

EFFECT OF VARIOUS AGENTS ON REMOVAL OF NICKEL FROM AQUEOUS SOLUTION USING POLYPYRROLE AS AN ADSORBENT

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Abstract

Removal of heavy metals is one of the applications of conducting polymers. In this study the preparation of polypyrrole (PPy) as an adsorbent is discussed and the capability of separating nickel from aqueous solution was studied. Polypyrrole was prepared by chemical oxidative polymerization of pyrrole using FeCl_3 as an oxidant. The effects of various agents such as pH of solution, dosage of adsorbent and contact time were investigated. The results compared with other adsorbents such as anthracite, purolite and activated carbon. This study indicated that removal percentage decreased by increasing concentration of adsorbent. The results show that high removal percentage obtained in alkaline solution. Scanning electron microscopy micrographs show that, surfactant plays a major role on the surface morphology and also the removal of nickel ions.

Keywords: Atomic absorption, pH, Polypyrrole, Nickel, Removal.

1. Introduction

The removal of toxic heavy metals such as cadmium, copper, lead, nickel, mercury, and zinc from aqueous environment has received considerable attention in recent years due to their toxicity and carcinogenicity which may cause damage to various systems of the human body. They also can be readily absorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [1]. Nickel ions are non-biodegradable toxic heavy metals and may cause dermatitis and allergic sensitization [2, 3]. According to the World Health Organization guidelines, the maximum permissible concentration of

nickel in effluents in the US from the electroplating process wastewater is 4.1 mg/l, while that in drinking water should be less than 0.1 mg/l [4]. Several environmental and health problems, associated with the metal contamination of the natural systems (soil and water) are arising from mining industries, smelting, brass, metal coating, silver refineries, electroplating and several other industrial activities [5, 6]. The main symptoms of nickel causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [7].

The major sources of nickel contamination to water comes from industrial process such as electroplating, batteries manufacturing, mine, metal finishing and forging. Different methods were investigated and applied to remove nickel ions from water such as adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis. Adsorption is widely used because it is cost-effective and simple.

Different adsorbents such as seaweeds [8], crab shell [9], dried aerobic activated sludge [10], loofa sponge-immobilized biomass of *Chlorella sorokiniana* [11], activated carbon prepared from almond husk [12], spent animal bones [13] and waste factory tea [14] have been used to remove nickel ions from aqueous water, but low adsorption capacities or efficiencies limit their applications. Therefore, investigating new adsorbents with higher adsorption capacities and efficiencies has been the aims of many researchers. Conductive electroactive polymers such as polypyrrole and polyaniline can be used for the removal of heavy metals from water and waste waters [15-17].

Amongst the important conducting polymers, polypyrrole (PPy) has potential applications in drug delivery [18, 19], sensors [20], biomolecules [21], adhesives [22], actuators [23], immunosensors [24] and corrosion protection [25]. Due to the intrinsic semiconducting properties, PPy has been used as an electronic component in electronic devices, e.g., photoelectrochemical devices [26], organic light-emitting diodes [27] and rectifying devices [28]. In this study effect of various agents such as pH, contact time and adsorbent concentration on removal percentage of nickel were characterized. Also the adsorption capacity of various adsorbents such as anthracite, activated carbon and purolite were compared with conductive electroactive polypyrrole composite in removal of nickel from water.

2. Experimental

2.1. Instrumentation

Magnetic mixer model MK20, digital scale model FR200, atomic absorption device perkin-elmer model 2380, pH meter model 211 HANNA, vacuum oven model Binder USA, differential scanning calorimeter model PL-DSC, fourier transform infrared (FTIR) spectrometer model shimadzu 4100 and scanning electron microscope (SEM) model LSM50A were employed.

2.2. Reagents and standard solutions

Materials used in this work were pyrrole ($d = 0.97$ g/mL), ethyl acetate, poly(vinyl alcohol) (PVA, $M_w = 72000$), anthracite, activated carbon, cation ion

exchangers (purolite) and ferric chloride, from Merck and Aldrich. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Pyrrole monomer was purified by simple distillation.

2.3. Synthesis of polypyrrole composite

The reaction was carried out 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 5.4 g of FeCl_3 as oxidant when the solution became homogen. After 5 hours, the polymer was collected by filtration, and in order to separate the oligomers and impurities, the product was washed several times in succession with deionized water. It was then dried in a vacuum oven at 40°C for 12 h.

