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Removal of trivalent chromium from aqueous solutions by amphiphilic core-shell poly(methyl acrylate)/silk sericin nanospheres

Summary — Well-defined, core-shell poly(methyl acrylate/silk sericin) (PMA-SS) nanospheres, ranging from 100 to 150 nm in diameter, were prepared *via* a direct graft copolymerisation of methyl acrylate (MA) with silk sericin (SS). The polymerisation was induced by a small amount of *tert*-butyl hydroperoxide (TBHP) in water at temp. 353 K. The PMA-SS core-shell nanospheres were used as adsorbent in a series of batch adsorption experiments for the removal of trivalent chromium from aqueous solutions. The experimental results showed that PMA-SS nanospheres were an effective adsorbent for trivalent chromium from aqueous solution, and the maximum amount of adsorption reached 4.876 mg Cr^{3+}/g of sorbent within the experimental range. With the increase in pH values of solutions, the adsorption increased obviously, while the addition of electrolyte had a little effect on the adsorption. The adsorption equilibrium was reached after about 3 h. The adsorption of trivalent chromium by PMA-SS nanospheres was significantly higher than that done by SS powder under the same adsorption conditions.

Key words: trivalent chromium ions, adsorption, silk sericin, poly(methyl acrylate), *tert*-butyl hydroperoxide, core-shell structure, nanospheres.

USUWANIE TRÓJWARTOŚCIOWEGO CHROMU Z ROZTWORÓW WODNYCH ZA POMOCĄ AMFIFILOWYCH NANOSFER TYPU RDZEŃ–OTOCZKA OTRZYMYWANYCH W WYNIKU KOPOLIMERYZACJI AKRYLANU METYLU Z SERYCYNĄ

Streszczenie — Metodą bezpośredniej kopolimeryzacji szczepionej akrylanu metylu (MA) na serycynie (SS) otrzymano nanosfery typu rdzeń–otoczka (PMA-SS) o średnicach zawierających się w przedziale 100—150 nm (rys. 1 i 2). Kopolimeryzację prowadzono w temp. 353 K w roztworze wodnym i inicjowano za pomocą wodoronadtlenku *tert*-butylu (TBHP). Zbadano zdolność otrzymanych nanosfer PMA-SS do adsorbowania Cr^{3+} z roztworów wodnych. Stwierdzono, że ilość zaadsorbowanego Cr^{3+} rośnie wraz ze wzrostem stężenia początkowego roztworu (C_0) osiągając wartość 4,876 mg Cr^{3+}/g sorbentu w temp. 293 K w przypadku roztworu o pH = 6,0 i C_0 = 3,5 mg Cr^{3+}/L (rys. 3). Zaobserwowano, że w badanym przedziale pH od 4,0 do 6,0 adsorpcja wyraźnie rośnie ze wzrostem pH (rys. 4). Badania wykazały także, że ilość zaadsorbowanego Cr^{3+} nieznacznie wzrasta pod wpływem dodania do roztworu niewielkiej ilości KCl jako dodatkowego elektrolitu (rys. 5). Na podstawie badań kinetyki adsorpcji określono, że równowaga jest osiągana po ok. 3 godz. Na zakończenie porównano wyniki adsorpcji Cr^{3+} za pomocą nanosfer PMA-SS z wynikami uzyskanymi w takich samych warunkach z zastosowaniem jako adsorbenta samego proszku SS i stwierdzono zdecydowanie większą efektywność adsorpcji w pierwszym przypadku.

Słowa kluczowe: trójwartościowe jony chromu, adsorpcja, serycyna, poli(akrylan metylu), nadtlenek *tert*-butylu, struktura typu rdzeń–otoczka, nanosfery.

