Preparation and characterization of polyaniline nanofiber and nanocomposites and their applications in removal of Cr(VI) and phosphate

Tariq S.Najim and Ali J.Salim

Polymer Research Unit, College of Science, Mustansiriya University, Baghdad Iraq

E-mail: tariq_pru@yahoo.com

ABSTRACT

Polyaniline (PANI) nanofiber was prepared by interfacial and rapid-mixing polymerization. PANI nanocomposites were prepared by insitu oxidative polymerization of aniline in acidic medium using ammonium persulfate as initiator in the presence of natural silica(PANIS), acid treated natural silica (PANISA), fiber glass (PANIFG), and poly(ethylene terephthalate) powder from waste bottles(PANIPET). The nanocomposites were used for removal of Cr(VI) and phosphate from aqueous solution. The PANI nanofiber and nanocomposite were characterized by FTIR, XRD and SEM. FTIR and XRD confirm the formation of PANI nanofiber, the SEM images clearly shown the formation of PANI nanofiber alone or in the nanocomposites. The adsorption experiments reveal that PANISA nanocomposite is potential for removal of Cr(VI) and phosphate in comparison with other nanocomposites. This behavior is attributed to the large surface area, due to, increase in number of pores and channels in the structure of PANISA. It was also found that the Pseudo-second-order kinetic model well fitted with the experimental data for all nanocomposites.

Keywords: Polyaniline nanofiber, Nanocomposites, Cr(VI) and phosphate adsorption, Scanning Electron Microscope, Natural silica.

1 INTRODUCTION

PANI nanofibers have received much attention owing to their superior properties compared to the conventional bulk PANI[1-3]. PANI nanofibers show enhanced water processability [4] and improved sensitivity and time response when they are exposed to chemical vapour as they embody porous characteristic resulting in large surface area. On the other hand, PANI nanofibers have numerous applications, including electric devices and flash welding [5], sensors and actuators [6,7], and rechargeable batteries [8]. In this work, PANI nanofibers were synthesized via interfacial and rapid mixing polymerization of aniline as well as its nanocomposites with the following materials: natural silica(S), natural silica pretreated with acid (SA), glass fiber powder (GF), and poly(ethylene terephthalate) PET from waste bottles. The application of these nanocomposites for removal of Cr(VI) and phosphate ions from aqueous solution have been investigated. Kinetic of the adsorption process was also investigated.

2 EXPERIMENTAL

2.1 Materials and instruments

Ammonium peroxydisulfate (APS), hydrochloric acid, sodium hydroxide were of analytical grade and used as received, aniline was double distilled under vacuum, deionized water was used through out this work. Powdered PET was obtained by grinding of waste bottles in a small grinder the particle size was about 500μm, washed several times with deionized water and acetone, then dried. Natural silica of particle size 150-200μm washed with deionized water and dried, acid treated natural silica SA was prepared by treating dried natural silica with 0.1M Hcl for overnight then washed with deionized water and dried, fiber glass was grounded and treated with acetone for 3 h and dried. Water bath shaker type Lab. Companion BS-11, digital scale KERB-ABS, UV-visible spectrometer, CARY 100 Conc, pH meter type Trans BP 300, Scanning Electron Microscope (SEM) model Philips XL series 30, Shimadzu 8400 FTIR and Shimadzu-XRD 6000 were employed.

2.2 Preparation of PANI nanofiber

PANI nanofibers were prepared by two methods: interfacial and rapid mixing polymerizations[9]. In the former toluene was used as an organic phase, in which aniline was dissolved and aqueous phase containing ammonium APS and the doping acid (hydrochloric acid). The aniline was polymerized at the interface between the two phases. In the later method the polymerization were performed by rapidly mixing of two solutions, aniline in acidic deionized water and APS in acidic deionized water, into a beaker and the mixture was stirred moderately with a magnetic bar at 5-10°C. In both methods the polymerization were lasted for 3 h, the doped PANI was filtered and washed with plenty of distilled water then with ethanol and acetone to remove all unreacted aniline, oligomers and impurities, then dried.