2.4. Method of nickel removal

Completely mixed batch reactor (CMBR) technique was used to remove nickel ions from water. For determining the amount of heavy metal removal by different adsorbents such as polypyrrole composite, anthracite, purolite and activated carbon, 50 ml of nickel solution was mixed with 0.5 g powder of adsorbents and then stirred using magnetic mixer for 30 min and then was filtered respectively. The nickel concentration was analyzed by atomic adsorption method.

In addition, for calibrating the atomic absorption device, four standard samples with concentration of 1, 2, 4 and 6 mg/L were prepared and the corresponding amounts of absorption for each concentration were measured. Then by considering the amount of absorption equivalent to each concentration the linear regression curve was drawn. After drawing the calibrating diagram, the samples were injected to the device and their absorption was calculated. Then by considering this diagram the nickel absorption determined for different adsorbents. All of the experiments were repeat two or three times.

3. Results and Discussion

3.1. Characterization of polypyrrole

In Figs. 1 and 2, scanning electron micrographs of polypyrrole composite were shown. The SEM micrographs characterized the morphology of the polymer. As can be seen, PVA as a stabilizing agent could affect the size, morphology and homogeneity of particles, because the surface active agents are adsorbed physically or chemically by the growing polymer.

Because of the surface active agents prevent gross aggregation of the particles PPy particles synthesized by suspension polymerization (without surfactant) are larger than the PPy particle, were obtained in the presence of PVA as a surface active agent.

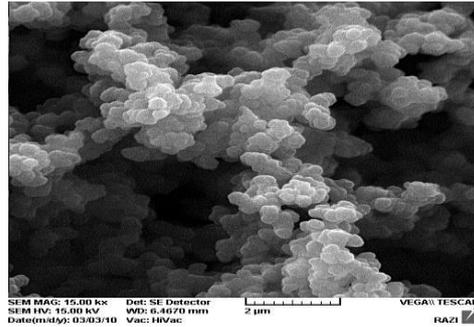


Fig. 1. SEM of Polypyrrole Nanocomposite Generated in Aqueous Media.
Reaction Conditions: $\text{FeCl}_3 = 54 \text{ g/L}$, Pyrrole Monomer = $14.45 \times 10^{-2} \text{ mol/L}$,
Volume of Solution = 100 mL, Reaction time = 5 h at Room Temperature.

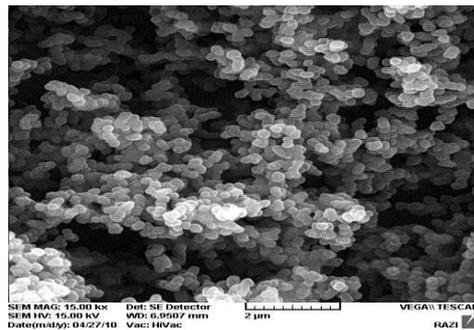


Fig. 2. SEM of Polypyrrole/PVA Nanocomposite Generated in Aqueous Media.
Reaction Conditions: $\text{FeCl}_3 = 54 \text{ g/L}$, Pyrrole Monomer = $14.45 \times 10^{-2} \text{ mol/L}$,
PVA = 2 g/L used as Surfactant, Volume of Solution = 100 mL, Reaction time = 5 h
at Room Temperature.

Figure 3 shows the SEM micrograph of PPy in aqueous/non-aqueous media. The micrograph shows that using water/ethyl acetate as solution the size of PPy particles decreases and homogeneity of particles increases.

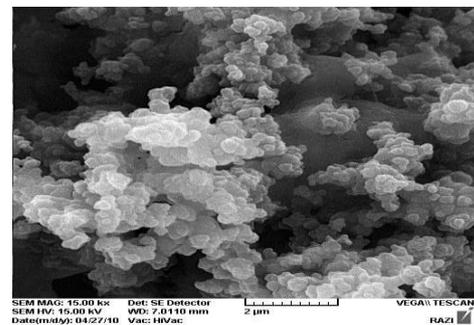


Fig. 3. SEM of Polypyrrole Nanocomposite Generated in Aqueous/Non-aqueous Media.
Reaction Conditions: $\text{FeCl}_3 = 54 \text{ g/L}$, Pyrrole Monomer = $14.45 \times 10^{-2} \text{ mol/L}$,
Volume of Solution = 100 mL, Reaction time = 5 h at Room Temperature.

