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Efficient removal of humic acid in aqueous solution using polyaniline adsorbent

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ABSTRACT

Polyaniline adsorbent prepared by chemical oxidation was developed to remove the humic acid (HA) in aqueous solution. The adsorbents showed the high adsorption capacity for aqueous HA with the maximum adsorption amount 126.58 mg g^{-1}, and the adsorption isotherm obeyed the Langmuir model. The adsorption kinetics followed an initial diffusion-controlled and then an attachment-controlled adsorption process. The HA adsorption was not much impacted in the presence of Na^+, K^+, while Ca^{2+} ion in aqueous solution can evidently enhance the HA adsorption. The HA adsorption on polyaniline decreased with increasing solution pH owing to the electrostatic interaction between imine and amine of polyaniline and disassociated HA. The HA molecules adsorbed on the polyaniline can be effectively desorbed in 0.1 M NaOH solution, and regenerated adsorbent can be repeatedly used in the subsequently adsorption–regeneration cycles.

Keywords: Polyaniline; Humic acid; Adsorption; Adsorption kinetics; Desorption; Electrostatic interaction; Water treatment

1. Introduction

Humic acid (HA) is one of major constituents of dissolved organic matter in natural water which is derived from soil humus and plants [1]. The presence of HA may pose several severe problems in drinking water production. For example, HA has been found to react with chlorine to form carcinogenic disinfection byproducts (e.g., trichloromethanes, haloaceticacids) [2]. Recent research showed that HA can cause membrane fouling during the filtration processes in drinking water treatment [3,4]. Therefore, it is desirable to remove HA in drinking water resources.

Due to its simplicity and high efficiency, adsorption is considered as the most practical approach for the removal of HA in natural water. Various adsorbents such as activated carbon [5–8], metal oxides [9–10], resins [11–12] and amino adsorbents have been developed to remove the aqueous HA [13–15]. Among them, amino-adsorbents have been found to have a strong affinity for aqueous HA owing to the strong interaction between the carboxyl and phenolic groups of HA molecules and the protonated amino groups of adsorbent [13–15]. For example, the aminopropyl functionalized mesoporous silica showed the high adsorption capacity for aqueous HA due to the electrostatic and hydrogen bonding interaction between surface aminopropyl groups and HA molecule [13]. Aminated polyacrylonitrile fibers prepared by surface modification were found to be very effective in removing aqueous HA [15]. The polypyrrole adsorbents with a high zero point of zeta potential were reported to be efficient for the removal of aqueous HA [16]. Chitosan hydrogel beads [17], chitosan coated polyethyleneterephthalate granules [18],

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the composite of chitosan and activated clay [19], and crosslinked chitosan epichlorohydrin beads [20] demonstrated high efficiencies to remove HA in aqueous solutions by the formation of organic complex between the protonated amino groups and HA. Amine-modified polyacrylamide–bentonite composite was found to be significantly effective for the removal of HA in aqueous solutions [21].

As a conducting polymer, polyaniline with controllable conductivity, excellent environmental stability, low cost and easy synthesis, has received great attention in many fields such as anticorrosion coating, charge storage systems and controlled drug delivery [22,23]. In recent years, polyaniline and its composites were developed to eliminate the inorganic and organic pollutants in wastewater because of its large amount of amine and imine nitrogens which can interact with heavy metals and organic pollutants [24]. For example, polyaniline and its composites have been found to efficiently remove heavy metals such as mercury [25], chromium [26], and arsenate [27] in aqueous solution. Fluoride in aqueous solution can also be eliminated by polyaniline adsorbent via doping [28]. Polyaniline modified mesoporous carbon (CMK-1) showed the significant adsorption efficiency for phenolic compounds such as phenol, resorcinol and *p*-cresol [29]. Polyaniline emeraldine salt synthesized by chemical oxidation was explored to be effective in removing the aqueous sulfonated dyes [30]. To our best knowledge, however, no studies have been found to remove the HA from aqueous solution by polyaniline and its composites.

