, the K(I) ions and Cu(II) ions exchange, so that the Cu(II) ions can be adsorbed onto the surface of the microspheres in a more facile method. This presumed process is illustrated in Scheme 2.



Scheme 2. Cu(II)-adsorption using ion exchange.

#### Conclusions

In this paper, we present a facile one-step solvothermal method for the preparation of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres from Fe(III) ions and PAAS. Compared to other methods for the production of polymer-Fe<sub>3</sub>O<sub>4</sub> composite microspheres, this process does not require the preparation Fe<sub>3</sub>O<sub>4</sub> particles beforehand. By adjusting the concentration of the PAAS solution,  $PI@Fe_3O_4$  composite microspheres with different sizes can be prepared. The saturation

magnetization of PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres was found to be decreased. However, PI coating on Fe<sub>3</sub>O<sub>4</sub> can effectively improve its stability. The adsorption capacity of Cu(II) ions can be improved by introducing K(I) ions to the composite microspheres via hydrolytic reactions.

#### Table 2. The adsorption capacity of pure Fe<sub>3</sub>O<sub>4</sub> and PI@Fe<sub>3</sub>O<sub>4</sub> composite microspheres.

Sample	Particle size	Adsorption
Fe <sub>3</sub> O <sub>4</sub>	200	10.56
PI@Fe <sub>3</sub> O <sub>4</sub> -1	300	5.81
PI@Fe <sub>3</sub> O <sub>4</sub> -4	1000	5.26
PI@Fe <sub>3</sub> O <sub>4</sub> -1H	300	24.63
PI@Fe <sub>3</sub> O <sub>4</sub> -4H	1000	24.44

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