The chemical structure of the obtained products was determined by FTIR spectroscopy, which has provided valuable information regarding the formation

of polypyrrole composite. The FTIR spectra analysis has been done to identify the characteristic peaks of products. The FTIR spectra in the 2500-450 cm^{-1} region for PPY composites were shown in Fig. 4.

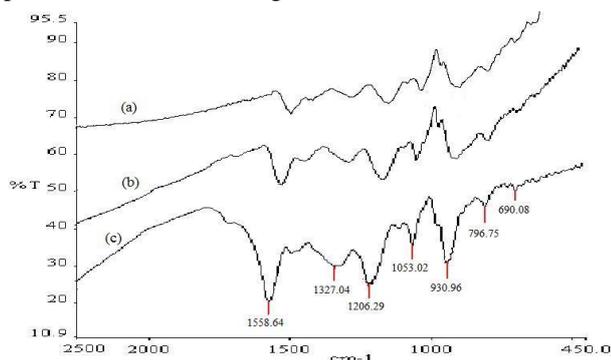


Fig. 4. FTIR Spectra of (a) PPY without Surfactant in Aqueous Media, (b) PPY without Surfactant in Aqueous/non-aqueous Media and (c) PPY/PVA (PVA used as Surfactant in Aqueous Media).

As can be seen, the FTIR spectrum changed when the composites were obtained in various conditions. As can be seen in Fig. 4(c) the peak related to pyrrole unit at 1558 cm^{-1} . The peaks are at 1327 cm^{-1} (C-N stretching vibration), 1206 cm^{-1} (C-H in-plane deformation), 1053 cm^{-1} (N-H in-plane deformation), 930 cm^{-1} (C-H out-of-plane deformation) and 796 cm^{-1} (C-H out-of-plane ring deformation). Comparison between Figs. 4(a) and (b) didn't show any significant variation and peaks are nearly similar, because there wasn't any surfactant in both of them. While in Fig. 4(c) because of the PVA presence intensity of peaks increased.

Thermal properties of polypyrrole have been studied using differential scanning calorimeter (DSC). The DSC thermogram of the polypyrrole was shown in Fig. 5. Normally, a glass transition appears temperature as a sudden change in slope in the DSC curve but sometimes it appears as an endothermic peak. The endotherm observed in thermogram (Fig. 5) is attributed to the glass transition temperature of the polypyrrole (189°C).

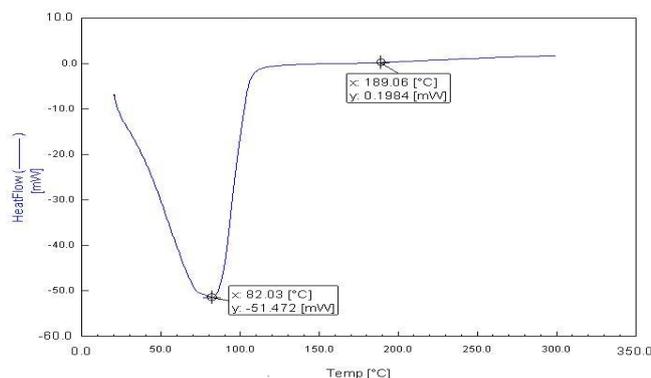


Fig. 5. DSC Thermogram of Polypyrrole Generated in Aqueous Media. Reaction Conditions: $\text{FeCl}_3 = 54 \text{ g/L}$, Pyrrole Monomer = $14.45 \times 10^{-2} \text{ mol/L}$, Volume of Solution = 100 mL, Reaction Time 5 h at Room Temperature.

3.2. Batch adsorption experiments

Adsorption experiments were performed by agitating 500 mg of nanocomposite with 50 mL of nickel ions solution of desired concentration at room temperature on a mixer. The mixer speed was 500 rpm throughout the study. At the end of predetermined time intervals, the solution was filtered and the concentration of nickel ions was determined.

All experiments were carried out twice and the adsorbed nickel ions concentrations were the means of duplicate experimental results. Experimental variables considered were initial concentration of nickel ions 100 mg/L; contact time between nanocomposite and nickel ions solution 5–60 min; pH of solution 2.55-12; dosage of adsorbent 1.25-7.5 g/L. The amount of adsorption at equilibrium (mg/g), was computed as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_o and C_e are the initial and equilibrium solution concentrations (mg/L), respectively, V is the volume of solution (L) and m (g) is the weight of adsorbent.