In this study, polyaniline was synthesized by chemical oxidation and characterized by IR spectra. Adsorption and desorption behavior of HA over polyaniline was evaluated by batch experiments, and the effect of solution chemistry properties such as solution pH and ionic strength were also discussed.

2. Materials and methods

2.1. Materials

HA of ACS reagent grade was purchased from Aldrich Chemical Co. All other reagents of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2. Preparation of adsorbent

Polyaniline was prepared by the chemical oxidation according to the procedure described by Shimano et al. [31]. Typically, 0.11 mmol of aniline was dissolved in 300 ml of 1 M HCl and cooled to 273–277 K. Then, 0.11 mmol of ammonium peroxodisulphate dissolved in 200 ml of 1.0 M HCl pre-cooled to 273–277 K was added to the above mixture under continuous stirring in an ice bath. After reaction for 2 h under N_2 protection, the dark-green precipitate was filtered and washed with copious deionized water until the filtrate became colorless. The resulting material was dried in a desiccator and referred to as PANI.

2.3. Characterization of material

Fourier transform-infrared (FT-IR) spectra was recorded in a Nicolet 5700 FT-IR spectrometer at 2 cm^{-1} resolution. The BET surface area was calculated from N_2 adsorption–desorption isotherms collected on a Micromeritics ASAP 2200 instrument. TEM observation was performed on a Hitachi H-800 transmission electron. The surface zeta potential of PANI was measured using a Zeta Potential Analyzer (Zeta PALS, Brookhaven Instruments Co., USA). Briefly, 0.04 g of nanoparticles were dispersed in 400 ml of 1 mmol l^{-1} NaCl solution and sonicated for 10 min. The desired pH values of the dispersion were adjusted with 0.1 mol l^{-1} HCl or NaOH. The dispersion was then settled for 24 h and the supernatant was used for zeta potential measurement.

2.4. Adsorption studies

The preliminary tests showed that the adsorption of HA on PANI adsorbent could reach equilibrium within 24 h under our tested experimental conditions. Therefore, the adsorption equilibrium time was 24 h for all adsorption experiments. Specifically, 25 mg of PANI was added to 60 ml flask containing 50 ml of HA solution with initial concentrations from 10 to 100 mg l^{-1} with pH 5.3 ± 0.3. The flasks were shaken on a shaker with 100 rpm and kept at 15, 25, and 35°C for 24 h, respectively. After achieving to adsorption equilibrium, the adsorbent particles were filtered with Whatman membrane filter (0.45 μm) and the residual concentrations of HA in every flasks were determined by a UV-Visual spectrometer at 254 nm. The equilibrium adsorption amounts of HA on PANI was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where q_e (mg g^{-1}) is the equilibrium adsorption amount of HA; C_0 (mg l^{-1}) is the initial HA concentration; C_e (mg l^{-1}) is the equilibrium concentration of HA; V (l) is the volume of HA solution; and M (g) is the adsorbent mass added to the flask.

For adsorption kinetic experiments, 250 mg of PANI was fast introduced into a 500 ml flask receiving 500 ml HA solution with the initial concentration of 25, 50, and

100 mg l^{-1}, respectively, and under strong continuous stirring at pH 5.4. The 4 ml of sample was withdrawn at different time intervals and filtered for spectrophotometrical determination of residual HA concentration.

In the pH effect experiments, a series of flasks receiving 25 mg of PANI and 50 ml of 50 mg l^{-1} HA solution were stirred at 25°C for 24 h. The solution pH was ranged from 3 to 10 pre-adjusted with 0.1 mol l^{-1} HCl or NaOH solution. After reaching adsorption equilibrium, the residual HA concentrations were determined spectrophotometrically and the adsorption amounts of HA were calculated using Eq. (1).

Effect of cations such as Na^+, K^+, Ca^{2+} on HA adsorption was studied by dispensing 25 mg of PANI to 50 ml of 100 mg l^{-1} HA solution with ionic concentrations ranging from 2.5 to 25 mmol l^{-1} at pH 5.8.

