PREPARATION OF NEW CONDUCTIVE POLYMER NANOCOMPOSITES FOR CADMIUM REMOVAL FROM INDUSTRIAL WASTEWATERS

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ABSTRACT

Different conductive polymer nanocomposites have been synthesized, characterized and tested, regarding the removal of cadmium from industrial wastewaters. The chemical structure and morphology are studied by FTIR spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The cadmium removal performance, using the produced polypyrrole, polyaniline and polythiophene nanocomposites, are about 40.2 %, 59 % and 99.94 %, respectively, suggesting the superior performance of synthesized polythiophene conductive nanocomposite for cadmium removal from industrial wastewaters. It is shown that the Langmuir adsorption model can be used for accurate description of cadmium removal mechanism using different synthesized conductive nanocomposites.

Keywords : wastewater, nanocomposite, polythiophene, cadmium removal, conductive polymer.

INTRODUCTION

Heavy metal pollution is a common environmental problem facing many places worldwide with the rapid development of economy and industry [1]. Numerous metals such as mercury, lead, cadmium, etc. are known to be highly toxic. Cadmium, like other heavy metals, can be introduced into surface waters by industrial effluents in amounts significant to human health [2]. The increasing presence of cadmium in the environment is mainly due to its use in phosphate fertilizer, stabilizers, alloys, ceramics, pigments, battery and electroplating plants [3 - 5]. Cadmium is a naturally occurring metal that is known to be extremely toxic in any of its different chemical forms such as chloride, sulfate, sulfide, carbonate, oxide, etc. [6].

Human toxicity with cadmium is usually related to smoking, refined foods, water pipes, coffee and tea, coal burning, and shellfish. High percent of accumulated cadmium is deposited and retained in the kidney and liver based on its strong ability to replace the essential mineral zinc in these organs of the human body [7]. Cadmium can cause serious damage to the liver and kidneys such as emphysema, bone disorders, cancer [8, 9], hypertension and testicular atrophy; it combines with the some of the chemical groups in protein and restrains the activity of enzymes [10].

The methods used for the removal of heavy metals are chemical precipitation, ion exchange [11-13], complexation using natural and synthetic reagents [14-16], reverse osmosis, electrodialysis, electro chemical reduction membrane processes, adsorption layer by layer chemical deposition technique [17], etc. Adsorption process is the most frequently applied method in

Various materials have been reported for the removal of cadmium from wastewaters such as natural soils [18], minerals [19], tailing wastes and biomasses [20 - 23], waste Fe (III)/Cr (III) hydroxide [24], red mud and fly ash [17], spent grain [25], silica gel and alumina [22], processed solid residue of oil mill products [26], tea industry waste [27], rice husk ash [28], calcite, hydroxyapatite (29), nanocrystallite hydroxyapatite (17), amino modified starch (30), olive leaves (31), activated carbon (32 - 35). New adsorbents that are locally available with high adsorption capacity and economic materials are still needed. Pore size, pore distribution and surface area, as well as pore surface chemistry, are the major factors in the adsorption [36].

In this research, different conductive polymer nanocomposites such as polypyrrole, polyaniline and polythiophene have been synthesized and tested regarding the removal of Cd(II) from aqueous solution.

EXPERIMENTAL

Materials

All the reagents used in the present study have been purchased from Merck and Aldrich companies. Stock solutions of cadmium have been prepared by dissolving cadmium chloride (CdCl₂, H₂O) in doubly distilled water, Other materials used are (NH₄)₂S₂O₈, NaOH, HNO₃, HPC, FeCl₃, H₂O₂ 30%, aluminum oxide and sulphuric acid, pyrrole (C₄H₅N), thiophene (C₄H₄S) and aniline (C₆H₇N). The monomers are distilled before the polymerization.

A magnetic mixer model MK20, digital scale model FR 200, atomic absorption device Perkin-Elmer model Thermo electron, pH meter model 211 HANNA, scanning electron microscope (SEM) model KYKY-EM3200 and Fourier transform infrared (FTIR) spectrometer have been employed.

Polyaniline nanocomposite preparation

For the preparation of polyaniline (PAn), 0.6 g KIO₃ was added to 100 mL sulphuric acid (1M) and the solution was maintained by a magnetic mixer. Then, 1 mL of the fresh distilled monomer was added to the stirred aqueous solution. The reaction was carried out for 5 h at room temperature. Consequently, the resulted polymer was filtered to separate the oligomers and impurities. The synthesized product was washed several times with deionized water and dried at room temperature.

Polypyrrole nanocomposite preparation

For the preparation of polypyrrole (PPy) 5.4 g FeCl₃ was added to 100 mL of water and the uniform solution was maintained by a magnetic mixer. Then, 1 mL fresh distilled monomer was added to the stirred aqueous solution. The reaction was carried out for 5 h at room temperature.