3.2.1. Effect of pH

The pH plays a major role on removal of metal ions. The effect of pH on the adsorption uptake of nickel ions was investigated in various pH regions with H_2SO_4 and NaOH solutions. The pH of solution affects the surface charge of the adsorbent and subsequently the removal percentage. Table 1 shows the effect of pH on the removal percentage of the studied metal ions. It is clear that removal percentage was poorly change at neutral and acidic pH. Maximum removal was achieved at alkaline pH for nickel. In alkaline pH the adsorption uptake increases due to the increase in the electrostatic attractive forces between OH^- and Ni^{2+} . Whereas at pH values below 3, the adsorption uptake was very weak due to the competition between Ni^{2+} and H^+ in the solution.

Table 1. Effect of pH on Removal Percentage of Nickel.

Adsorbent	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Removal percentage (% w/w)
PPy	2.55	100	25.72	74
	5.67	100	25.94	74
	7.28	100	23.96	76
	9.84	100	20.47	79
	12	100	16.05	84

3.2.2. Effect of contact time

For performing this experiment, 0.5 g PPy was treated with 50 mL of 100 mg/L nickel solution for different time periods (5-60 min) accompanied by stirring at room temperature. The adsorption profile obtained from the analysis of unabsorbed nickel solution is shown in Fig. 6. As the results indicate, removal of nickel using the PPy occurs quickly and it is not a highly time-dependent process.

It was found that about 74% removal of nickel occurs within 30 min. This confirms a high and rapid adsorption of nickel by PPy adsorbent.

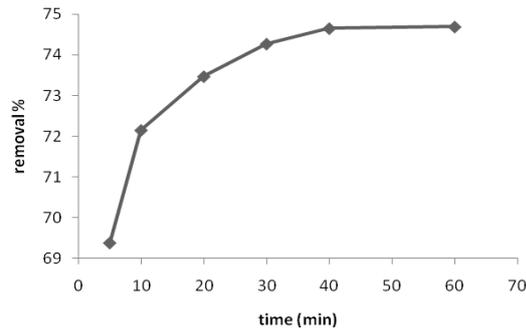


Fig. 6. Effect of Contact Time on Removal Percentage of Nickel Using PPy.

3.2.3. Effect of adsorbent dosage

The effect of adsorbent dose on the amount of nickel ions removal was studied at room temperature and at initial nickel solution concentration of 100 mg/L by allowing a contact time of 30 min. The results are presented in Fig. 7. It is evident from the figure, the amount of nickel ions uptake per gram of adsorbent increased by increasing the amount of adsorbent dose. This is due to the availability of higher number of polypyrrole ions per unit volume of solution.

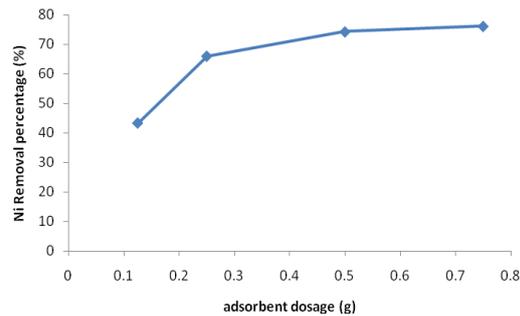


Fig. 7. Effect of Adsorbent Dosage on Removal Percentage of Nickel using PPy.

3.2.4. Comparison of adsorbent type on removal percentage

The adsorption capacity of polypyrrole for removal of nickel has been compared with other adsorbents such as PPy/PVA composite, PPy in aqueous/non-aqueous solution, activated carbon, anthracite and purolite. The effect of different adsorbents in nickel removal is demonstrated in Table 2. As it can be seen, the maximum removal percentage was obtained 97% (w/w), for purolite. The PPy/PVA composite in alkaline media has a desirable adsorption capacity than the other adsorbents. By using PVA as a surfactant the removal percentage increases, because the total surface area of adsorbent increases as the particle size decreases. Also PPy synthesized in water/ethyl acetate solution has an acceptable removal percentage and also it's because of increasing in adsorption surface area.

Table 2. Effect of Adsorbent Type on Removal Percentage of Nickel.

