

POLYMER ADSORBENT FOR THE REMOVAL OF LEAD IONS FROM AQUEOUS SOLUTION

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Abstract— Polypyrrole (PPy) conducting polymer prepared by chemical oxidation using FeCl₃.6H₂O as an oxidant has exhibited 100% adsorption efficiency for the removal of Pb(II) ions from aqueous solution. Batch adsorption results showed that pH plays a major role on lead ion adsorption. At pH 7, 100% lead absorption was found as measured by atomic absorption spectrophotometry. At both acidic and alkaline solutions, the adsorption efficiency of PPy was substantially lowered. The effects of other important parameters such as the initial concentration of lead stock solution, the sorbent dosage and the contact time on the uptake of Pb(II) ions were also investigated to identify the optimum adsorption. The experimental data fitted well to the Langmuir isotherm. The FTIR and EDX results confirmed the presence of Pb(II) ions in the polymer matrix after adsorption. The prepared PPy adsorbent showed a surface area of 5.04 m²/g as measured by BET analysis. The SEM micrographs looked similar for both the post and pre-adsorption of lead ions by the polymer.

(key words) polypyrrole, adsorption, conducting polymer, wastewater, heavy metals.

I. INTRODUCTION

The presence of heavy metals in the aqueous stream is a great health concern around the world. Heavy metals being toxic and lethal to the human beings and aquatic lives have attracted much attention for its removal from aqueous stream [1-4]. Heavy metals like lead, mercury, zinc, copper, nickel etc. are widely used in industries in various manufacturing processes. These heavy metals tend to accumulate in living bodies through the food chain and direct uptake. It may cause hypertension, reproductive disorders, neurological and metabolic problems for human beings [5].

Various techniques have been employed for the removal of heavy metals from water environment including precipitation, adsorption, ion-exchange and reverse osmosis [6]. Among these, adsorption is one of the most extensively used methods. Many adsorbents have been studied for the removal of heavy metals from wastewater and industrial effluents such as activated carbon [7-8], silicates [9-10], natural zeolite [11], clinoptilolite [12], peat [13], chitosan polymer [14-15] and biomass [16-18].

However, as a new type of polymer adsorbent, conducting polymers have drawn much attention to the researchers for the removal of various heavy metals, dyes and organic pollutants from various water sources due to its ion exchange and adsorption properties [2-4, 19-21]. Polypyrrole and polyaniline conducting polymers coated individually on sawdust via cast method were investigated for the removal of heavy metals and organic pollutants from paper mill wastewater [20]. Polypyrrole-sawdust nanocomposite was also studied for the removal of Zn from aqueous solution with an efficiency of 95.7% [21].

A lot of efforts have been made to remove hexavalent chromium ion from wastewater using conducting polymers and its composites [22-24]. Selective adsorption of Cr(VI) ion from

aqueous solution was achieved in the presence of other co-existing ions using polypyrrole-polyaniline (PPy-PANI) nanofiber [1]. The maximum adsorption capacity of the PPy-PANI nanofibers for Cr(VI) was 227 mg/g. PPy nanoclusters have been found to remove 3.47 mmol/g of Cr(VI) ion in aqueous solution at pH 5 which was higher than the commercial activated carbon and traditional PPy nanoparticles [25].

Polyaniline [26] and its composites [27] were used to remove mercury from wastewater. Wang et al., [26] reported 58% removal of mercury from water solution at pH 5.5 using polyaniline prepared by chemical oxidation method. The removal of arsenic from wastewater using different composites of PPy has been reported by Eisazadeh [28]. The composites of PPy with polyvinyl alcohol, polyethylene glycol, activated carbon and bentonite have shown the arsenic removal efficiency of 64.66%, 83.33%, 6.44% and 97.33%, respectively, from wastewater. Polypyrrole-impregnated porous carbon has been shown to adsorb heavy metals like Hg, Pb and Ag ions from solutions with 20 times higher capacity than that of adsorbents with amine functional groups such as chitosan-containing membranes [19].