2.5. Desorption and regeneration tests

Prior to regeneration of adsorbent, desorption kinetic was studied. Briefly, 100 mg of PANI was added to a 250 ml flask receiving 200 ml of 50 mg l^{-1} HA. After 24 h adsorption, the saturated adsorbent was separated centrifugally and washed for several times. The HA loaded adsorbent was dispensed in 200 ml of 0.1 mol l^{-1} NaOH under strong stirring. The 4 ml of the mixture was withdrawn at different time intervals and separated for determination of desorbed HA concentration.

Adsorption of HA and regeneration of HA loaded PANI was conducted with four consecutive cycles. In each cycle, 25 mg of PANI adsorbent was dispensed in 50 ml of 50 mg l^{-1} HA solution at pH 6.0 for 24 h, and HA saturated PANI was separated by centrifuge and regenerated in 50 ml of 0.1 mol l^{-1} NaOH for 2 h. Then regenerated adsorbent was separated centrifugally and washed thoroughly with deionized water till pH 6.0 for next adsorption–regeneration cycle.

3. Results and discussion

3.1. Material characterization

FT-IR spectra of PANI was illustrated in Fig. 1. From the results, the peaks at 1575 and 1496 cm^{-1} are attributed to the C=C stretching vibrations of quinine ring and benzene ring vibrations, which suggests that as-synthesized PANI is in its oxidation state. The peaks at 1301, 1245, 1105 and 804 cm^{-1} are assigned to C–N stretching vibration connected with benzene ring, $C–N^+$ stretching vibration, C=N stretching vibration connected with quinine ring, and C–H out of plane bending vibration, respectively. The results showed that the material was in its emeraldine salt state. The BET surface area of PANI is 29.97 m^2 g^{-1}.

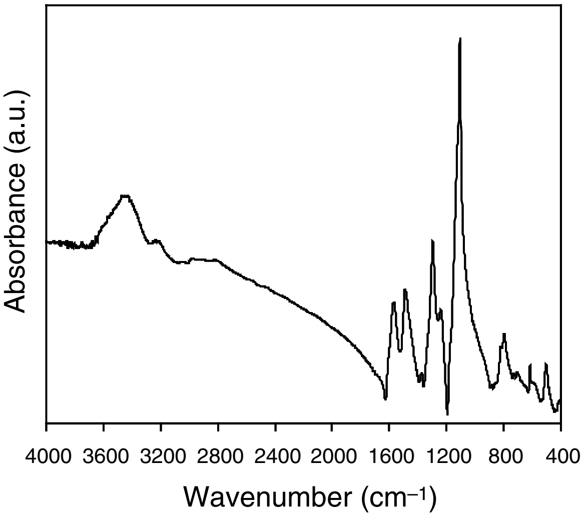

Fig. 1. Fourier transform infrared (FTIR) spectra of PANI.

3.2. Adsorption isotherms

Adsorption isotherms of aqueous HA adsorption on PANI at different temperature (15, 25, and 35°C) were illustrated in Fig. 2. It is evident that HA adsorption amounts increased with increasing adsorption temperature and the maximum adsorption amounts of HA on PANI at 15, 25, and 35°C are 85.47, 91.74, 126.58 mg g^{-1}, respectively, suggesting that HA adsorption process on PANI is endothermic reaction. The high adsorption capacity of HA on PANI was comparable with other adsorbents reported in literatures such as activated carbon 2.51 mg g^{-1} [8], aminopropyl functionalized SBA-15 117.6 mg g^{-1} [13], aminated polyacrylonitrile fibers

