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Removal of copper ions from aqueous solutions using polypyrrole and its nanocomposites

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ABSTRACT

In this article, preparation of polypyrrole and its nanocomposites as adsorbents were discussed and the capability of separation of copper ions from aqueous solution were studied. Polypyrrole was prepared by chemical oxidative polymerization method of pyrrole using $FeCl_3$ as an oxidant. The removal of Cu (II) was investigated using PPy, PPy/TiO_2 and $PPy/TiO_2/DHSNa$ nanocomposites. The products were investigated in terms of morphology and chemical structure with scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Batch studies were performed to evaluate the influence of various experimental parameters such as pH, ion dosage and contact time. Optimum conditions for copper ions removal were found to be pH 3, ion dosage of 50 mg L^{-1} and the equilibrium time equals to 30 minutes. It was also found that the equilibrium adsorption isotherm was better described by Freundlich adsorption isotherm model.

1. Introduction

The removal of toxic heavy metals from aqueous streams is an important issue faced in industries discharging effluents bearing heavy metals. Copper is an essential element but its concentration on air, water, and food should be below the tolerance limits; otherwise it would be harmful to humans and animals [1]. The removal of copper ions from wastewaters has received considerable attention in recent years. Extensive investigations have been carried out to identify suitable adsorbents which are capable of removing significant quantities of copper ions. Table 1 shows a number of previously reported adsorption capacities of various adsorbents. Various techniques such as chemical sedimentation, oxidation/reduction, membrane filtration/osmosis, ion exchange, and adsorption can be used for the removal of metal ions. Each process has its advantages and disadvantages, but ion exchange/adsorption methods offer the most direct method of treated water production with the highest quality [2, 3]. Conducting polymers can be used effectively for removal of some toxic metal ions from aqueous solutions [4]. Conducting polymers such as polyacetylene, polyaniline, polypyrrole, and polythiophene have attracted much research interest for a wide range of applications such as rechargeable batteries [5], conductive paints [6], membranes [7], optical devices [8], sensors and biosensors [9,10], electromagnetic interference (EMI) shieldings [11], biomedical applications [12], and removal of heavy metal ions [13,14]. Polypyrrole as one of the most promising conducting polymers has received comprehensive interest due to its excellent characteristics including easy preparation, environmental stability, high conductivity and so on [15,16]. PPy is a conjugated polymer with alternating single and double bonds. Polypyrrole can be prepared by plasma and vapor phase polymerization techniques. In applications such as coating the dielectric materials, the most suitable process is in situ chemical polymerization, because it provides

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Table1. Previously reported adsorption capacities of various adsorbents for Cu (II)

q_m (mg/g)	Material	Reference
38.7	Soybean hulls	[25]
19.1	Cottonseed hulls	[25]
16.4	Sphagnum moss peat	[26]
10.8	Apple wastes	[27]
11.7	Tree fern	[28]
8.18	Chitosan-coated sand (CCS)	[29]
1.79	Sawdust	[30]
9.59	LS (Shells of lentil)	[31]
17.42	WS (Shells of wheat)	[31]
2.95	RS (Shells of rice)	[31]
8.64	Tea-industry waste	[32]
1.62	Low-rank Turkish coals	[33]
15.82	PPy//TiO2/ DHSNa	In this study

relatively high conductivity as well as suitable and uniform film thickness [17]. Most of the optical, electrical, and morphologic properties of the PPy depend on the synthesis procedure as well as on the dopant nature [18]. The main purpose of this paper is the removal of copper ions by using adsorption and determining the ability of PPy, PPy/TiO_2 and PPy/TiO_2/DHSNa nanocomposite to remove Copper ions from aqueous solutions. Additionally, effects of pH, ion dosage, and contact time variation have been investigated.

2. Mathematical and Methods

2.1 Instruments

A magnetic mixer of model MK20 (Germany), digital scale of model FR 200 (Germany), scanning electron microscope (SEM) of model XL30 (Netherland), pH meter model HANNA 211 (Italy), and fourier transform infrared (FTIR) spectrometer of model spectrum one (Germany), and atomic absorption device of model perkinelmer 2380 (Germany) were employed.