Many efforts have been done so far to remove heavy metals from aqueous environment using various polypyrrole composites. But very little effort has been done to use polypyrrole alone as an adsorbent without forming any composites for the removal of lead ions from aqueous solution. Since the heavy metal removal efficiency depends on the synthesis conditions of conducting polymer, hence, our present effort has been made to evaluate polypyrrole alone as an effective adsorbent for the removal of lead ions from aqueous solution without forming any of its composites.

II. EXPERIMENTAL

All the reagents used were of high purity. The monomer pyrrole (Sigma-Aldrich) was distilled prior to use. Ferric chloride (FeCl₃.6H₂O) (Sigma Aldrich) was used as an oxidant. Stock solutions of lead were prepared by dissolving lead nitrate in distilled water. HCl (Sigma Aldrich) and NaOH (Sigma Aldrich) were used to control the pH of the stock solution.

III. CHARACTERIZATION

The concentration of heavy metals in aqueous samples was analyzed by using an atomic absorption spectrophotometer (VARIAN Spectra A-10 PLUS) in an air-acetylene and nitrous oxide-acetylene flame. To determine the calibration curve, different concentrations of lead stock solutions were prepared. The correlation coefficient of the plot was 0.9998 which reflects the accuracy of the analysis. The Fourier-transform infrared (FT-IR) analysis was performed in wavenumbers ranging from 400-4000 cm⁻¹ using a FTIR-400, Perkin Elmer spectrophotometer. The surface area and pore volume were measured by Brunauer Emmett Teller (BET) surface area

analyzer (Autosorb 6B, Quanta chrome). A scanning electron microscope PHENOM PROX was used to look into the morphology of PPy adsorbent before and after adsorption.

IV. SYNTHESIS OF THE ADSORBENT

Generally, polypyrrole can be formed chemically through the oxidative polymerization of pyrrole monomer using various oxidants in aqueous and non-aqueous solutions [29]. The final form of polypyrrole is a long conjugated backbone of pyrrole monomer (Fig. 1). In this present effort, polypyrrole has been prepared by chemical method using FeCl₃.6H₂O as an oxidant in aqueous solution. In a typical experiment, 0.33 g of pyrrole and 1.35 g of FeCl₃.6H₂O (1:1 mole ratio of monomer to oxidant) was taken in 50 ml of distilled water under stirring condition. The color of the mixture gradually changed from green to black showing that polymerization was in progress. After 1 h of polymerization, the polymer mixture was filtered. The black polymer mass was then washed several times with deionized water and dried in an oven at 60 °C for 24 hours.

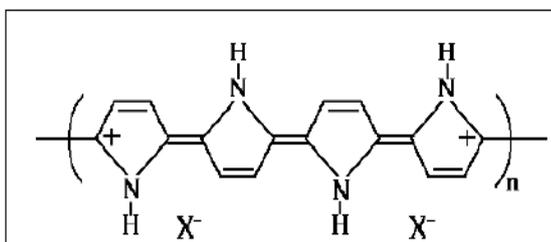


Fig.1. Structure of polypyrrole formed through oxidative polymerization.

V. BATCH ADSORPTION EXPERIMENTS

The batch adsorption experiments were carried out with 0.08 g of polypyrrole adsorbent added in 25 ml of lead solution having a concentration of 1, 5, 10 and 15 ppm in the pH range of 2-8 in a shaker operated at 200 rpm for 8 hours. Later the solution was filtered. The concentration of lead in the filtrate was determined by atomic adsorption spectroscopy (AAS).

The lead ion removal efficiency, E, was determined by using Eq. (1).

$$E = \frac{C_0 - C_e}{C_0} \times 100 \quad \dots\dots\dots \text{Eq. 1}$$

Where C₀ and C_e are the initial and equilibrium concentrations (mg/L) of lead ions, respectively.

A. Effect of initial concentration

The effect of initial lead ion concentration on the percentage of lead ion removal from aqueous solution is shown in Fig. 2. It shows that the efficiency of lead ion removal gradually decreased from 100% to 88% with the increase in the initial lead ion concentration from 1 ppm to 15 ppm. This is due to the fact that the higher number of lead ions per unit mass of adsorbent restricts its adsorption.