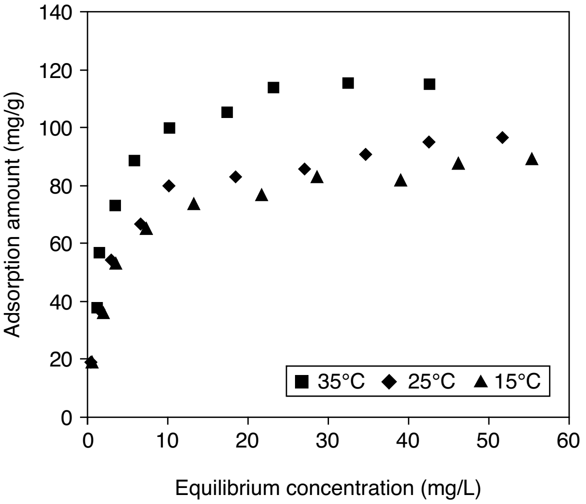

Fig. 2. Adsorption isotherms of HA on PANI at 15, 25 and 35°C.

16.22 mg g^{-1} [14], polypyrrole coated glass beads 0.396 mg g^{-1} [16], chitosan coated PET granules 0.407 mg g^{-1} [18], irradiation-crosslinked carboxymethylchitosan 57.14 mg g^{-1} [32].

To further describe the adsorption isotherms, the experimental datas were fitted by Langmuir and Freundlich model which are expressed as follows:

Langmuir Equation [33]:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

where q_e (mg g^{-1}) is the equilibrium adsorption amount; C_e (mg l^{-1}) is the equilibrium concentration of HA; q_m (mg g^{-1}) is the theoretical maximum adsorption capacity of adsorbent for HA; and b (l mg^{-1}) is the affinity coefficient.

Freundlich Equation [34]:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

where K_f ($mg^{1-1/n}\ l^{1/n}\ g^{-1}$) is the Freundlich constant; and $1/n$ is the heterogeneity factor.

The simulated parameters for HA adsorption isotherms at 15, 25, and 35°C by Langmuir and Freundlich equations are listed in Table 1. From the results, The R^2 of Langmuir model (0.99) was higher than that of Freundlich model (0.94), indicating that HA adsorption over PANI can be better fitted using Langmuir model than Freundlich model and the adsorption of HA on adsorbent is a monolayer adsorption.

Separation factor constant R_L is the characteristic parameter of Langmuir isotherm, which was frequently used to describe the affinity between adsorbate and adsorbent [35]. R_L is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

where C_0 (mg l^{-1}) is the initial HA concentration in aqueous solution and b is the Langmuir constant. Adsorption process with $0 < R_L < 1$ is favorable, and that with $R_L > 1$ is unfavorable. The calculated values of R_L at different initial concentration and adsorption temperature are shown in Fig. 3. As illustrated, within the tested initial concentration ranging from 10 to 100 mg l^{-1}, the R_L are between 0.018 and 0.21, indicating that HA adsorption on PANI is favorable. Additionally, the R_L values decrease with increasing initial concentration of HA, suggesting higher adsorption amount at higher HA initial concentration.

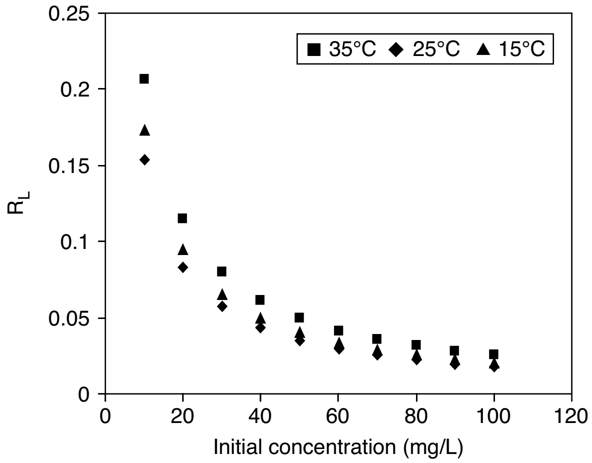

Fig. 3. Separation factor (R_L) values for the adsorption of HA on PANI.