Industrial wastewater effluents from metal-finishing and mining-metallurgical sectors often contain high levels of heavy metal concentrations and thus create serious environmental pollution hazards. Trivalent chromium is an important pollutant introduced into natural waters by various industrial wastewaters coming from plating, leather tanning, mining, steel or pigments productions, which have significant impacts on human health and other living organisms in the environment [1, 2]. Current technologies of trivalent chromium removal such as chemical precipitation and ion exchange with synthetic resins, not only entail operational costs but also create sludge disposal problems [3]. These processes also fail to meet the requirements of legislation for its discharge which are from 0.1 to 3 mg/l of metal concentration [4]. However, adsorption can provide a new, less expensive way to remove toxic heavy metals even from diluted industrial wastewaters [5]. Recently, natural materials [6, 7] that are available in large quantities, or certain waste products [8, 9] from industrial or agricultural operations catch much more attention, due to their low

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cost [10, 11]. These materials can serve as effective adsorbents after being modified a little.

Silk sericin (SS) is a family of natural macromolecular proteins derived from silkworm *Bombyx mori*, and comprises 20—30 wt. % of silk [12]. Most of SS must be removed during raw silk production at the reeling mill and other stages of silk processing, and is included in silk processing wastewater. However, the unique properties of SS, such as high hydrophilicity and affinity to skin and hair, biocompatibility, and antioxidant activity, have recently attracted much attention [13]. Considering the economics and environmental protection, recovery of SS from silk industrial wastewater will be important. SS contains a lot of polar groups, including hydroxyl, carbonyl, carboxyl and amino ones, and these groups can react with heavy metal ions to form stable complexes within a certain range of pH values, which is the chemical basis of SS to be used as adsorbent for heavy metal ions. Additionally, the wastewaters containing SS were treated expensively; meanwhile the cost of SS recovery is low by freezing-thawing methods. Therefore, SS can be a potential and cheap adsorbent for heavy metal ions. However, SS has some drawbacks, such as instability in water, tendency to being invaded by microbes, poor mechanical properties, etc. which limits its using as adsorbent directly. Modification of SS by graft copolymerisation can improve those unfavourable factors.

In our previous works [14] well-defined core-shell poly(methyl acrylate)/silk sericin (PMA-SS) nanospheres were prepared *via* a direct graft copolymerisation of methyl acrylate (MA) with silk sericin (SS) initiated by a small amount of *tert*-butyl hydroperoxide (TBHP), in water at 80 °C. In this study, the removal of trivalent chromium from aqueous solutions by the PMA-SS nanospheres was investigated. The effects of initial Cr^{3+} concentrations, pH and addition of electrolyte on the adsorption performance were studied in detail. Additionally, dynamic study of adsorption was carried out, and the comparison of adsorption behavior of PMA-SS nanospheres and SS powder towards trivalent chromium was also carried out. PMA-SS nanospheres will be a potential and cheap adsorbent for removal of trivalent chromium from aqueous solutions.

EXPERIMENTAL

Materials

Silk sericin purchased from Huzhou Atesi Biochemical Co. (Huzhou, China), was used without further purification.

Methyl acrylate, obtained from Chengdu Kelong Chemical Co. (Chengdu, China), was of analytical grade, and was distilled before use.

Tert-butyl hydroperoxide (70 % solution in water) was used as received from Lancaster Synthesis Ltd (Lancaster, England).

Freshly deionized water was used as the dispersion medium.

$CrCl_3 \cdot 6H_2O$, obtained from Chongqing Jiulong Chemical Agent Factory was of analytical grade.

Other chemicals were of analytical grade and used without further purification, and twice deionized water was used in all batch adsorption experiments.

Preparation of PMA/SS core-shell nanospheres

The PMA/SS nanoshperes with core-shell structures were prepared according to our method described previously [14]. For a total of 100 mL of solution, SS (1.0 g) and sodium carbonate (0.4 g) were first dissolved in water at 323 K and then mixed with purified MA monomer (4.0 g) in a four-necked flask equipped with a thermometer, condenser, stirrer, and nitrogen inlet. The stirred mixture was purged with nitrogen for 30 min at temp. 353 K. The appropriate concentration of TBHP solution was then added, and the mixture was allowed to react for 2 h under nitrogen. The MA conversion was then determined gravimetrically. The nanospheres were purified using a dialysis membrane and dialyzed against 1L of twice deionized water, which was changed each 12 h for 72 h at room temperature to remove the water-soluble impurities.