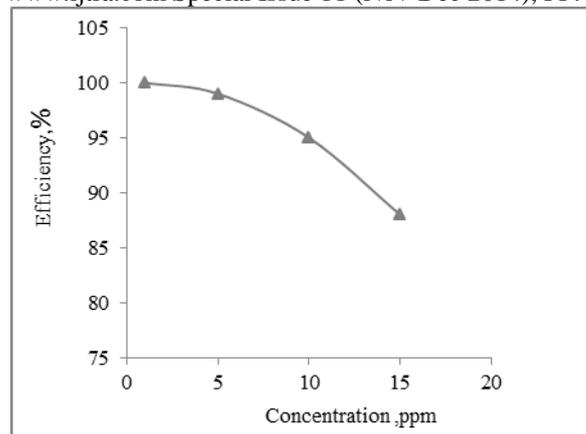


Fig.2. Effect of concentration of lead stock solution on the removal of lead ion from aqueous solution.

B. Effect of pH

One of the important controlling parameters in adsorption is pH. The effect of this factor is shown in Fig. 3. It is evident that the highest percentage (100%) of lead ion removal was found at pH 7. At lower level of pH (pH=2), no adsorption was recorded but with the increase in pH to 7, the efficiency increased up to 100%. Later the adsorption decreased with further increase in pH. At lower pH, mostly amine sites in polypyrrole adsorbent are protonated and cannot facilitate the chelation process. With the increase in pH from 2 to 7, protons are released from the amine functional groups of polypyrrole adsorbent which causes more available active amine sites for the adsorption of lead ions from aqueous solution. With further increase in pH above 7, lead hydroxide formation renders the low adsorption of lead ions by the adsorbent. The similar declining trend of adsorption with the increase in pH above 5 was observed for the removal of heavy metals from aqueous solution by other researchers [1, 3, 30].

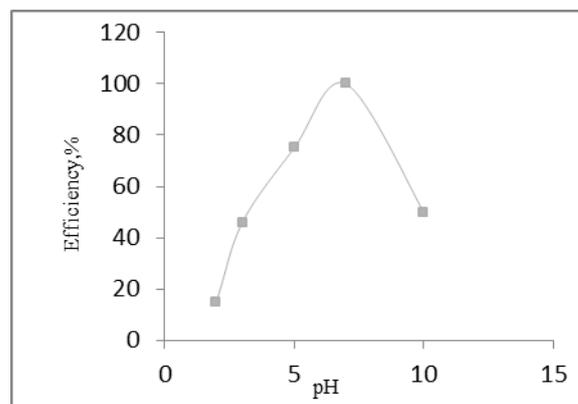


Fig.3. Effect of pH on the removal of lead from aqueous solution.

C. Effect of contact time

Adsorption efficiency of lead ions was measured as a function of time between 30 min to 24 hours by keeping all of the other parameters constant. The effect of contact time on adsorption is shown in Fig. 4. The plot shows that the adsorption efficiency increased with the increase in contact time. The maximum level of efficiency was found in 8 hours at which equilibrium was attained.

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 adsorption capacity (mg/g) of the adsorbent PPy; K_L is the Langmuir adsorption constant (L/mg). When C_e/q_e is plotted against C_e , a straight line with slope $1/q_m$ and the intercept of $1/q_m K_L$ is obtained.

The favorability of an adsorption process can be represented in terms of the dimensionless separation factor R_L , which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \dots \text{Eq.3}$$

Where C_0 the initial cation concentration (mg/L) and K_L is the Langmuir constant (L/mg). The value of R_L represents the adsorption process to be unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $R_L < 1$ and irreversible when $R_L = 0$ [31]. The results of adsorption process carried out at 25 °C, 35 °C and 45 °C. R_L values were found to be between 0 and 1 which confirms that adsorption process is favorable in Langmuir model and the reaction is endothermic. The adsorption isotherm shows the monolayer adsorption properties (Fig. 6).