2.2 Reagents and Standard Solutions

Materials used in this work were pyrrole, sodium dodecylhydrogensulfate (DHSNa), titanium dioxide, and ferric chloride from Merck. All reagents were used in their analytical grade without further purification, otherwise it is stated. Distilled water was used throughout this work. Monomer of pyrrole was purified by simple distillation. Stock solutions of copper ions were prepared by dissolving $CuSO_4$ in doubly distilled water.

2.3 Nanocomposite preparation

2.3.1 Preparation of polypyrrole in aqueous media

The polypyrrole particles were synthesized by iron (III) catalyzed oxidative polymerization in aqueous media using pyrrole as a monomer and $FeCl_3$ as an oxidant. For the typical synthesis, 1 mL of pyrrole monomer was added to a stirred aqueous solution (100 mL) containing 5.5 g of $FeCl_3$. After 5 hours, the polymer was collected by filtration. In order to separate the oligomers and impurities, the product was washed several times in succession with deionized water. It was then dried at the temperature of about 60 ˚C in oven for 24 hrs.

2.4 Preparation of polypyrrole nanocomposite

The reaction was tested in an aqueous media at room temperature for 5 hours. In a typical experiment, 1 mL of pyrrole monomer was added to a stirred aqueous solution (100 mL) containing 5.5 g of $FeCl_3$, 0.5 g of titanium oxide, and 0.5 g of DHSNa. After 5 hours, the polymer was collected by filtration. In order to separate the oligomers and impurities, the product was washed several times in succession with distilled water. It was then dried at about 60 ˚C in oven for 24 hrs.

2.5 Batch adsorption experiment

Completely mixed batch reactor (CMBR) technique was used to remove Cu(II) from water. 25 mL of solution was added to the beaker containing of the desired adsorbent. At the end of predetermined time intervals, the sorbate was filtered and the concentration of Cu(II) was determined. All experiments were carried out twice and the adsorbed copper ions' concentrations were given by the means of duplicate experimental results. Experimental variables were considered as the following: initial concentration of Cu(II) 50, 100, 150, and 200 ppm; contact time between polypyrrole and its nanocomposites with Cu(II) solution 15-45 mins; pH 3, 4, 5, 6, and 7 and dosage of adsorbent 250 mg/25 mL. The equilibrium adsorption capacity of adsorbent was calculated by equation (1). Where qe is the equilibrium adsorption capacity of adsorbent in mg metal/g adsorbent. C_0 is the initial concentration of metal ions in mg.L^{-1}, C_e is the equilibrium concentrations of metal ions in mg.L^{-1}, V is the volume of metal ions solution in L, and m is the weight of the adsorbent in g.

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

3. Results and Discussion

3.1 Morphology of nanocomposite

The chemical method can be a general and useful procedure to prepare conductive polymer and its composites. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters [19]. The yield, particle size, and morphology are dependent on the presence of TiO_2 and surfactant, because the surfactant adsorbes physically to the growing polymer [20]. The morphology of nanocomposites was studied, using scanning electron microscope. Figs. 1-3, show the morphologhy of pure polypyrrole, PPy/TiO_2 and PPy/TiO_2 nanocomposite using DHSNa as a surfactant, respectively. As it can be seen in micrographs, the nanocomposites obtained using surfactant DHSNa exhibit spherical particles. Also, surface active agents affect the physical and chemical properties of the solution. It is apparent that using the surfactant decreases the tendency to form agglomerates which leads to more homogeneous distribution, because surfactant prevents the gross aggregation of particles.