Method of characterization of nanospheres

Transmission electron microscopy (TEM) images of PMA-SS core-shell nanospheres were obtained using a JEM 100 CX transmission microscope at an accelerating voltage of 100 kV. The samples were prepared by wetting a carbon-coated grid with a small drop of the dilute latex solution. Upon drying, it was stained with a small drop of 2 % phosphotungstic acid (PTA) for 30 min and dried at room temperature before analysis. The particle size and its distribution of PMA-SS core-shell nanospheres were measured using a MASTERSIZER 2000 particle size analyzer with poly(vinyl alcohol) standard sample. Separation operation was carried out by Anke TDL-40B. The pH was measured with a Beckman model 71 pH-meter.

Adsorption experiment

Batch adsorption experiments were carried out in 50 mL flasks, contained 10 mL of chromium solution prepared from $CrCl_3 \cdot 6H_2O$. A specified amount of amphiphilic PMA-SS nanospheres (0.1 g of dry substance) was added into a flask, and the total volume of solution was 20 mL. The contents of the flask was stirred using a thermostatic magnetic stirrer at 293 K and 120 rpm for 6 h (well above the adsorption equilibrium time of about 3 h). After 6 h the amphiphilic PMA-SS nanospheres in the flask were precipitated by adjusting the pH value of the contents with 6 N HCl, and were immediately centrifuged at 3000 rpm using a centrifuge Anke TDL-40B, China. Subsequently, the upper filtrate was analysed for final chromium concentration using UV spectrophotometer. Further studies on chromium removal were carried out using the constant amount of adsorbent equal to 0.1 g. The initial concentration of trivalent chromium ranged from 15 mg/L to 35 mg/L. The pH of the contents varied from 4.0 to 6.0 for the initial concentration 25 mg/L of trivalent chromium. The contact time in batch varied from 30 to 360 min. Additionally, the effect of electrolyte (KCl) on adsorption equilibrium was studied, and KCl concentration in the adsorption system was 0.005 mol/L.

Determination of Chromium

The chromium concentration, before and after being adsorbed by PMA-SS nanospheres, was determined by UV-VIS spectrophotometric method. Trivalent chromium concentrations were determined colorimetrically using 4-(2-pyridylazo)-resorcinol (PAR) and triethanolamine (TEA) in the presence of cetyltrimethylammonium bromide (CTMAB) to form red colored complexes [15]. The detailed operation was carried out as follows. First the certain sample and 5.0 mL of buffering solution of pH = 7.2, 5.0 mL of $5.0 \cdot 10^{-4}$ mol/L solution of PAR and 1.0 mL of $2.5 \cdot 10^{-2}$ mol/L solution of CTMAB were added into a 25 mL color comparison tube, and then shaked it to make these solutions mixed enough. Then the color comparison tube was heated for about 20 min in boiling water bath. After the mixture in the tube was cooled, 2.0 mL of $1.0 \cdot 10^{-2}$ mol/L solution of EDTA was added. Finally the solution in the color comparison tube was diluted to a constant volume. The absorbance of the colorful complexes was measured in a double beam spectrophotometer (Hitosho UV-1010 spectrophotometer), at a wavelength of 540 nm, and chromium concentration of tested samples was determined using a calibration curve prepared by measurements for standard solutions of concentrations of trivalent chromium from 0.08 to 0.8 mg/L. Runs were triplicated. The specific uptake by the sorbent (q in mg/g of dry sorbent) was calculated using the following equation:

$$q = \frac{V(C_0 - C_1)}{W} \tag{1}$$

where: C_0, C_1 — *initial and final metal concentrations, respectively, V — solution volume, W — amount of dry adsorbent used.*

Additionally, q_e can be defined as the equilibrium uptake of the sorbent.