3.3. Adsorption kinetics

Adsorption kinetics of HA adsorption on PANI at the initial concentrations of 25, 50 and 100 mg l^{-1} are shown in Fig. 4a. From the plot, adsorption amounts of HA over adsorbent increase sharply within 60 min and then become slowly with the progress of adsorption. Moreover, adsorption equilibrium is almost achieving within 240 min, which is advantageous for practical application.

Generally, adsorption of organic macromolecules on various adsorbents usually follows two-stage process [36]. In the early stage, the adsorbent surface is vacant and HA molecules reaching the adsorbent surface will be attached immediately. Therefore, HA adsorption on

Table 1
Langmuir and Freundlich model parameters for HA adsorption on PANI at 15, 25 and 35°C

Temperature (°C)	Langmuir model parameters			Freundlich model parameters		
	q_m (mg g^{-1})	b (l mg^{-1})	R^2	n	K_f	R^2
15	85.47	0.478	0.992	3.21	55.82	0.936
25	91.74	0.551	0.996	3.19	29.02	0.909
35	126.58	0.385	0.991	2.75	37.05	0.872

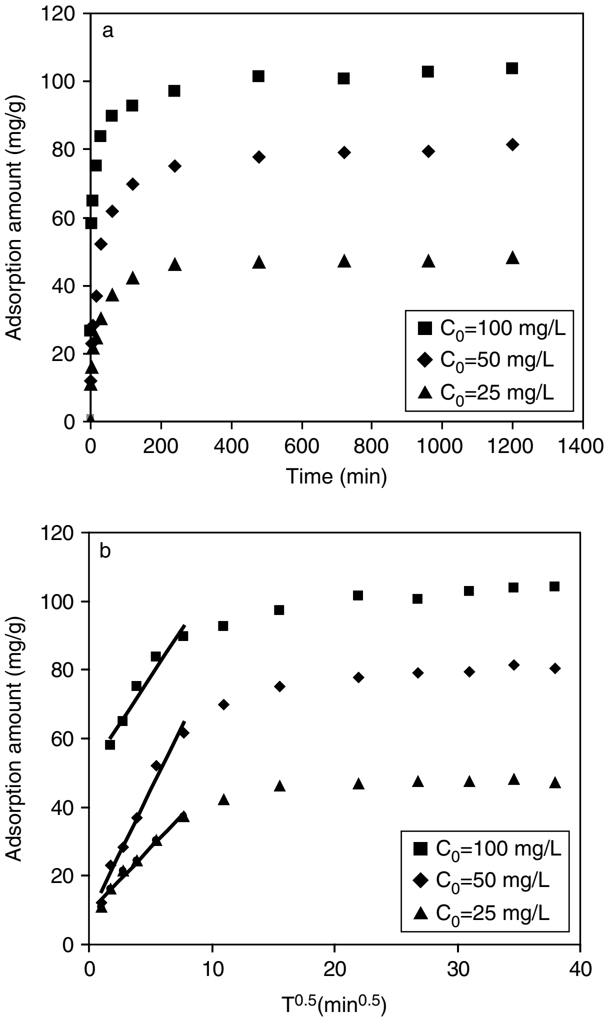

Fig. 4. Adsorption kinetics of HA on PANI at the initial concentration of 25, 50, and 100 mg l^{-1}.

adsorbent is controlled by diffusion of HA molecules from the solution to adsorption sites of adsorbent surface [14]. The diffusion controlled kinetics can be described by the Fickian diffusion equation defined as [18]:

$$q_t = \frac{2}{\sqrt{\pi}} C_0 S \sqrt{Dt} = k t^{\frac{1}{2}} \qquad (5)$$

where q_t (mg g^{-1}) is the adsorption amount of HA on PANI at equilibrium concentration (mg g^{-1}); C_0 (mg l^{-1}) is the initial concentration of HA in the solution; S (m^2 g^{-1}) is the specific surface area of adsorbent; D (m^2 s^{-1}) is the diffusion coefficient of HA in the solution; and k = a constant.

