Removal of anionic contaminants by surfactant modified powdered activated carbon (SM-PAC) combined with ultrafiltration

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ABSTRACT

A variety of inorganic contaminants may form toxic oxyanions in aqueous systems which pose significant hazard to human health and the ecosystem. In order to remove the oxyanions from aqueous stream effectively, surfactant-modified powdered activated carbon (SM-PAC) combined with ultrafiltration (UF) was proposed in this study. As the cationic surfactant, cetylpyridinium chloride (CPC), adsorbs on the surface of PAC, the zeta potential of PAC increases to +40 mV. Oxyanions such as chromate, ferricyanide and arsenate bind on SM-PAC by electrostatic interaction, then the contaminants bound with SM-PAC can be separated by UF membrane. 0.3 mM of chromate and ferricyanide are removed completely with 4.0 g/L of SM-PAC. In case of arsenate, the removal efficiency was lower than chromate and ferricyanide. It is considered that the competition occurs among anionic pollutants on the limited binding sites of SM-PAC and lower valence of arsenate results in the lower removal efficiency. High permeate flux is maintained during filtration. The spent SM-PAC was regenerated by the concentrated Cl⁻ solutions. NaCl solution whose molar Cl⁻ concentration is 1.4 times higher than the contaminants bound on SM-PAC was optimal for the regeneration. Regenerated SM-PAC exhibited similar adsorption capacity to fresh SM-PAC. SM-PAC combined with UF can effectively remove anionic contaminants. Moreover, the simple and efficient regeneration process is proposed.

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1. Introduction

Hazardous inorganic contaminants such as arsenate ($H_2AsO_4^-$), perchlorate (ClO_4^-), chromate (CrO_4^{2-}) and bromate (BrO_3^-) in aqueous stream seriously threaten human health and ecosystem. Ion exchange (IX) is one of the most attractive methods for the removal of ionic pollutants [1–4]. However, IX resin is relatively expensive and it is not effective on the organic contaminants which are frequently present in aqueous stream. Studies on the alternative materials of IX resin have been carried out extensively [5–7]. Cao modified fly ash with a cationic polyelectrolyte, polydimethydially-lammonium chloride (PDMDAAC) and the modified fly ash removed anionic dye by electrostatic interaction [8]. Mohd Yusof removed the Cr(VI) and As(V) using the cationic surfactant-modified zeolite [9].

Because activated carbon (AC) has been implemented in most water and wastewater treatment processes, modification of AC and its application to the removal of ionic pollutants has been widely studied. Thermal treatment enlarges the specific surface area of AC and acidic treatment activates the functional groups of AC. Basic treatment enhances the adsorption of phenolic compounds [10]. Also adsorptive capacity of AC on hazardous substances can be substantially boosted by impregnation with suitable chemicals such as metal and surfactant. Surfactant can enhance the ion exchange property of AC. Basar removed chromate using AC modified by cetyl trimethyl ammonium bromide (CTAB) [11]. Perchlorate can also be removed by the surfactant-modified AC [12]. So far, the studies on surfactant-modified AC have been mostly focused on the removal of contaminants and considerations on the actual operation process are still insufficient.

In this study, surfactant-modified powdered activated carbon (SM-PAC) combined with ultrafitration (UF) was proposed for the removal of ionic contaminants. PAC modified with cationic surfactant exhibits positive surface charge and anionic compounds can bind on it by electrostatic interaction or ion exchange. The contaminants bound on SM-PAC can be separated from aqueous phase by UF membrane. Series operation of removal and regeneration of SM-PAC was designed and optimal regeneration condition was determined. Specific objectives of this study are as

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follows:

1. To synthesize and characterize SM-PAC.
2. To develop UF process combined with SM-PAC to remove inorganic pollutants from water.
3. To investigate optimal regeneration condition of spent SM-PAC in the hybrid UF process.