RESULTS AND DISCUSSION

Characteristic of PMA-SS core-shell nanospheres

PMA-SS nanospheres with core-shell structure were prepared *via* a direct graft copolymerisation of methyl acrylate (MA) and silk sericin (SS), initiated by a small amount of TBHP. The TEM images of PMA-SS nanospheres, as illustrated in Figure 1, showed a well-defined core-shell morphology, where the PMA cores were coated with SS shells. The diameters of PMA-SS nanospheres were about 100—150 nm.

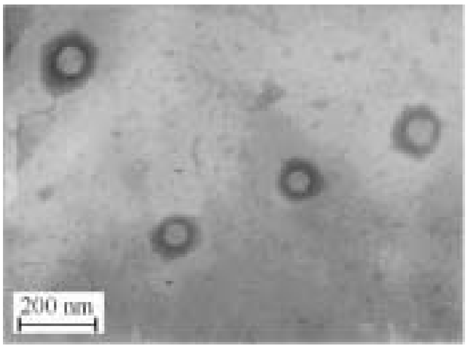

Fig. 1. TEM micrographs of PMA-SS particles treated with 2 % phosphotungstic acid

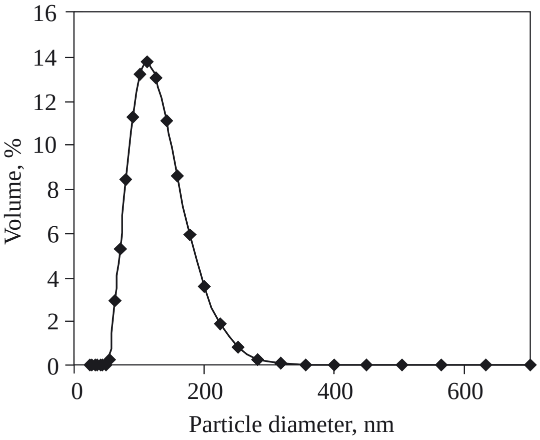

Fig. 2. Size dispersion of PMA-SS nanospheres

Figure 2 shows the size dispersion of PMA-SS nanoshperes. The average diameter of particles in volume was 115 nm in addition to narrow distribution, which was basically in agreement with the results of TEM.

SS shells of PMA-SS nanoshperes contain a lot of polar groups including hydroxyl, carboxyl, amino and carbonyl ones, which can react with many heavy metal ions to form stable complexes [16—18]. Moreover, SS used as the main material for preparation of PMA-SS nanospheres, is a kind of reproducible bioresources with low recovery cost. Therefore PMA-SS nanospheres are potential novel and cheap adsorbent for the removal of heavy metals from aqueous solutions. Such measures will be significant for both natural bioresources savings and environment protection.

Effect of initial trivalent chromium concentration on adsorption performance

Figure 3 shows the results of measurements of adsorption of the trivalent chromium at pH = 6.0 and temp. 293 K dependent on initial concentration of solutions. It can be seen from figure that the adsorption performance

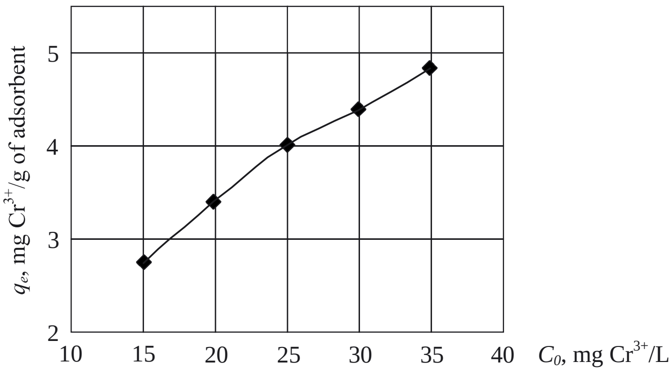

Fig. 3. Effect of Cr^{3+} initial concentrations on adsorption equilibrium of Cr^{3+} ions from aqueous solutions at pH = 6.0 and temp. 293 K

improved with the initial metal loadings of the trivalent chromium species into the adsorption system. The maximum adsorption reached 4.876 mg Cr^{3+}/g of sorbent, which is a little higher than that of an effective adsorbent for trivalent chromium described in [19], which was a *aqave lechugnilla* biomass.