The plot of q_t versus $t^{0.5}$ in initial 60 min was shown in Fig. 4b. The linear dependence of q_t on $t^{0.5}$ for the experimental data is clearly observed, which indicates that HA adsorption in initial 60 min is diffusion-controlled. After fast adsorption process, some HA molecules are attached on the adsorbent surface and occupy the most of active sites on the adsorbent. Hence, other HA molecules have to find the available active sites and overcome the electrostatic repulsive force from the HA molecules adsorbed on the adsorbent. The increasing adsorption amount with adsorption time will become much slower, and HA adsorption on the adsorbent has been shifted from the initial diffusion controlled to attachment-controlled [15]. The adsorption will last for another several hours until adsorption equilibrium is achieved, which suggests that the attachment-controlled process dominates the adsorption process.

3.4. Effect of ionic strength and solution pH

The cations such as Na^+, K^+, Ca^{2+} are present in natural water, which may be interacted with HA molecules and effect the HA adsorption on PANI. Fig. 5 shows the effect of Na^+, K^+, Ca^{2+} on HA adsorption. From the results, no apparent effect on HA adsorption was observed in the presence of Na^+, K^+, however, Ca^{2+} can efficiently improve the HA adsorption amount on PANI. The HA adsorption amounts increase from 82.14 to 95.30 mg g^{-1} with Ca^{2+} concentration from 0 to 5 mmol l^{-1}, and gradually become constant at Ca^{2+} concentration higher than 5 mmol l^{-1}. The augment of HA adsorption in the presence of Ca^{2+} may be attributed to the weakening of the repulsive interaction between HA molecules adsorbed on the surface of the adsorbent and HA molecules in solution. Additionally, Ca^{2+} may be directly interacted with the HA molecules bounded to the adsorbent, and Ca^{2+} adsorbed on the adsorbent may again adsorb the HA molecules in solution, leading to the enhanced HA adsorption [11]. Moreover, the increasing solubility of

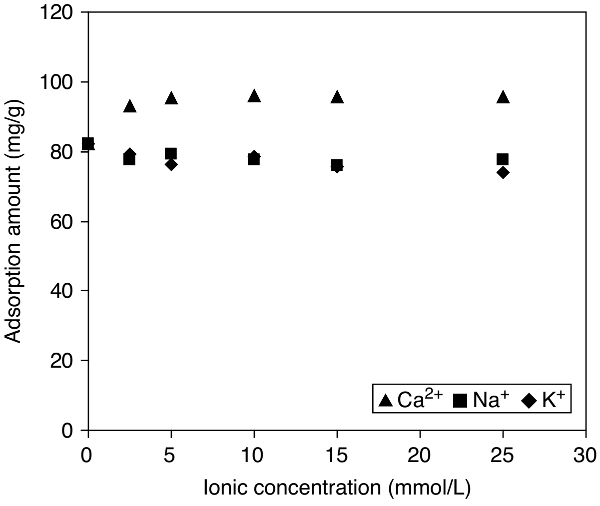

Fig. 5. Effect of ionic strength on HA adsorption over PANI at 25°C.

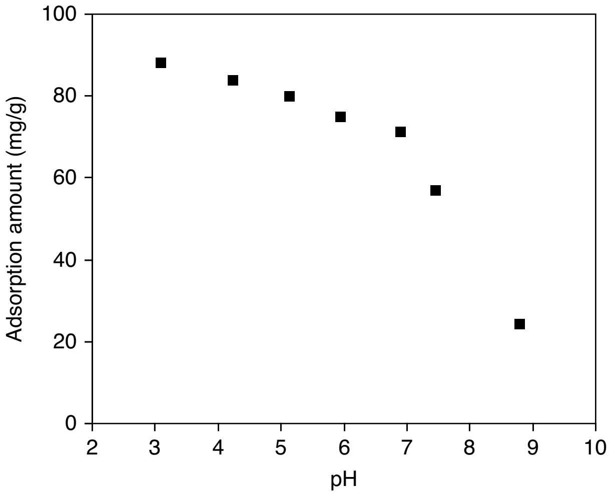

Fig. 6. Effect of solution pH on HA adsorption over PANI at 25°C.