2. Experiment

2.1. Materials

Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), sodium chromate (Na_2CrO_4) and potassium ferricyanide ($K_3Fe(CN)_6$) were used as anionic contaminants. Each compound ionizes to mono-, di- and tri-valent ion, respectively, in aqueous phase. PAC (Darco G-60) was modified by the cationic surfactant, ceptylpyridinium chloride (CPC). Critical micelle concentration (CMC) of CPC was 0.9 mM at 25 °C [13]. All chemicals were purchased from Sigma–aldrich, USA. Experiments were conducted in dead-end UF cell (Millipore) and volume of UF is 350 mL. The molecular weight cut-off (MWCO) of UF membrane (Amicon) was 500,000 Da.

2.2. Synthesis of SM-PAC

2 g/L of PAC was mixed with 10 mM of CPC solution for 12 h at 25 °C. The modified PAC was recovered by centrifugation at 15,000 rpm for 30 min. Supernatant (CPC solution) was reused for the modification of fresh PAC. The prepared SM-PAC was thoroughly washed with distilled water in order to get rid of unbound CPC molecules.

2.3. Series operation of removal–regeneration

4 g/L of SM-PAC was used to remove anionic contaminants. Arsenate ($H_2AsO_4^-$), chromate (CrO_4^{2-}) and ferricyanide ($Fe(CN)_6^{3-}$) were mixed in solution and concentration of each pollutant was 0.3 mM. 300 mL of contaminated water was mixed with SM-PAC and filtered through UF membrane at 1 bar. HCl and NaCl were tested for the regeneration of spent SM-PAC. To find the optimum ratio of regenerant to SM-PAC, various concentrations (1 and 5 M) and the different volume (300, 200 mL) of regenerant was applied to the spent SM-PAC. Regenerant was mixed with spent SM-PAC for 12 h. Fig. 1 illustrates the series operation of removal–regeneration process.

2.4. Analytical methods

Zeta potential of the suspended SM-PAC solution (2 g/L) was measured by zeta potential analyzer (Brookhavern Instrument, USA). Concentrations of chromate and ferricyanide were analyzed by UV–vis spectrometer (Hewlett Packard 8452A, USA) as described [14]. Arsenate concentration was determined by either inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer Elan 6000) or inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3300DV). Detection limit of As on ICP-MS was 100 ng/L. Because concentration of cationic surfactant in aqueous phase was negligible, pretreatment was not necessary for the sample analysis. Removal efficiency of contaminants and regeneration efficiency of adsorbent can be determined by the following equations, respectively.

$$Removal \ (\%) = \left(1 - \frac{C_{final}}{C_{initial}} \right) \times 100$$

$$Regeneration \ (\%) = \frac{Q_{release}}{Q_{adsorb}} \times 100$$

where C_{final} and $C_{initial}$ indicate the final and initial concentration, respectively. Q_{adsorb} and $Q_{release}$ denote adsorbed and released mass of contaminant after regeneration (mmol/g), respectively. Also permeate flux, J, can be calculated as the following:

$$J \ (L \, m^2 \, h) = \frac{V_p}{A \times t}$$

where V_p indicates volume of permeate (L) and A denotes effective membrane area (m^2) and t is time (s or h). Permeate flux is expressed with volume reduction of retentate which is defined as the volume ratio of feed (V_{feed}) to retentate ($V_{retentate}$).

3. Results and discussions

3.1. Characteristics of SM-PAC

Sorbed amount of CPC strongly affects the adsorption capacity of SM-PAC. The major driving force of adsorption is hydrophobic interaction between hydrocarbon chain of CPC and PAC. Fig. 2 shows the adsorption isotherm of CPC on PAC. The adsorbed amount of CPC increased rapidly and reached to the first plateau (~0.9 mmol/g) at ca. 0.06 mM of equilibrium CPC concentration. At higher equilibrium CPC concentration (0.4 mM), the sorbed amount of CPC increased again. It reveals that two different driving forces exert on the adsorption of CPC [15]. Interaction between adsorbate and adsorbent occurs at first. When the surface of PAC is completely covered by surfactant molecules, adsorption isotherm may reach to plateau. Then, adsorbate–adsorbate interaction between CPC molecules occurs predominantly. CPC molecule in liquid phase interacts with already adsorbed surfactant and forms surfactant double layer or hemi-micelles on the surface of PAC. It results in another increase in the adsorbed amount of CPC and the second plateau value.