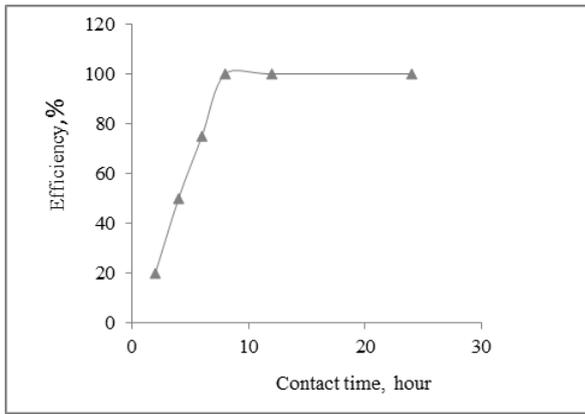


Fig.4. Effect of contact time on the removal of lead from aqueous solution.

D. Effect of initial concentration

The effect of dosage of PPy on the removal of lead ions has been studied (Fig.5). The dosages were varied from 0.04 g to 0.16 g. The equilibrium value was obtained from using 0.08 g of PPy per 25 mL of lead solution at room temperature for 8 hours as it exhibited the highest removal efficiency of 100%. It was observed that with further increase in adsorbent from 0.08 g to 0.16 g, the adsorption efficiency of PPy gradually decreased. This decrease may be due to the reduction of available active sites resulting from PPy agglomeration upon higher dosages of PPy. The same declining trend with the increase in adsorbent after the equilibrium was observed by Karthikeyan *et. al.*, [31] for the removal of fluoride ions from aqueous solution by polypyrrole adsorbent.

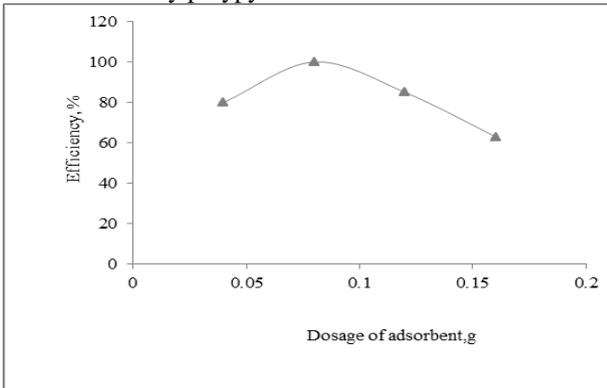


Fig.5. Effect of dosage of adsorbent for the removal of lead ion from aqueous solution.

E. Adsorption isotherm

The distribution of sorbent between the solid and the solution interface at equilibrium has been described by the Freundlich and Langmuir equations. These two models are widely used, the former being purely empirical and the latter assuming that maximum adsorption occurs when the surface is covered by adsorbate [31].

To explore the capacity and thermodynamics of lead ion adsorption by the PPy conducting polymer, adsorption isotherms were studied at three different temperatures, namely, 25 °C, 35 °C and 45 °C.

The linearized Langmuir equation is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \dots \text{Eq.2}$$

Where C_e is the equilibrium cation concentration in liquid phase (mg/L), q_e denotes the equilibrium cation concentration on the adsorbent (mg/g), q_m is the maximum monolayer

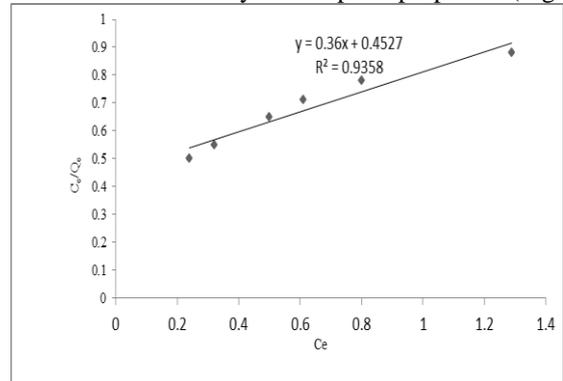


Fig. 6. Langmuir adsorption isotherm.

Freundlich isotherm shows the multilayer heterogeneous adsorption properties. The Freundlich model is mathematically expressed in logarithmic form as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \text{Eq. 4}$$

Where K_f and $1/n$ are the Freundlich isotherm parameters related to multilayer adsorption capacity (mg/g) and intensity of adsorption, respectively.