Fig. 1. Schematic illustrations of polymer repeat units for (I) emeraldine base, (II) polaron form of emeraldine salt, and (III) bipolaron form of emeraldine salt.
temperature. Consequently, the resulted product was filtered to separate the oligomers and impurities. The synthesized product was then washed several times with deionized water and dried at room temperature.

**Polythiophene nanoparticles preparation**

The polythiophene (PT) nanoparticles are synthesized by iron (III) catalyzed oxidative polymerization in aqueous medium using thiophene as monomer, FeCl$_3$ as an oxidant and H$_2$O$_2$ as a co-oxidant. For a typical synthesis, the thiophene monomer (2 mL) is dissolved in 50 mL distilled water and after 15 min, the co-oxidant H$_2$O$_2$ (7.5 mL) is added to the solution. FeCl$_3$ (0.02 gr) is also dissolved in 50 ml deionised water and after 15 min, the aluminum oxide (1g) is added to the resulting solution. After 15 min, the mixture is then added to the first one. The reaction is carried out for 5 h at room temperature. After 5 hours a dark-brown precipitate of polythiophene is obtained. Finally, the product is dried at 60°C in an oven for 12 h.

**Nanocomposite characterization**

**Morphology**

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 [14]. Polyaniline (PAn) has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. The amine group of aniline is transformed into protonated form by sulfuric acid [11]. The surface morphology of products was studied, using scanning electron microscope. As shown in Figs. 2 - 5, the size and homogeneity of particles are dependent on the type of surfactant. Comparing the results in Figs. 3 - 5 it is evident that the surfactant strongly influence the particle size and homogeneity of particles. Conductivity of PAn increases by using DBSNa, because DBSNa is an ionic surfactant. As shown in Figs. 2 - 5, the size and homogeneity of particles are dependent on the additive and steric stabilizer. This is presumably due to the amount of adsorbed chemically surfactant to the polyaniline particles. Surface active agents affect the physical and chemical properties of the solutions. The surfactant is known to influence the rate of polymer formation, particle size, size distribution, morphology and homogeneity.

**FTIR spectroscopy**

The structure of the obtained product is determined by FTIR spectrum. The peak locations, related to the corresponding chemical bonds, are in a good agreement with those reported in the literature [15]. FTIR spectra in the 3000 - 450 cm$^{-1}$ region, for pure PAn and for other nanocomposite, are shown in Fig. 6. As can be seen, the FTIR spectrum changes when the composite was formed using a surfactant. For instance, pure PAn polymer shows the presence of characteristic absorption bands at 1563 cm$^{-1}$ (C=C stretching vibration of the quinoid ring), 1469 cm$^{-1}$ (stretching vibration of C=C of the

![Fig. 2. SEM image of pure PAn.](image1)

![Fig. 3. SEM image of PAn/Al$_2$O$_3$.](image2)
benzenoid ring), 1298 cm\(^{-1}\) (C-N stretching vibration), 1055 cm\(^{-1}\) (C-H in-plane deformation), 882 cm\(^{-1}\) (C-H out-of-plane deformation).

**X-ray diffraction**

Polyaniline is inherently amorphous and hence there are no sharp peaks for polyaniline. All peaks in the XRD pattern are in agreement with the literature values of aluminium nanoparticles [16] and are indexed in the terms of the face-centered cubic (FCC) structure of aluminium. The main peaks in the XRD pattern of pure PAN are observed at \(2\theta = 17.8^\circ, 25.15^\circ,\) and \(32.6^\circ\). The characteristic peaks ascertained for PAN/Al\(_2\)O\(_3\) nanocomposite are at \(2\theta = 29.2^\circ, 40.8^\circ, 43.22^\circ\) and \(50.74^\circ\). These extra peaks in the XRD pattern of nanocomposites verify the presence of aluminium nanoparticles in the polyaniline matrix. The broad peak with \(2\theta = 25.15^\circ\) is connected with the diffraction of amorphous polyaniline. The diffraction peak at the \(2\theta = 25.15^\circ\) of PAN/Al\(_2\)O\(_3\) nanocomposite is relatively more intense compared to the polyaniline’s one. A probable reason is the increase of effective delocalization in polymer chains in pres-
ence of negatively charged aluminium nanoparticles. All diffraction peaks observed in the XRD pattern of aluminium nanoparticles correspond to the crystalline phase. It should be noticed that the diffraction peaks of aluminium are relatively wide due to the nanosize of the crystalline particles. The average crystallite size is estimated from the integral intensity of the X-ray diffraction peak maximum using the Scherrer’s equation [16]:

$$\beta = k\lambda / D\cos\theta$$  \hspace{1cm} (1)