Fig. 3 shows zeta potential changes of PAC with the adsorbed amount of CPC. Virgin PAC indicates slightly negative charge
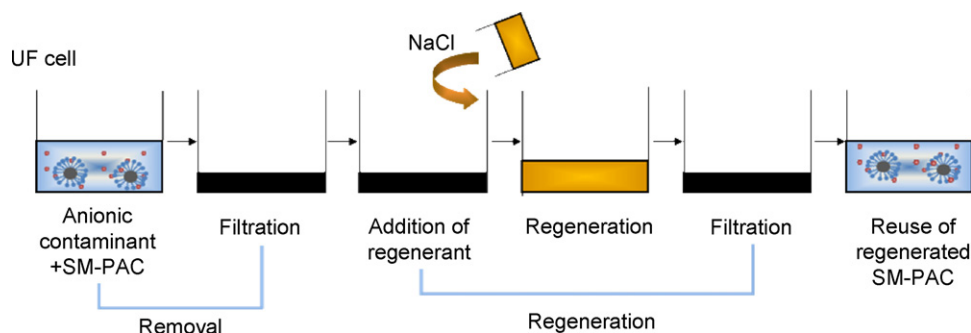

Fig. 1. Schematic diagram of series operation of SM-PAC combined with UF for removal and regeneration.
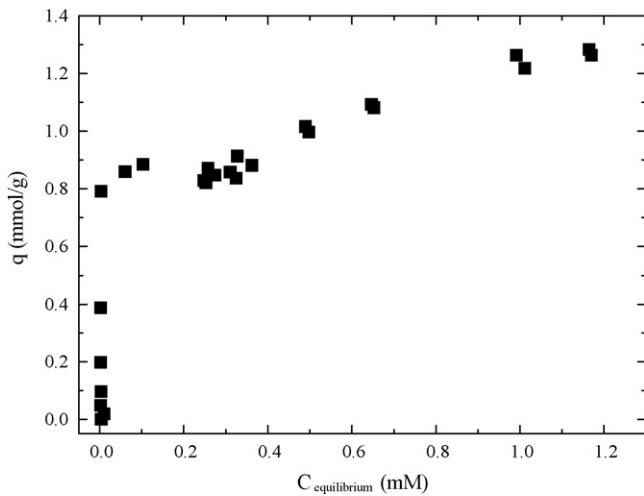
Fig. 2. Adsorption isotherm of CPC on PAC (25 °C).

(−40 mV) in water due to acidic functional groups such as quinone and hydroquinone [10]. As surfactant adsorbs on the surface of PAC, zeta potential increases to positive potential. Finally, +40 mV of zeta potential is obtained as 1.2 mmol/g of CPC is adsorbed on PAC. The positive zeta potential enables SM-PAC to bind with anionic pollutants. It is consistent with literatures. For example, Basar and his coworkers reported that zeta potential of AC increased proportionally with adsorbed CTAB [16].

Because PAC has large surface area (987 m²/g), significant amount of CPC can be adsorbed on PAC. Maximum adsorbed amount of CPC was approximately 1.2 mmol/g after 12 h reaction.