The correlation coefficient (R^2) for Langmuir and Freundlich equations were found to be 0.9356 and 0.9186, respectively, which indicate that the equilibrium adsorption data is working well under both equation. However, the higher value of R^2 indicates Langmuir as the favorable model for the removal of lead ions from aqueous solution (Fig. 7).

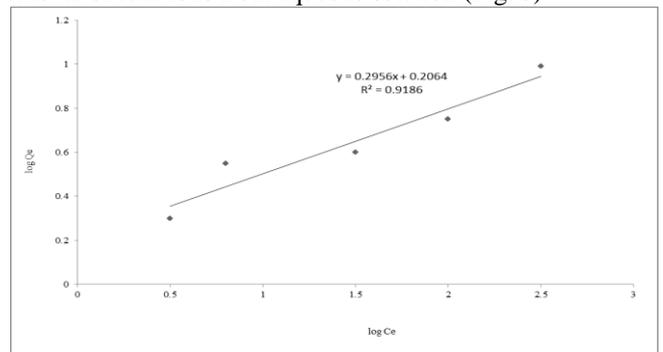


Fig. 7. Freundlich adsorption isotherm.

F. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of PPy before and after lead ion adsorption are shown in Fig. 8. In the spectrum of PPy before lead ion adsorption, it shows that the band at 1520 cm⁻¹ is due to C-C and C=C backbone stretching of PPy and refers to the quinoid formation of polypyrrole. The band at 1432 cm⁻¹ corresponds to the C-N stretching of PPy and refers to the benzenoid form of the polypyrrole. The band at 1276 cm⁻¹ is attributed to C-H and C-N in-plane deformation modes of pyrrole [21]. The band at 1126 cm⁻¹ is related to C-C stretching of pyrrole [29]. The band at 1015 cm⁻¹ is due to N-H wagging and C-H stretching. The band at 756 cm⁻¹ is attributed to C-H wagging vibration. Thus, it shows that all the corresponding bands of PPy (Bhaumik et al., [1]) are present in the spectrum.

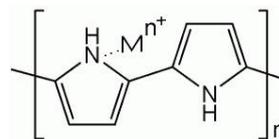


Fig. 9: Schematic diagram of possible metal ion adsorption on the surface of nitrogen functional groups in polypyrrole conducting polymer.

F. Morphology

The SEM micrographs show the morphologies of PPy before and after adsorption of lead ions (Figs. 10 and 11, respectively). There are no significant changes that can be observed from these SEM micrographs except some white patches on the PPy surface after lead ions adsorption. However, clear evidence of lead ions adsorption has already been shown in EDX spectrum (Fig.12). The BET surface area of the prepared PPy adsorbent was found to be 5.04 m²/g.