2.3 Preparation of nanocomposites

The polyaniline nanofiber composites were prepared by insitu oxidative polymerization of aniline in the presence of S, SA, GF and PET in hydrochloric acid solution by rapid addition of a specified amount of APS in Hcl to the mixture then moderatly stirred using magnetic bar. After 3 h, The product was filtered and washed with distilled water then ethanol and acetone to remove unreacted aniline, oligomers and impurities then dried in an oven at 80°C for 6 h and stored in a sealed container.

2.4 Adsorption experiments

A stock solution of potassium dichromate and potassium dihydrogen phosphate of 1000 mg/L were prepared. From this solution, dilute concentrations of Cr(VI) and phosphate were prepared by dilution of specified volume of stock solution. 50 ml of certain concentration of Cr(VI) and phosphate were stirred with certain amount of nanocomposite in a water bath shaker for definite time interval. At the end of each adsorption experiment the solution was made alkaline at pH $\geq$ 12, and the residual

Cr(VI) was determined using UV-Visible spectrophotometer [10]. Residual phosphate was also determined spectrophotometrically after complexation with ammonium molybdate and sodium sulfide in concentrated sulfuric acid. For calibrating the UV-Visible spectrophotometer, standard samples of dichromate and phosphate were prepared and the corresponding absorption for each concentration were measured at λ_{max} 372nm and λ_{max} 715nm respectively.

3   RESULTS AND DISCUSSIONS
3.1   Characterization of PANI nanofiber

The analysis of the prepared PANI nanofibers were carried out by Scanning Electron Microscope, X-ray diffraction and FTIR. The presence of the characteristic adsorption peaks of PANI in the FTIR spectrum indicates the successful polymerization of aniline via interfacial and rapid mixing methods, as shown in Figure 1, the C=C stretching vibration of benzenoid ring appear at 1555 cm^{-1} and that for quinoid ring at 1476 cm^{-1}, C-N stretching vib. at 1296 & 1244 cm^{-1} and that for C-H bending vib. of aromatic ring appear at 1114cm^{-1}, about the same peaks that obtained by Wei et al.[11]. In case of nanocomposites, due to, the low yield of PANI in comparison to the large quantity of fillers in each composite (20g), the final percentage ratio of filler to PANI was about (97 : 3), so, the absorption peaks of PANI nanofiber was weak and about the same position of pure PANI.
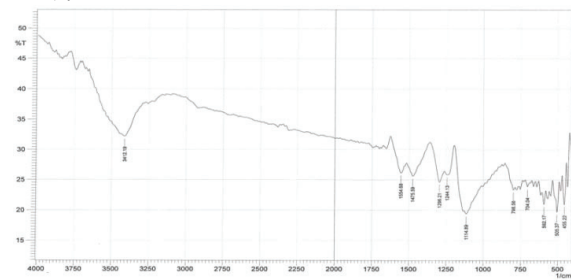
Figure 1 FTIR of PANI Nanofiber by Interfacial Polymerization

The X-ray diffraction confirm the formation of PANI, two characteristic peaks around $2\theta = 25^o$ and around $2\theta = 20^o$ presented in the XRD pattern of the PANI nanofiber, figure is not shown, the same XRD pattern of PANI nanofiber was obtained by Yangyong et al.[12]. A ccording to the studies carried out by Luzny et al.[13,14] and Chaudhari et al.[15], the nanofibers has partial crystallinity. Scanning Electron Microscope (SEM) was used to show images of PANI nanofiber after completion of polymerization by interfacial and rapid-mixing techniques as well as nanocomposites, as shown in Fig. 2. The images clearly shown the formation of PANI nanofibers with diameter of 30-80 nm.