3.2. Removal of ionic pollutant by UF process combined with SM-PAC

Fig. 4 shows removal efficiencies of arsenate, chromate and ferricyanide using SM-PAC combined with UF. Removal efficiencies of all pollutants are proportional to the dose of SM-PAC. With UF only, the removal efficiencies were just 20% for all contaminants. The introduction of SM-PAC in UF significantly enhanced the removal efficiencies. 4 g/L of SM-PAC removed chromate and ferricyanide by ca. 95%. However, the removal efficiency of arsenate was lower than that of chromate or ferricyanide. At neutral pH, arsenate exists as mono-valent ion ($H_2AsO_4^-$) while chromate and ferricyanide form
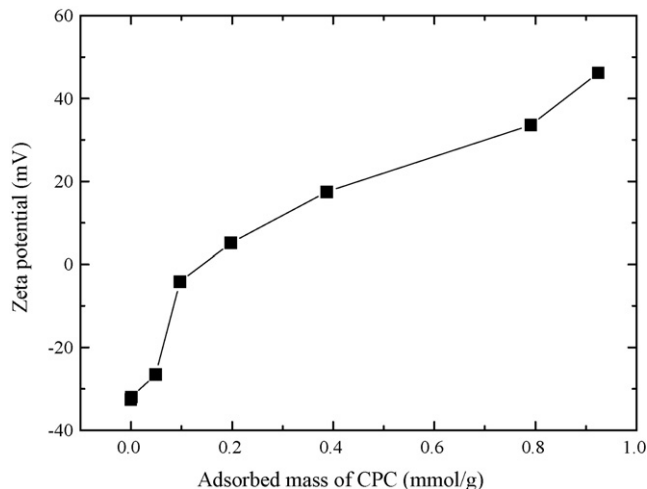

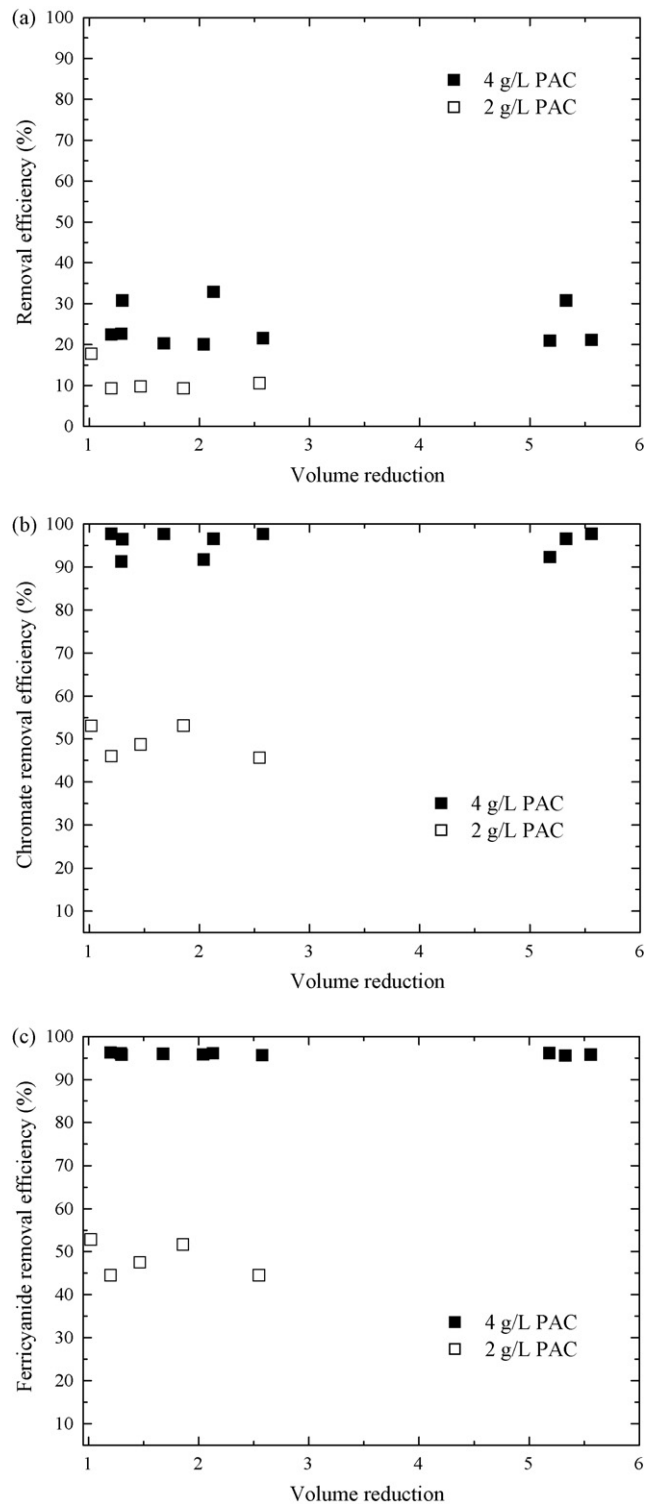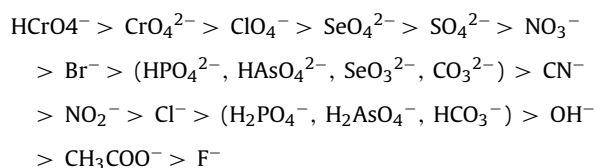**Fig. 3.** Zeta potential change of PAC with the sorbed amount of CPC.