Effect of pH on adsorption equilibrium

The value of adsorption of chromium strongly depends on pH of solution. The results of adsorption obtained for the solutions with pH values from 4.0 to 6.0 (further pH increase was not realized due to the possibility of precipitation close to pH 7 and above) at temp. 293 K are shown in Figure 4. It can be seen that the adsorption of trivalent chromium species increased with the increase in solution pH values. The maximum adsorption value was 4.008 mg Cr^{3+}/g of adsorbent. This effect of pH may be ascribed to existence form of Cr^{3+} and charge property covered with the surface of PMA-SS nanospheres [2]. The Cr (III) species in aqueous solution may take the forms of Cr^{3+}, Cr(OH)$^{2+}$, or Cr(OH)$_2^+$, depending on the solution pH values. As these species normally carry positive electric charges, they are relatively easy to be adsorbed on the negatively charged surface of adsorbents. PMA-SS nanospheres are amphiphilic, and theirs isoelectric point is at pH = 3.4. For pH < 3.4, the surface of PMA-SS nanospheres mainly exhibited positive charges, what is unfavorable to the adsorption of metal ions with positive charges. For pH > 3.4, the charges on the surface of PMA-SS nanospheres are mainly negative, what is advantageous for the adsorption of metal ions with positive charges. Raising the pH values in the adsorption system increases the negative charges on the surface of amphiphilic PMA-SS nanospheres, which leads to increasing adsorption of trivalent chromium on PMA-SS nanospheres. Considering the two above aspects, the optimum pH value of adsorption system is 6.0, and it is different from the other adsorption systems for the trivalent chromium [20, 21].

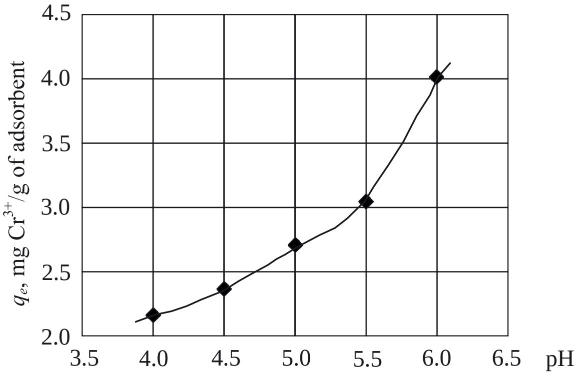

Fig. 4. Effect of pH on adsorption equilibrium of Cr^{3+} ions from aqueous solutions at C_0 = 25 mg Cr^{3+}/L and temp. 293 K

Effect of KCl in solution on adsorption equilibrium

The effect of additional electrolyte (KCl) on adsorption equilibrium was also investigated. The experimental results presented in Figure 5 suggested that the adsorption increased a little with the addition of KCl in concentration of 0.005 mol/L. This may be ascribed to the raised activity of trivalent chromium, due to the increase in ion strength in adsorption system caused by the addition of KCl, which leads to the increase in adsorption value [22].

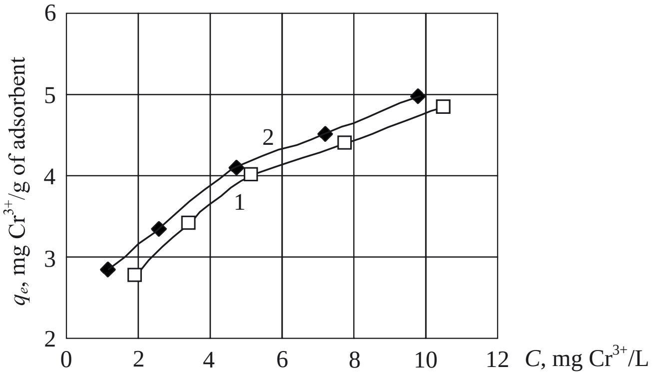

Fig. 5. Effect of the addition of KCl on adsorption equilibrium of Cr^{3+} ions from aqueous solutions at pH = 6.0 and temp. 293 K: 1 — without KCl, 2 — with KCl concentration 0.005 mol/L in solution