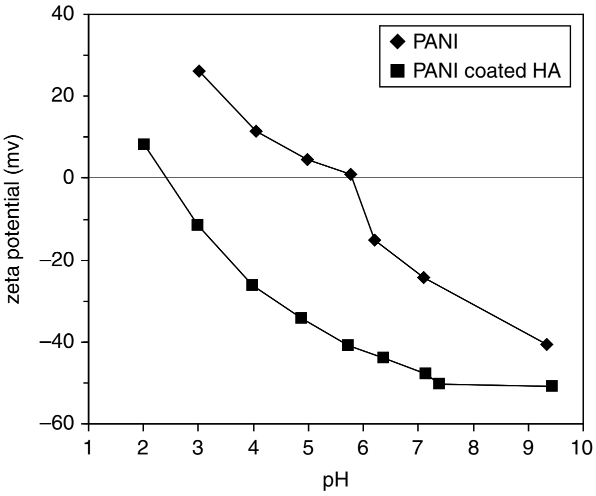

Fig. 7. Zeta potential of PANI before and after HA adsorption.

aqueous HA in high Ca^{2+} concentration may favor the mass transfer of HA from the solution to adsorbent surface, which may be another reason for the increased adsorption of HA [1].

The effect of solution pH on HA adsorption over PANI is illustrated in Fig. 6. It is shown that the HA adsorption over PANI decreases monotonously with increasing pH within the tested pH range. In addition, HA adsorption amount increases slightly with decreased pH at pH below 6.0, but decreases sharply with increasing pH when pH is more than 6.0. The distinct impact of solution pH on HA adsorption on PANI can be described by the physicochemical properties of PANI and HA molecules. According to the result of Tao et al. [13], the isoelectric point (IEP) of HA is about 1.9, and HA have the negative charges owing to deprotonation of carboxyl groups or phenolic groups in tested pH range. Whereas, the IEP of PANI illustrated in Fig. 7. is about 5.8, which is identical to the result of Wang et al. [24]. At pH below 5.8, PANI adsorbent carries positive charges due to the protonation of the imine and amine groups, and with the increasing pH, the adsorbents become less positively charged owing to the deprotonation of imine and amine groups until pH 5.8 [24]. Hence, the electrostatic interaction between positive charged PANI and negative charged HA leads to the enhanced HA adsorption on PANI. At pH above 5.8, increasing pH results in the adsorbent negatively charged due to the competitive adsorption of OH^- on imine and amine groups of adsorbent [37], therefore, the electrostatic repulsive force between negative charged PANI and disassociated HA may cause the decreased HA adsorption over PANI. Additionally, increasing of HA molecular size from a spherical structure at lower pH to a linear or stretched structure at higher pH may suppress the HA adsorption on PANI [38], which may be another reason for decreasing of HA adsorption with increasing of solution pH. In conclusion, the observations from the effect of solution pH and ionic strength on HA adsorption suggest that electrostatic interaction may play a crucial role in HA adsorption on PANI.

3.5. Zeta potential of PANI before and after HA adsorption

Zeta potentials of the adsorbents before and after HA adsorption are compiled in Fig. 7. It is evident that in all pH tested, zeta potential of PANI after HA adsorption are lower than PANI before HA adsorption, and the IEP of PANI after HA is about 2.4, which is higher than the IEP of HA but lower than that of PANI before adsorption, which indicates that HA molecules are conjugated the adsorbent surface. The significant zeta potential difference of PANI before and after HA adsorption at pH below 6.0 may account for the enhanced HA adsorption on PANI at low pH.