Fig. 4. Removal efficiency of arsenate (a), chromate (b) and ferricyanide (c) by SM-PAC combined with UF.

divalent (CrO_4^{2-}) and trivalent ion ($Fe(CN)_6^{3-}$), respectively. Higher valence anion has stronger electrostatic attraction to SM-PAC and the adsorption of arsenate was restricted in the competition with other higher valent anions.

2 g/L of SM-PAC could simultaneously adsorb 3.0×10^{-2} mmol arsenate/g, 7.5×10^{-2} mmol chromate/g and 7.5×10^{-2} mmol ferricyanide/g. When SM-PAC dose was increased from 2 to 4 g/L, the adsorption of chromate and ferricyanide did not increase.

But the adsorption of arsenate was doubled (6.0×10^{-2} mmol/g). It implies that the adsorption sites in 2 g/L of SM-PAC are not enough to bind all anionic contaminants completely. Adsorption of arsenate is restricted due to its weak affinity. Higher SM-PAC dose (4 g/L) results in increase of adsorption sites and improves the adsorption of arsenate.

The functional group of SM-PAC is similar to strong base IX resin. Most of strong base IX resin has quaternary ammonium as a functional group and Cl^- as a counter ion. The affinity of anions for most strong-base IX resins is given below [17].

$HCrO4^- > CrO_4^{2-} > ClO_4^- > SeO_4^{2-} > SO_4^{2-} > NO_3^-$

$> Br^- > (HPO_4^{2-}, HAsO_4^{2-}, SeO_3^{2-}, CO_3^{2-}) > CN^-$

$> NO_2^- > Cl^- > (H_2PO_4^-, H_2AsO_4^-, HCO_3^-) > OH^-$

$> CH_3COO^- > F^-$

Strong base IX resin shows higher affinity to chromate than arsenate and it seems that the order of affinity is similar between anion exchange resin and SM-PAC in general. It was observed that chromate had higher affinity to SM-PAC than ferricyanide and the removal efficiency of arsenate was still lower than others. Those results are consistent with the affinity order of anion exchange resin.

Moreover, SM-PAC can remove organic pollutants. In batch tests, the removal efficiency of humic acid (HA) by SM-PAC was as high as that by pure PAC. In the presence of anionic pollutant, the removal of both HA and anion pollutant increased due to the complexation of them (Figs. S-1 and S-2). It is remarkable that SM-PAC can adsorb ionic pollutant as well as organic pollutant.