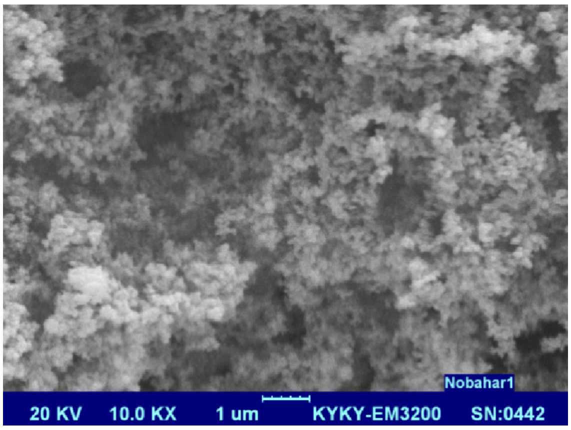

Fig. 1 Scanning electron micrograph of pure PPy generated in aqueous media. Reaction conditions: $FeCl_3$ = 55 g L^{-1}, pyrrole monomer 14.45×10^{-2} mol L^{-1}, volume of solution 100 mL, reaction time 5 hrs at room temperature.

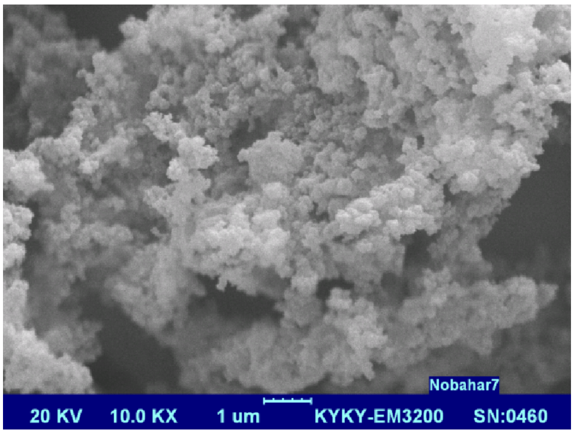

Fig. 2 Scanning electron micrograph of PPy/TiO_2 generated in aqueous media. Reaction conditions: $FeCl_3$ = 55 g L^{-1}, pyrrole monomer 14.45×10^{-2} mol L^{-1}, titanium oxide = 0.5 g , volume of solution 100 mL, reaction time 5 hrs at room temperature.

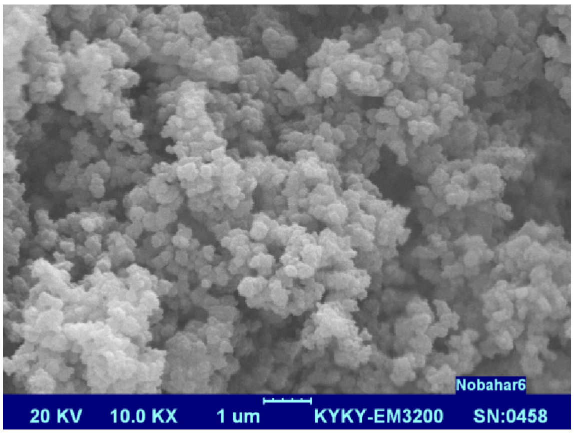

Fig. 3 Scanning electron micrograph of PPy/DHSNa/ TiO_2 generated in aqueous media. Reaction conditions: $FeCl_3$= 55 g L^{-1}, pyrrole monomer 14.45×10^{-2} mol L^{-1}, Titanium oxide = 0.5 g , sodium dodecylhydrogenSulfate = 0.5 g L^{-1} volume of solution 100 mL, reaction time 5 hrs at room temperature.

3.2 FTIR spectroscopy

Fig. 4, represents the FTIR spectra of the pure polypyrrole, polypyrrole/TiO_2 composite, and the polypyrrole/TiO_2 composite with DHSNa as a surfactant. The FTIR spectroscopy has provided valuable information regarding the formation of polypyrrole composites. FTIR analysis has been done to identify the characteristic peaks of the product. As shown in this figure, the FTIR spectrum of the polymer and its composites depend on the type of solution and the additive. As it can be seen in Fig. 4(c), the peaks related to pyrrole unit appear at 1539 cm^{-1}. The peaks are at 1307 cm^{-1} (C-N stretching vibration), 1165 cm^{-1} (C-H in-plane bending), 1043 cm^{-1} (N-H in-plane bending), 889 cm^{-1} (C-H out-of-plane bending), and 787 cm^{-1} (C-H out-of-plane ring bending) [21].Also, All bands in