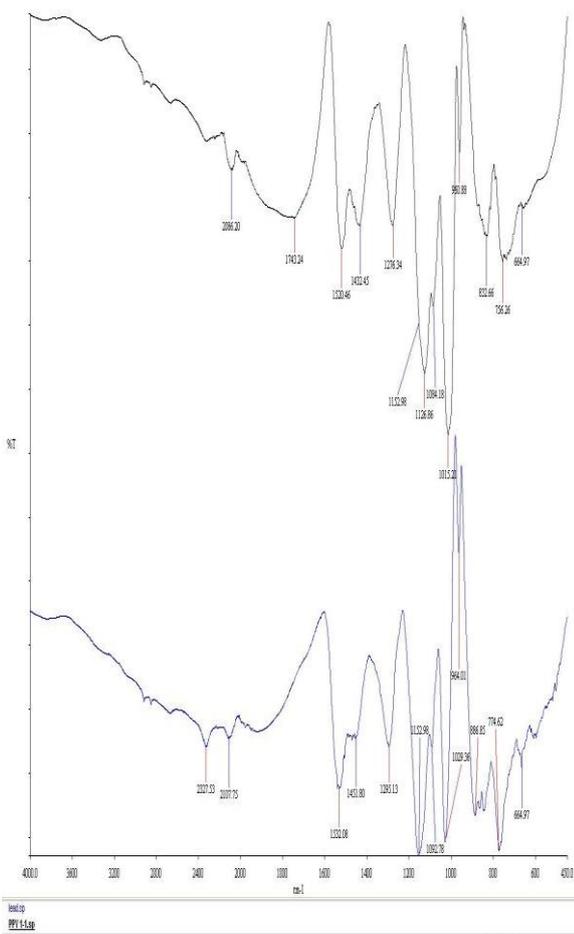


Fig.8. FT-IR spectra of PPy before and after adsorption of lead ions from aqueous solution.

The entire peak positions observed for PPy before adsorption have shifted to higher wavenumbers in the spectrum of PPy after adsorption. The bands at 756 cm⁻¹, 1015 cm⁻¹, 1126 cm⁻¹, 1276 cm⁻¹, 1432 cm⁻¹ and 1520 cm⁻¹ observed in PPy spectrum before adsorption have shifted to 774 cm⁻¹, 1029 cm⁻¹, 1152 cm⁻¹, 1295 cm⁻¹, 1451 cm⁻¹ and 1530 cm⁻¹, respectively, after adsorption. The red shift of all these bands in PPy spectrum after adsorption and the distinct peak observed at 774 cm⁻¹ due to metallic bond formation clearly indicates the adsorption of lead ions by PPy conducting polymer. Furthermore, the bands at 1015 cm⁻¹ due to N-H wagging and 1276 cm⁻¹ due to C-N in-plane deformation shifted to 1029 cm⁻¹ and 1295 cm⁻¹, respectively, after lead ion adsorption, again shows the evidence of the metallic bond linkage of lead ions

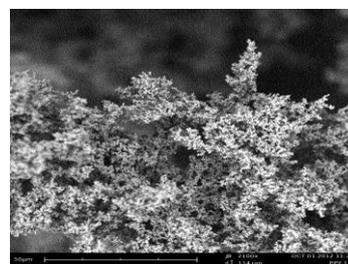


Fig.10. Scanning electron micrograph of PPy before adsorption.

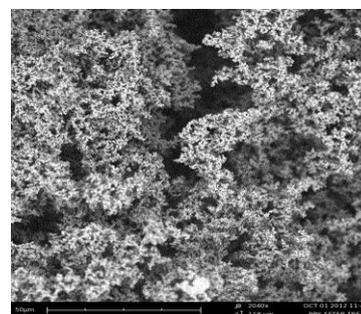


Fig.11. Scanning electron micrograph of PPy after adsorption.

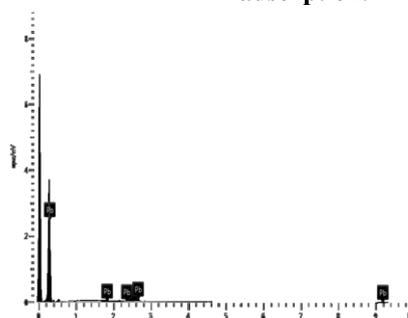


Fig. 12. EDX analysis of the constants of lead ion (count per second) per energy (KeV), inside the PPy after adsorption.

VI. CONCLUSIONS

Polypyrrole conducting polymer was successfully prepared by chemical method using ferric chloride as an oxidant. The adsorption ability due to the presence of nitrogen in amine functional group of polypyrrole structure made it an effective adsorbent for the removal of lead ions from aqueous solution. The preparation conditions of polypyrrole had a great influence on the adsorption efficiency for the removal of lead ions from aqueous solution. The complete removal (100%) of lead ions from aqueous solution by polypyrrole was achieved by controlling the essential parameters such as contact time, adsorbent dosage, pH and initial concentration of lead ions in aqueous solution. The isothermal study of adsorption process indicates that the experimental data for the removal of lead ions from aqueous solution fitted well to the Langmuir isotherm. FTIR results confirm the adsorption of lead ions by polypyrrole. Our findings show that polypyrrole alone without forming any of its composites was capable of removing heavy metal ions like lead from aqueous solution with 100% efficiency.

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