3.3. Flux

Fig. 5 indicates flux change of UF process with volume reduction ($V_{feed}/V_{retentate}$) during the filtration process. As filtration proceeded, the retained SM-PAC accumulated on the surface of membrane and it resulted in flux decline. After half of the solution was filtered, flux reached equilibrium. The flux decline was not severe. At 2 g/L of SM-PAC, flux declined from 3500 to 2700 L/m^2 h. Increase of SM-PAC dose from 2 to 4 g/L causes flux reduction to 2500–1600 L/m^2 h. Because operating pressure is low and the UF membrane with relatively high MWCO is applied, this process shows higher flux compared with other membrane processes such as NF, RO and MEUF (micellar enhanced ultrafiltration) [18,19]. Although both SM-PAC and UF membrane were used repeat-
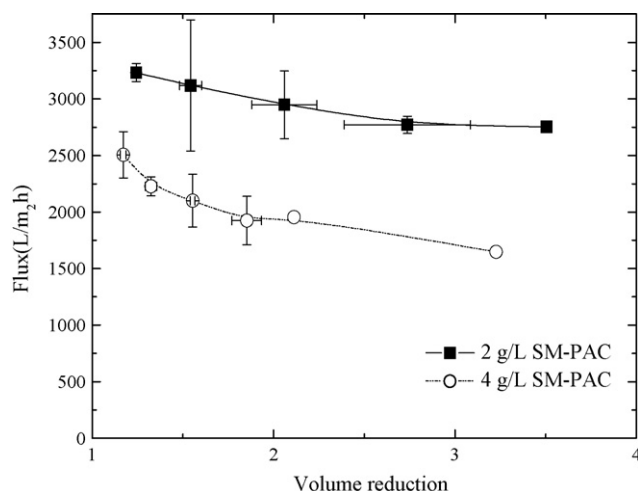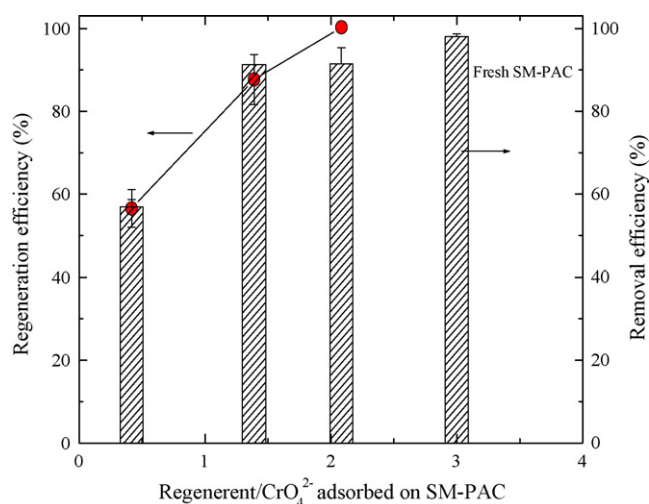

Fig. 6. Regeneration efficiency at various molar ratio of NaCl and adsorption capacity of the regenerated SM PAC at 1 mM CrO_4^{2-}.

edly after regeneration, significant flux decline was not observed throughout the experiments.

3.4. Regeneration of SM-PAC

To find out better regenerant, SM-PAC saturated with arsenate, chromate and ferricyanide was treated by 1 M NaCl or HCl solution. NaCl regenerated 60% of chromate and ferricyanide bound with SM-PAC while the efficiency of HCl was less than 40% (not shown). Different from chromate and ferricyanide, HCl resulted in higher regeneration efficiency than NaCl for the arsenate-bound SM-PAC. HCl reduces pH and arsenate ($H_2AsO_4^-$) is protonated as H_3AsO_4. As arsenate loses its negative charge, it is liberated from SM-PAC.