3.2   Adsorption of Cr(VI) and phosphate

The adsorption is the affinity of interaction between the adsorbent active sites on it's surface and the adsorbate molecules. The PANI nanocomposites (PANIS, PANISA, PANIFG, PANIPET) were used in this work for removal of Cr(VI), whereas, PANIS and PANISA were used for removal of phosphate from aqueous solution. The pH of solution is an important factor that controlled the adsorption process
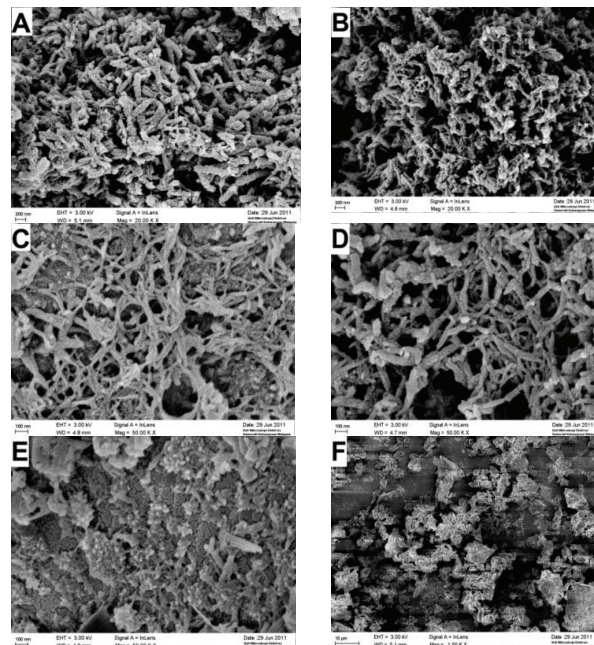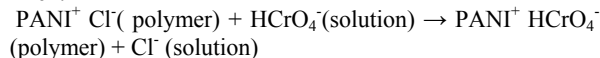
Figure 2 SEM images of: A) PANI nanofiber by interfacial polym. B) PANI nanofiber by rapid mixing C) PANIFG D) PANIPET E) PANISA F) SA.

, therefore, the effect of pH on adsorption was investigated. It was observed that higher adsorption of Cr(VI) was obtained at pH 2 for all nanocomposites, while, the higher removal of phosphate was obtained at pH 1 onto PANIS and PANISA. The removal percentage decreased with increasing pH for both adsorbate, the removal percentage of Cr(VI) onto PANIS was reduced from 95% at pH 2 to 34% at pH 6, from 99% at pH 2 to 55% at pH 6 onto PANISA, from 84% at pH 2 to 36% at pH 6 onto PANIFG and from 84% at pH 2 to 34% at pH 6 onto PANIPET, when the nanocomposites weight was 4g/L. Whereas, the removal percentage of phosphate onto PANIS was reduced from 21% at pH 1 to 7% at pH 6 and from 40% at pH 1 to 16% at pH 6 onto PANISA.

It seems that the mechanism of Cr(VI) and phosphate ions sorption onto nanocomposites, mostly occurred via anion exchange process. When the Hcl doped PANI is treated with an aqueous solution of Cr(VI) or phosphate (PO_4^{-3}) ions in acidic media, the chloride ion (mobile dopant anion) in the polymer is readily exchanged for chromate or phosphate ions, so the removal of Cr(VI) or phosphate results[10]. At pH$\leq$ 2 the dichromate is converted to chromate $HCrO_4^-$ ions as follows:

$$Cr_2O_4^{-2} + H^+ \rightarrow 2 HCrO_4^- + H_2O$$

Then:
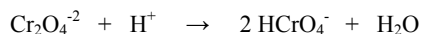
PANI$^+$ Cl$^-$(polymer) + HCrO$_4^-$(solution) → PANI$^+$ HCrO$_4^-$ (polymer) + Cl$^-$ (solution)

The low removal percentage of phosphate anion PO$_4^{-3}$ onto nanocomposites in comparison to chromate anion HCrO$_4^-$ can be attributed to the difficulty in replacing monovalent anion for trivalent anion unless more doped PANI is required. The effect of contact time for Cr(VI) adsorption was also investigated, all nanocomposites take about 90 min to reach equilibrium except PANISA, where the adsorption was very rapid, and takes about 2 min. to attain equilibrium. This behavior and the higher removal of Cr(VI) and phosphate onto PANISA are attributed to the large surface area of PANISA, due to, increase in number of pores and channels in the structure of PANISA after treatment with acid, these pores and channels is clearly shown in Figures 3E & 3F. The foregoing attribution was also confirmed by the effect of adsorbent weight for removal of Cr(VI). It was found that, 4g/L of PANISA can remove more than 99% of chromate anion, 10g/L of PANIS, PANIPET and PANIFG can remove about 95% and about 93% of chromate anion respectively.