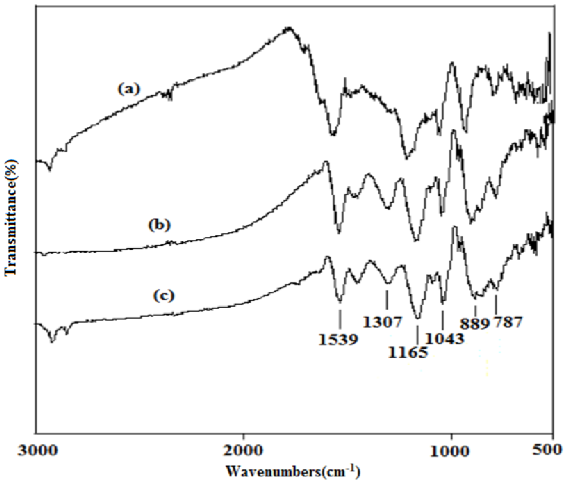

Fig. 4 FTIR spectra of (a) pure PPy, (b) PPy/TiO_2 and (c) PPy/TiO_2 with DHSNa.

composites are slightly shifted, which shows that there is some interaction between polypyrrole, titanium oxide, and surfactant.

3.3 Effect of pH

The pH value of the aqueous solution is an important controlling parameter in the adsorption process. These pH values affect the surface charge of adsorbent, the degree of ionization, and speciation of adsorbate during the process. At high pH values, de-doping process occurred in polymer (PPy), and then desorption of Cu(II) became the predominant process. No measurable Cu(II) sorption was observed when the treatment media was neutral or alkaline. Under alkaline conditions (pH>7), the polymer (PPy) became completely undoped and the polymer changed into its deprotonated emeraldine base form, with no counter anions in the polymer to be exchanged with Cu(II) ion in the solution [22]. In order to evaluate the influence of this parameter on the adsorption, the experiments were carried out at different initial pH = 3, 4, 5, 6, and 7. The experiment was done by PPy, PPy/TiO_2 nanocomposite, and PPy/TiO_2 nanocomposite with DHSNa as surfactant with an initial copper ions concentration of 50 mg.L-1 at room temperature with contact time of 30 minutes. The results are shown in Fig. 5. Removal of copper ions increases with decreasing solution's pH. Besides, in pH=7 the copper ions were existing in the solution by sediments, and a maximum value was reached at an equilibrium pH of around 3.

As it can be seen in Fig. 5, removal efficiency of PPy/TiO_2/DHSNa is higher than PPy and PPy/TiO_2.

3.4 Effect of initial concentration of Cu(II) on the adsorption

In order to evaluate the influence of this parameter on the adsorption, the experiments were carried out at different initial concentrations, 50, 100, 150, and 200 mg.L^{-1} of Cu(II) from aqueous solutions at pH of 3. The amount of adsorbent was adjusted to 250 mg/25 mL. As it can be seen in Fig. 6, by increasing the initial concentration of Cu(II), the removal efficiency of copper ions was reduced. Since the amount of consumable adsorbent used in the experiments had been constant, the active levels of the adsorption remained uncheanged. So, increasing the concentration of the copper ions existing in the solution resulted in the reduction of deletion percentage. Additionally, an increase in the competition among the absorbed molecules, collision, and repulsion among them, are other factors of this decreasing process. Taking into account these results, initial concentration of Cu(II) was chosen 50 mg.L^{-1} for further experiments.