where $\lambda$ is the X-ray wavelength, $k$, the shape factor, $D$, the average diameter of the crystals in angstroms, $\theta$, the Bragg angle in degree, and $\beta$ is measured by half-height in radians. The value of $k$ depends on several factors, including the miller index of inflection plane and the shape of the crystal. If the shape is unknown, $k$ is often assigned a value of 0.89. The crystallite size of aluminium in the nanocomposite, calculated by eq. (1), is about 80 nm. When the reflecting peak at $2\theta = 29.2^\circ$ is chosen for calculating the average diameter, the average size of the PAN/Al$_2$O$_3$ produced particles is about 86 nm. X-ray scattering patterns of pure PAN, Al$_2$O$_3$ and PAN/Al$_2$O$_3$ are shown in Figs. 7 - 9.

**Batch Adsorption Experiment**

Completely mixed batch reactor (CMBR) technique is used to remove cadmium from aqueous solution. A 25 mL of solution is added to the beaker containing 0.25 g of the adsorbent. At the end of predetermined time intervals, the sorbate is filtered and the concentration of Cd (II) is determined. All experiments are carried out two times. Experimental variables considered are initial concentration of Cd (II), contact time between adsorbent with cadmium solution, solution pH and dosage of adsorbent. Atomic fluorescence spectrophotometer is used for the analysis of Cd (II) in the aqueous solution.

**RESULTS AND DISCUSSION**

The solution pH is one of the most important variables governing the metal adsorption. This is partly due to the fact that hydrogen ions themselves are strong competing ions and partly that the solution pH influences the chemical speciation of the metal ions as well as the ionization of the functional groups onto the adsorbent surfaces. The pH of the solution affects the charge on
the surface of the adsorbents, so the change in pH also affects the adsorption process and the H\(^+\) ion may react with the functional groups on the active sites on the adsorption surface.

To evaluate the influence of this parameter on the cadmium adsorption, the experiments are carried out at different initial pH (3, 5, 7, 10) values. The effect of pH on adsorption efficiencies with PAN/Al\(_2\)O\(_3\)-HPC (hydroxypropylcellulose) nanocomposite is shown in Table 1. Removal of cadmium ions increases with the decreasing of the solution pH and a maximum value is always reached at an equilibrium pH of around 3. The cadmium ions adsorption may be due to the complexation between cadmium ions and the nitrogen atoms of the -N=C- groups through sharing their one lone pair of electrons. Comparison of PAN and PAN/Al\(_2\)O\(_3\)-HPC nanocomposite regarding the removal of Cd ions from aqueous solution suggests that the PAN/Al\(_2\)O\(_3\)-HPC nanocomposite has better effectiveness for the removal of Cd ions from aqueous media in comparison with polyaniline as adsorbent.

The performance of the synthesized nanocomposite adsorbents regarding cadmium removal from aqueous solutions are also displayed in Table 2. As shown, the maximum adsorption efficiency, 99.94\%, is obtained with the polythiophene nanocomposite. This shows the possibility of polythiophene conductive nanocomposite for complete removal of cadmium from the wastewaters.

The more common models used to investigate the adsorption isotherm are Langmuir and Freundlich equations. The experimental results of this study are fitted with these two models. The equilibrium adsorption capacity of the adsorbent is calculated by:

\[
q_e = \frac{(C_o - C_e)V}{m}
\]

where \(q_e\) is the equilibrium adsorption capacity of adsorbent in mg cadmium/g adsorbent, \(C_o\) is the initial concentration of the cadmium ions in mg/L, \(C_e\) is the equilibrium concentration of metal ions in mg/L, \(V\) is the volume of cadmium ions solution in L, and \(W\) is the mass of the adsorbent in g. The equilibrium adsorption capacity of a typical synthesized nanocomposite is always measured after a long time when the equilibrium condition is maintained.

The accuracy of the Langmuir adsorption equation for description of cadmium adsorption process using the synthesized nanocomposites is examined in this work. The Langmuir equation is given as:

\[
C_e = \frac{1}{q_mK_L} + \frac{C_e}{q_m}
\]

where \(q_m\) is the monolayer capacity of the adsorbent (mg/L) and \(K_L\) is the Langmuir equilibrium constant.

Table 1. Effects of the adsorbents and pH regarding Cd(II) removal.

<table>
<thead>
<tr>
<th>Type of adsorbent</th>
<th>pH</th>
<th>Removal percent (%) w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>PAN/Al(_2)O(_3)-HPC</td>
<td>3</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>32</td>
</tr>
</tbody>
</table>
(L/mg). Using the linear form of this isotherm, the plot of \( C_e/q_e \) versus \( C_e \) gives a line with a slope of \( 1/q_m \) and an intercept of \( 1/q_mK_L \). Linear plots of \( C_e/q_e \) versus \( C_e \) regarding three different synthesized nanocomposites are displayed in Fig. 10. The best fitted values of the model parameters obtained by linear regression analysis and the corresponding correlation coefficients (R²) are presented in Table 3. The R² values regarding polyaniline (PAn), polypyrrole (PPy) and polythiophene (PT) nanocomposites are about 0.9893, 0.9638 and 0.9927, respectively. For the special case of polythiophene (PT), the Langmuir model is in excellent agreement with the measured data.