3.6. Desorption and regeneration

The suppressed HA adsorption on PANI observed at high pH implies that desorption of HA loaded adsorbent in alkali solution is a feasible approach. The 0.1 mol l^{-1} NaOH solution was used to regenerate the HA saturated PANI, and the desorption kinetics was compiled in Fig. 8. From the results, the desorption process was fairly fast in initial 20 min and the desorption percentage was 92.4% at 20 min. After a few hours, desorption reach a plateau and the maximum desorption percentage was 97.6%. The fast desorption of HA adsorbed on the adsorbent in alkali solution may be attributed to the superior adsorption of OH^- anions on the imine and

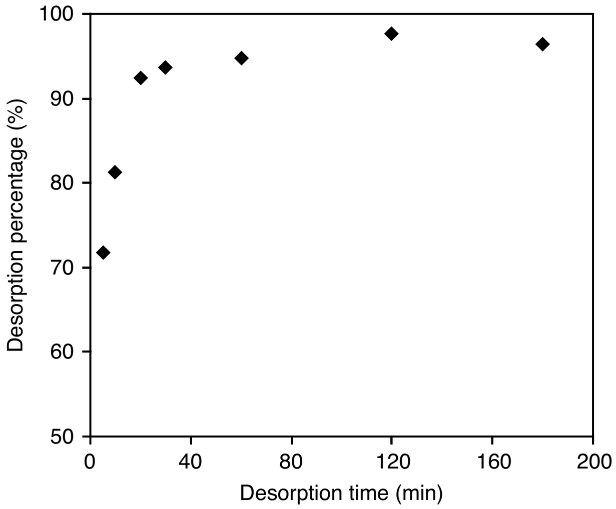

Fig. 8. Desorption kinetic of HA saturated PANI at 25°C in 0.1 mol l^{-1} NaOH solution.

amine groups of PANI compared with disassociated HA molecules [24].

The adsorption capacity of regenerated adsorbent was investigated and compiled in Fig. 9. It is found that the adsorption capacity of regenerated PANI degrades to 63.63 and 44.88 mg g^{-1} after the initial two adsorption-regeneration cycles, while in the subsequent cycles, no apparent decrease was observed, which implies that the regenerated adsorbent still possesses the high HA adsorption amount, therefore, the adsorbent can be used repeatedly to remove the HA from aqueous solution.

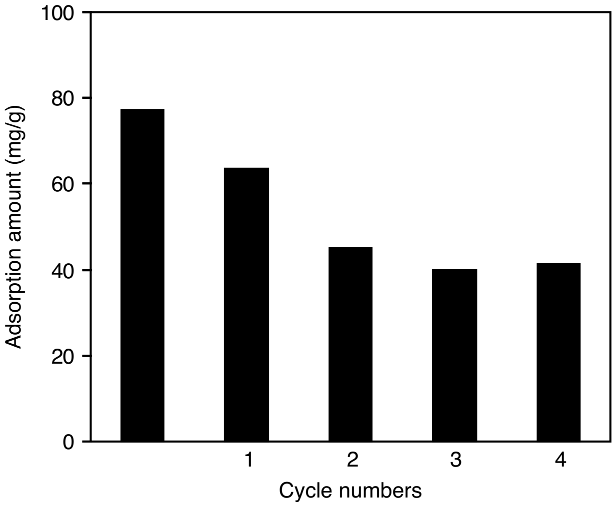

Fig. 9. HA adsorption on virgin and regenerated PANI adsorbent with four adsorption–regeneration cycles at 25°C.

4. Conclusions

Polyaniline prepared by chemical oxidation exists in emeraldine salt state. As synthesized material shows the strong affinity for the HA in aqueous solution, and HA adsorption process on PANI is endothermic. Increased Ca^{2+} concentration markedly increased the HA adsorption on PANI, while no apparent effect is observed in the presence of Na^+ and K^+. HA adsorption over PANI is highly dependent on solution pH and the adsorption amount of HA decreases with increasing of solution pH owing to the electrostatic interaction between imine and amine of PANI and disassociated HA. The HA saturated PANI is desorbed rapidly in alkali solution and regenerated adsorbent can be repeatedly used. The results highlight that PANI adsorbent is an available alternative in water treatment for the removal of HA.

Acknowledgements

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