The effectiveness of the regeneration process was evaluated at different NaCl concentration and the regenerated SM-PAC was reused for the chromate removal (Fig. 6). Regeneration efficiency increases with NaCl concentration. When the molar ratio of Cl^- ion to the chromate adsorbed on SM-PAC was 0.4 (NaCl/CrO_4^{2-}-SM-PAC $\approx$ 0.4), regeneration efficiency was only 56.5%. The efficiency was enhanced to 87.7% at higher Cl^- concentration (NaCl/CrO_4^{2-}-SM-PAC $\approx$ 1.4). Further increase in Cl^- concentration (NaCl/CrO_4^{2-}-SM-PAC = 2.1) resulted in a complete regeneration of the chromate-saturated SM-PAC. It reveals that the equimolar amount of Cl^- is insufficient for the complete regeneration because of the high binding affinity of chromate. Although further increase of NaCl/CrO_4^{2-}-SM-PAC ratio from 1.4 to 2.1 enhanced the regeneration efficiency, it did not affect the removal efficiency of chromate in the reuse test. Both of SM-PACs, which were regenerated at NaCl/CrO_4^{2-}-SM-PAC of 1.4 and 2.1, removed chromate by 91%. Although complete regeneration can be obtained at high NaCl concentration, it may result in a higher residual NaCl concentration in retentate. The residual NaCl after regeneration may interrupt the removal of chromate.

Therefore, the optimal regeneration condition is determined as the ratio of NaCl/CrO_4^{2-}-SM-PAC to 1.4. Compared with the fresh SM-PAC, the regenerated SM-PAC has similar adsorption capacity for chromate.

The optimum regeneration condition (NaCl/CrO_4^{2-}-SM-PAC = 1.4) is applied to the spent SM-PAC which is saturated with mixed anions. Then, the SM-PAC is reused for the removal of mixed contaminants. The reuse of SM-PAC showed similar removal efficiency with fresh SM-PAC (Fig. 7). In the reuse of SM-PAC, chromate and ferricyanide are completely removed and the removal efficiency of arsenate was ca. 30%.
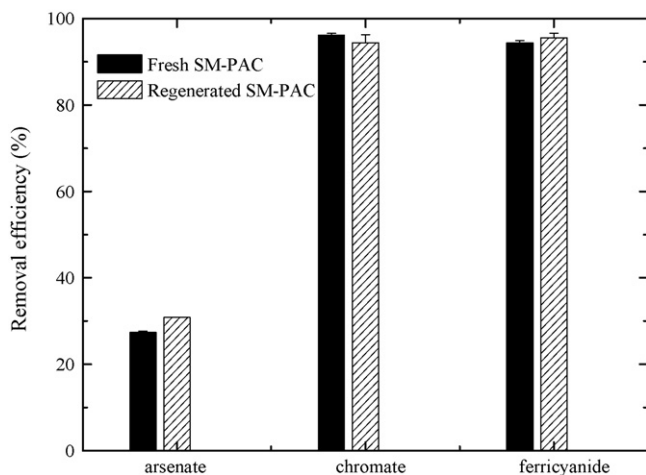

Fig. 5. Flux change with volume reduction.

Fig. 7. Removal efficiency of arsenate, chromate and ferricyanide with fresh and regenerated SM-PAC.

4. Conclusion

SM-PAC combined with UF was investigated for the removal of anionic contaminants. The adsorbed CPC increased the zeta potential of adsorbent to +40 mV. While UF was unable to remove the oxyanions – arsenate, chromate and ferricyanide, SM-PAC combined with UF showed high removal efficiencies. 4 g/L of SM-PAC can completely remove 1 mM of chromate and ferricyanide simultaneously. In case of arsenate, the removal efficiency was lower than chromate and ferricyanide. It is considered that the competition occurs among anionic pollutants on the limited binding sites of SM-PAC and the lower valence of arsenate results in lower removal efficiency. SM-PAC can remove the typical organic contaminant, humic acid and anionic pollutant simultaneously. High permeate flux is observed during filtration.

NaCl shows a better regeneration performance than HCl. Approximately 91% of regeneration efficiency was obtained when the molar ratio of NaCl to the adsorbed anionic contaminant is 1.4. The regenerated SM-PAC shows similar adsorption capacity to the fresh one. SM-PAC combined with UF can effectively remove anionic contaminants. Moreover, the simple and efficient regeneration process is proposed.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.05.108.

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