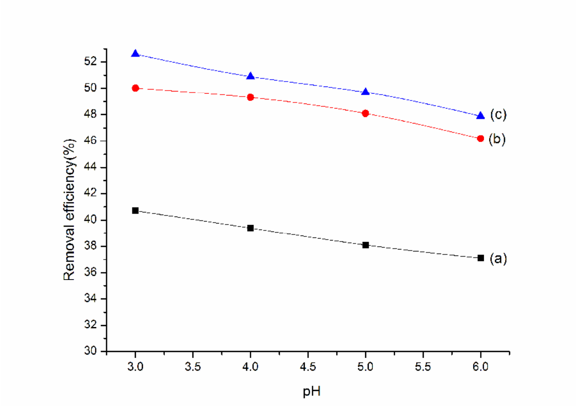

Fig. 5 The Effect of pH on the removal efficiency with: (a) pure PPy, (b) PPy/TiO_2 and (c) PPy/TiO_2 with DHSNa (initial concentration, 50 mg L-1; contact time, 30 minutes).

3.5 Effect of contact time

Fig. 7 shows the influence of contact time on the sorption of copper ions by PPy, PPy/TiO_2 and PPy/TiO_2/DHSNa. For these cases, initial copper ions' concentration was 50 mg.L^{-1} and pH of 3 was used for copper ions solution. Also, PPy, PPy/TiO_2 and PPy/TiO_2/DHSNa dose of 0.25 g in 25 mL was utilized. When contact time was 30 minutes, little change of sorption rate was observed. This result demonstrated that the adsorption of copper ions was fast and the equilibrium was obtained after 30 minutes of contact time. Taking into account these results, a contact time of 30 minutes was chosen for further experiments.

3.6 Adsorption Isotherms

The adsorption isotherm for the removal of copper ions was studied using concentration level of 50-200 mg.L^{-1} and adsorbent dosage of 250 mg/25 mL. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent (q_e) and the solute concentration for the solution at equilibrium (C_e).

3.7 Langmuir Adsorption Isotherm

The data obtained were fitted into the Langmuir adsorption isotherm [23] applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a limited number of same sites and is represented as following:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{C_e}{q_m} \qquad (2)$$

A linear plot of C_e/q_e versus C_e in Fig. 8 was utilized to determine the value of q_m (mg/g) and K_l (L/mg). The data obtained with the correlation coefficients (R^2) was listed in Table 1.

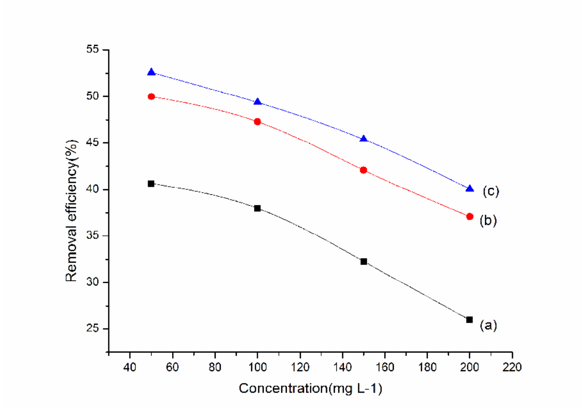

Fig. 6 The Effect of initial concentration of Cu(II) on the removal efficiency with: (a) pure PPy, (b) PPy/TiO_2 and (c) PPy/TiO_2 with DHSNa (pH, 3; contact time, 30 minutes).

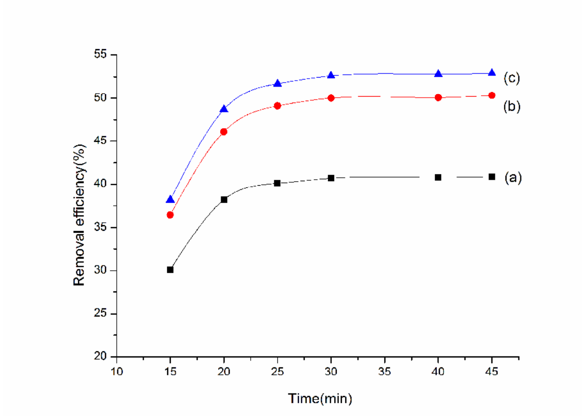

Fig. 7 The Effect of contact time on the removal efficiency with: (a) pure PPy, (b) PPy/TiO_2 and (c) PPy/TiO_2 with DHSNa(pH, 3; initial concentration, 50 mg L^{-1}).