Type of Adsorbent	pH	Initial concentration (mg/L)	Final Concentration (mg/L)	Removal percentage (% w/w)
PPy prepared in aqueous media	12	100	16.05	84
PPy/PVA prepared in aqueous media		100	9.18	91
PPy prepared in aqueous/non-aqueous media		100	11.87	88
Activated carbon		100	20.14	79
Anthracite		100	18.33	81
Purolite		100	2.14	97

3.2.5. Equilibrium studies

In order to optimize the design of a sorption system to remove chromium, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested in the present study, namely; Langmuir and Freundlich. The goodness of fit between experimental data and the model predicted values was expressed by the correlation coefficient (R^2 , values close or equal 1).

(a) The langmuir Isotherm

The widely used Langmuir isotherm has found successfully application in many real sorption processes [29-35] and is expressed as:

$$q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (2)$$

A linear form of this expression is:

$$\frac{1}{q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m} \quad (3)$$

where C_e (mg/L) is the equilibrium liquid phase concentration of total chromium, q_e (mg/g) is the total chromium adsorption capacity at equilibrium, Q_m the monolayer adsorbent capacity and b is the energy constant of adsorption. The values of the Langmuir constants were presented in Table 3 and the theoretical Langmuir equation was shown in Fig. 8.

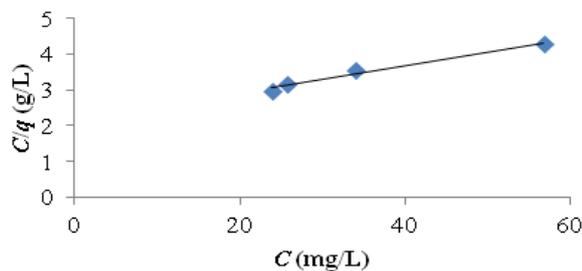


Fig. 8. Langmuir Isotherm for the Removal of Nickel.

(b) The Freundlich Isotherm

The well known Freundlich isotherm is often used for heterogeneous surface energy systems [29, 31, 36]. The Freundlich equation is given as:

$$q_e = KC_e^{1/n} \quad (4)$$

A linear form of this expression is:

$$\log q_e = \log K + \frac{1}{n} \log C \quad (5)$$

where K is the Freundlich constant and n the Freundlich exponent. K and n can be determined from the linear plot of $\log q_e$ versus $\log C_e$. The values of the Freundlich constants were presented in Table 3 and the theoretical Freundlich equation was shown in Fig. 9.

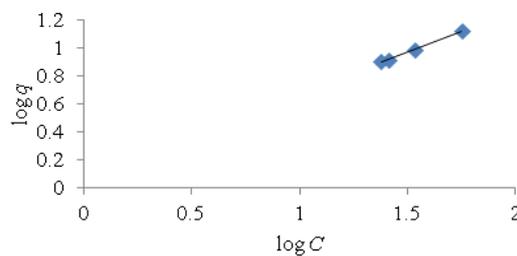


Fig. 9. Freundlich Isotherm for the Removal of Nickel.

Table 3. Isotherm Model Constants and Correlation Coefficients for Adsorption of Nickel.

Model					
Langmuir			Freundlich		
R^2	Q_o (mg/g)	b (L/mg)	R^2	k	n
0.986	26.37	0.017	0.998	1.677	1.191

4. Conclusions

Polypyrrole conducting polymer can be easily synthesized via chemical polymerization. In this study, the effect of various agents on removal of nickel from water using PPy was investigated and the results were compared with various adsorbents such as anthracite, purolite and activated carbon. The study indicated the suitability of the adsorbents used for removal of nickel aqueous solution. The polypyrrole composite has shown considerable potential for the removal of nickel from aqueous solution. The results may be summarized as follows:

- The results indicate that the pH of solution had an effect on the amount of adsorption. Alkaline pH range was found as the favourable condition for maximum nickel removal.

- Because of the availability of higher number of polypyrrole ions per unit volume of nickel solution, the amount of nickel ions uptake per gram of adsorbent increased by increasing the adsorbent dose.
- Surfactant as a stabilizing agent could affect the size, morphology and homogeneity of particles, because the surface active agents are adsorbed physically by the growing polymer.
- The adsorption isotherm studies shown that Langmuir and Freundlich adsorption isotherm model fits well with the experimental data.
- Comparison between all adsorbents, the results show that a desirable adsorption capacity for polypyrrole composites especially for PPy/PVA composite.

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