3.3 Kinetic Study

In order to define the adsorption kinetics of Cr (VI) and phosphate onto nanocomposites, the experimental data were regressed against the pseudo-first order model represented by the following linear equation [16]:

$$\log(q_e - q_t) = \log q_e - (\frac{K_1}{2.303})t$$

And pseudo-second-order kinetic model [17]:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t)$$

Where q$_e$ and q$_t$ are the adsorption capacity at equilibrium and time t respectively. k$_1$ and k$_2$ are the rate constants of the pseudo-first-order and pseudo-second-order kinetics. In the first-order kinetic model log (q$_e$-q$_t$) was plotted against time t. A linear curves were obtained when t/q$_t$ was plotted against time, for the adsorption of Cr(VI) and phosphate onto nanocomposites Figures 3 and 4. The results reveal that the second-order kinetic model is well fitted with the experimental data for adsorption of Cr(VI) onto PANIS, PANIFG and PANIPET, and phosphate onto PANIS and PANISA, due to the good correlation coefficient obtained from second-order plot R^2 = 0.9999 as well as the close match between the values of q$_e$(cal) and q$_e$(exp) for the second-order kinetic model.
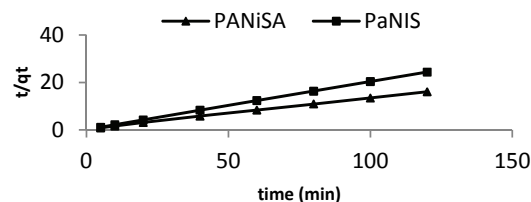

Figure 3 Second-order plot of adsorption of Phosphate onto Nanocomposites.
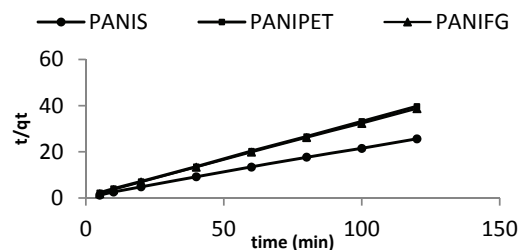

Figure 4 Second-order Plot of adsorption of Cr(VI) onto Nanocomposites.

4 REFERENCES

[1] S. Virji, J. Haung, R.B. Kaner, B.H. Weiller, Nano Letter. 4, 491, 2004.
[2] J. Wang, S. Chan, R.R Carison, Y. Luo, G. Ge, R.S. Ries, J.R Heath, H.R. Tseng, Nano Letter. 4, 1693, 2004.
[3] J. Haung, S. Virji, B.H. Weiller, R.B. Kaner, Chem. Eur.J. 10, 1314, 2004.
[4] D. Li, R.B. Kaner, Chem. Commun., 3286, 2005.
[5] J. Huang, J. Appl. Chem. 78, 15, 2006.
[6] N. Densakulprasert, L. Wannatong, D. Chotpattananont, P. Hiamtup, A. Sirivat, J Schwank, Mater. Sci. Eng., B117, 276, 2005
[7] J. Gao, J.M. Sansinena, H.L. Wang, Synth. Met. 135-136, 809, 2003.
[8] K. Ghanbari, M.F. Mosavi, M.J. Shamsipur, Power Sources. 170, 513, 2007.
[9] H. Jiaxing, B.K. Richard, Angew. Chem. Int. Ed. 43, 5817, 2004.
[10] A. Reza, Acta Chim. Slov. 53, 88, 2006.
[11] L. Wei, Z. Qinghua, C. Dajun, L. Lan, J. Macromol. Sci., part A, 43, 1815, 2006.
[12] W. Yangyong, J. Xinli, Mat. Sci. & Eng. B, 138, 95, 2007.
[13] W. Lunzy and E. Banka, Macromolecules. 33, 425, 2000.
[14] E. Banka and W. Luzny, Synth. Met. 101, 715, 1999.
[15] H.K. Chaudhari and D.S. Kelkar, J. Appl. Polym. Sci. 62, 15, 1996.
[16] S. Langergren, Handlinger. 24, 1, 1898.
[17] Y.S. Ho and G. Mckay, Water Res 33, 578, 1999.