3.8 Freundlich Adsorption Isotherm

The adsorption data obtained were then fitted the Freundlich adsorption isotherm [24] which is stated by the following equation:

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

A linear form of this expression is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

The Freundlich isotherm constants KF and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. The constants KF and n were computed from Eq. (4) using Freundlich plots as displayed in Fig. 9. The values for Freundlich constants and correlation coefficients (R^2) for the adsorption process are also exhibited in Table 1. The values of n between 1 and 10 (i.e., 1/n less than 1) represent a positive adsorption. The n values obtained for the adsorption process showed an advantageous adsorption. As it can be seen in Table 2, experimental data are better fitted to the Freundlich (R^2=0.9908) than the Langmuir (R^2=0.9798) adsorption isotherm.

4. Conclusions

In this work, polypyrrole nanocomposites were successfully fabricated and applied as adsorbent to remove copper ions. The SEM micrographs indicate that the morphology and particle size of products are dependent on the presence of surfactant. The comparison of figs. 2 and 3 shows that, particle size decreased by using DHSNa. The molecular structures of the products were determined by FTIR spectroscopy. The results indicate that the intensities of the peaks are dependent on the surfactant. Batch technique was adopted to investigate the adsorption of Cu(II) from aqueous solution onto nanocomposite as a function of various environmental factors such as pH, ion dosage, and contact time under ambient conditions. Optimum conditions for copper ions removal were found to be pH 3, ion dosage of 50 mg.L^{-1} and equilibrium time of 30 minutes. A comparison between PPy, PPy/TiO_2 and PPy/TiO_2/DHSNa in removal of copper ions indicated

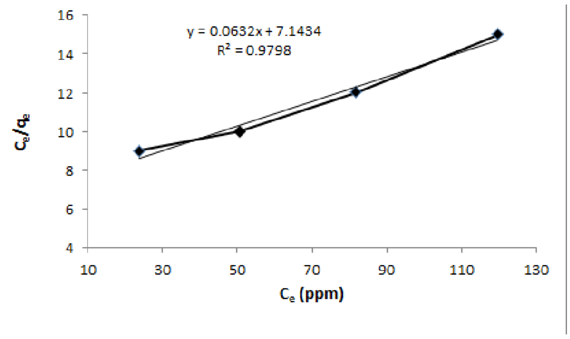

Fig. 8 Langmuir plot for the adsorption of copper ions by PPy/TiO_2 with DHSNa: pH, 3; initial concentration, 50 mg L^{-1}; contact time, 30 minutes.

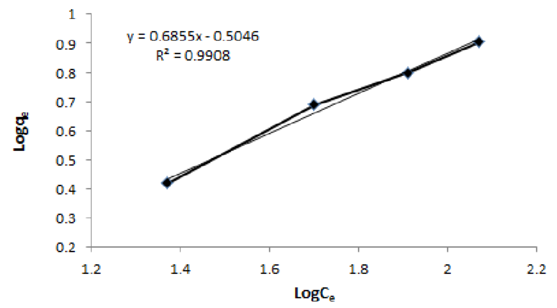

Fig. 9 Freundlich plot for the adsorption of copper ions by PPy/TiO_2 with DHSNa: pH, 3; initial concentration, 50 mg L^{-1}; contact time, 30 minutes.

Table2. Langmuir and Freundlich adsorption isotherm constants for copper ions on PPy//TiO_2/ DHSNa.

Langmuir constants		Freundlich constants	
q_m (mg.g^{-1})	15.820	K_F ((mg.g^{-1})/ (mg.L^{-1})$^{1/n}$)	0.31
K_l (L.mg^{-1})	0.0088	n	1.4580
R^2 0	0.9798	R^2	0.9908

that the removal efficiency of PPy/TiO_2/DHSNa nanocomposite is higher than the PPy and PPy/TiO_2 in all experiments. It was also found that the equilibrium data followed the Freundlich isotherm better than the Langmuir model at a constant temperature.

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