Adsorption kinetics

Figure 6 shows the results of adsorption dynamics of Cr^{3+} ions on PMA-SS nanospheres at an adsorption system at pH = 6.0. It is observed that the adsorption velocity was very high firstly, and above 45 min the adsorption velocity was low. Furthermore, the adsorption equilibrium values were reached only about 3 h, which shows the facile adsorption of trivalent chromium on PMA-SS nanospheres. Adsorption process is generally known to be controlled by the transport of the species to be ad-

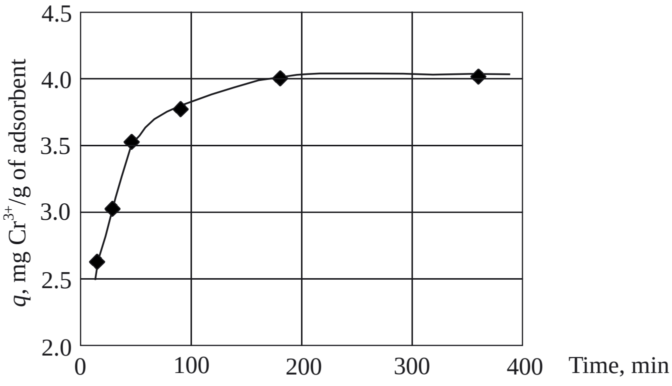

Fig. 6. Dynamic curve of adsorption of Cr^{3+} ions on PMA-SS nanospheres from the solutions with initial concentration C_0 = 25 mg Cr^{3+}/L and pH = 6.0 at temp. 293 K

sorbed from the solution to the surface of the adsorbent, and then the attachment of the transported species on the surface of the adsorbent [2]. Due to PMA-SS nanospheres' large surface, a lot of polar groups in SS, located at the shell of PMA-SS nanospheres, were exposed in solution, which make the chromium ions adsorbed quickly by PMA-SS nanospheres. As the adsorption proceeds, the adsorption velocity got slow due to the electrostatic repulsion among adsorbed chromium ions on the adsorbent and free chromium ions around the adsorbent. Additionally, the amount of chromium ions in solution reduced, which leads to the low adsorption velocity.

Comparison of adsorption properties of PMA-SS and SS

Additionally, the comparison of adsorption properties was carried out between SS powder and PMA-SS nanospheres for trivalent chromium at the same conditions (C_0 = 25 mg Cr^{3+}/L, pH = 6.0, 293 K). The results showed that the remained chromium concentrations after using SS powder as adsorbent were significantly higher than those after using PMA-SS nanospheres as adsorbent. The adsorption values obtained for SS and PMA-SS nanospheres are 2.640 mg Cr^{3+}/g of adsorbent and 4.008 mg Cr^{3+}/g of adsorbent, respectively. This can be explained by the larger surface of PMA-SS nanospheres compared with SS powder. Therefore polar groups of SS, located at the shell of PMA-SS nanospheres, have a lot of chances to contact with trivalent chromium in solution, which results in the high adsorption at PMA-SS nanospheres.

CONCLUSIONS

Amphiphilic core-shell PMA-SS nanoshperes were prepared by graft copolymerisation of methyl acrylate and silk sericin using *tert*-butyl hydroperoxide as initiator. The diameter of PMA-SS nanospheres ranged from 100 to 150 nm, and their average size was 115 nm with narrow distribution. The PMA-SS nanospheres were found to be effective in the adsorption of trivalent chromium from aqueous solutions, and the maximum adsorption observed was 4.876 mg Cr^{3+}/g of adsorbent. The adsorption equilibrium can be reached after about 3 h. With the increase in pH values, the adsorption increased obviously. The addition of KCl had a little effect on the adsorption equilibrium. Furthermore, the values of adsorption obtained with using PMA-SS nanospheres were significantly higher that with SS powder use. The PMA-SS nanospheres are considered to have potential applications in wastewater treatment for the removal of heavy metal ions such as trivalent chromium species.

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