Freundlich equation is also examined regarding the cadmium adsorption on nanocomposites synthesized in this work. The Freundlich equation is as follows:

\[
q_e = K_F C_e^{1/n}
\]

The linear form of the above expression is:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \( q_e \) (mg/L) is the amount adsorbed at the equilibrium concentration \( C_e \) (mg/L), \( K_F \) is the Freundlich constant (L/g) which represents the strength of the adsorptive bond, \( n \) is the heterogeneity factor, which represents the bond distribution. According to Eq. (4), the plot of the log \( q_e \) versus log \( C_e \) gives a straight line and \( K_F \) and \( n \) values can be determined from the intercept and slope of a straight line, respectively.

Linear plots of log \( q_e \) versus log \( C_e \) regarding three different synthesized nanocomposites are displayed in Fig. 11. The best fitted values of the model parameters obtained by linear regression analysis and the corresponding correlation coefficients (R²) are presented in Table 4. The R² values regarding polyaniline (PAn),

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial concentration (ppm)</th>
<th>Final concentration (ppm)</th>
<th>Removal percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline nanocomposite (PAn)</td>
<td>50</td>
<td>25.6</td>
<td>59</td>
</tr>
<tr>
<td>Polypyrrole nanocomposite (PPy)</td>
<td>50</td>
<td>29.9</td>
<td>40.2</td>
</tr>
<tr>
<td>Polythiophene nanocomposite (PT)</td>
<td>50</td>
<td>0.03</td>
<td>99.94</td>
</tr>
</tbody>
</table>

Table 2. Cadmium removal by the synthesized conductive nanocomposites.

<table>
<thead>
<tr>
<th>Langmuir parameters</th>
<th>PAn nanocomposite</th>
<th>PPy nanocomposite</th>
<th>PT nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_m (mg g⁻¹)</td>
<td>13.7741</td>
<td>6.4683</td>
<td>17.4825</td>
</tr>
<tr>
<td>K_L (L mg⁻¹)</td>
<td>0.0134</td>
<td>0.0205</td>
<td>0.251</td>
</tr>
<tr>
<td>R²-value</td>
<td>0.9893</td>
<td>0.9638</td>
<td>0.9927</td>
</tr>
</tbody>
</table>

Table 3. Langmuir adsorption isotherm constants regarding cadmium uptake by PAn, PPy and PT nanocomposites.
polypyrrole (PPy) and polythiophene (PT) nanocomposites are 0.9876, 0.8336 and 0.9739, respectively. Since the $R^2$ values according to the Langmuir model are always higher than those of Freundlich model, it can be concluded that the cadmium adsorption mechanism for the synthesized nanocomposites can be accurately described by the Langmuir adsorption model. For the special case of polythiophene (PT) nanocomposite, the predicted results according to the cadmiums, the Langmuir adsorption model is in excellent agreement with the measured data with the $R^2$ value of 0.9927.

<table>
<thead>
<tr>
<th>Freundlich parameters</th>
<th>PAN nanocomposite</th>
<th>PPy nanocomposite</th>
<th>PT nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_F$</td>
<td>0.6884</td>
<td>0.4821</td>
<td>8.2110</td>
</tr>
<tr>
<td>$n$</td>
<td>1.9153</td>
<td>2.1358</td>
<td>6.4766</td>
</tr>
<tr>
<td>$R^2$-value</td>
<td>0.9876</td>
<td>0.8336</td>
<td>0.9739</td>
</tr>
</tbody>
</table>

Table 4. Freundlich adsorption isotherm parameters regarding cadmium uptake by PAN, PPy and PT nanocomposites.
CONCLUSIONS

Three conductive polymer nanocomposites have been synthesized and tested regarding the removal of Cd(II) from industrial wastewaters. The cadmium removal performance using the produced polypyrrole, polyaniline and polythiophene nanocomposites is 40.2 %, 59 % and 99.94 %, respectively. It is shown that the cadmium adsorption mechanism of the synthesized nanocomposites can be described by the Langmuir adsorption model. For the case of polythiophene (PT) nanocomposite, the predicted results according to the proposed Langmuir adsorption model, is in excellent agreement with the measured data with the R² value of 0.9927. The synthesized polythiophene (PT) conductive polymer nanocomposite with 99.94 % removal efficiency, is an excellent alternative for cadmium removal from industrial wastewaters.

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