

Adsorption of Pb (II) ions from aqueous solutions using polycresol film fabricated by cyclic voltammetry

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Abstract: Polycresol *p* (*o*-cresol) has been synthesized by cyclic voltammetry technique in acidic medium using sulfuric acid as an electrolyte at 30°C. The electrosynthesized polymer was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The adsorption properties of the fabricated polymer were investigated for adsorptive removal of Pb (II) ions from aqueous solutions. Various physico-chemical parameters such as pH, initial metal ion concentration, and equilibrium contact time were studied. Optimum conditions were found to be 6 for pH and 4 h for contact time. In addition, the adsorption isotherms were obtained using Pb(II) solutions of concentrations ranging from 50 to 250 mg/l. The adsorption process was found to follow pseudo-second-order reaction kinetics and Freundlich adsorption isotherms.

Keywords: *P*(*o*-cresol); cyclic voltammetry; adsorption; lead ions

I. Introduction

Water pollution by heavy metal ions has become a serious environmental issue especially due to their toxicity and tendency to bioaccumulation [1]. The heavy metal ions are not only toxic to living organisms in water, but also cause harmful effects to humans through food chain transfers. In living organisms, heavy metal ions can particularly bind to nucleic acids, proteins, and small metabolites. The contaminated organic cells are altered or missed their biological functions with losing the homeostatic control of essential metals, resulting in fatal health problems [2]. Pb(II) is a highly toxic substance and exposure to which can produce a wide range of adverse health effects for both adults and children. At high levels of exposure, a child may become mentally retarded, fall into a coma, and even die from lead poisoning. In adults, lead can increase blood pressure and cause fertility problems, nerve disorders, muscle and joint pain, irritability, and memory or concentration problems [3]. Therefore, it is necessary to eliminate such hazardous heavy metal ions in wastewater before discharging it into the ecosystem. The contamination of wastewater and surface water by toxic heavy metals is worldwide environmental problem. The most commonly applied physicochemical treatment methods are (i) precipitation as hydroxides, carbonates or sulfides and subsequent liquid-solids separation by gravity settling, flotation or filtration, (ii) sorption (adsorption, ion exchange), (iii) membrane processes, (iv) electrolytic recovery, and (v) liquid-liquid extraction [4-7]. However, each method has its merits and limitations in applications and they are often limited by technical and economical issues [7, 8]. The adsorption process with activated carbon is attractive to many scientists because of the effectiveness of the removal of heavy-metal ions at trace quantities [9, 10]. However, the process has not been used extensively because of its high cost [9-11]. Therefore, the use of low-cost materials as sorbents for removing the heavy metal ions from wastewater has been a focal point of many researchers. Low cost bio-sorbents may be an alternative wastewater treatment technology because they are inexpensive and capable of removing trace levels of heavy-metal ions [12, 13]. However, to improve their absorption capacity and enhance the separation rate, the design and exploration of novel adsorbents are still necessary.

Polymeric adsorbent is one of the most suitable materials in the adsorption of heavy metals because of their easy regeneration and strong mechanical properties in comparison with other adsorbents such as activated carbon, cellulose and silica gel. Despite the fact that polymers are preferably utilized to adsorb heavy-metal ions, the higher costs of these materials may hinder their employment as cost-effective adsorbents for the large-scale production of heavy-metal free water [14]. In this work, polycresol has been synthesized by cyclic voltammetry technique and characterized by XRD and SEM. The adsorption properties of the fabricated polymer were investigated for adsorptive removal of Pb (II) ions from aqueous solutions of different concentrations and pH values.

II. Materials and Methods

2.1. Materials

The o-cresol and sulfuric acid solution 98 % were purchased from Merck, Germany. All solutions were prepared by using freshly double-distilled water.

2.2. Electropolymerization of o-cresol

Electropolymerization of monomer and formation of the polymer film were carried out using potentiodynamic technique. The electrochemical cell was made from transparent perspex trough which has inside dimensions of 8 cm length, 2.5 cm width, and 3 cm height. The cell consists of three electrodes. The working electrode (WE) was a platinum sheet with dimensions of 1cm length and 0.5 cm width. The auxiliary (counter) electrode (CE) was a platinum foil with the same dimensions as the WE. A saturated calomel electrode (SCE) was used as a reference electrode. Electrochemical experiments were performed using the Potentiostat / Galvanostat Wenking PGS 95. Electropolymerization of o-cresol on platinum electrode was carried out from aqueous solution containing 0.6 M H₂SO₄ at 313 K in the presence of monomer and the potential was swept linearly from -500 to +1600 mV(vs. SCE) with scan rate of 30 mVs⁻¹.

2.3. Characterization of the electro-prepared polymer

Scanning electron microscopic (SEM) analysis was carried out on the as-prepared polymer film deposited on Pt-working electrode surface using a JSM-T20 Electron Probe Microanalyzer (JEOL, Tokyo, Japan). The X-ray diffraction analysis (XRD) was carried out by X-ray diffractometer (Philips 1976 Model 1390, Netherlands) and operated under the following conditions that were kept constant for all the analysis processes: X-ray tube, Cu; scan speed 8 deg min⁻¹; current 30 mA; voltage 40 kV; and preset time 10 s.

2.4. Adsorption of lead Pb (II) ions

The adsorption of lead was studied by a batch operation at room temperature. The batch mode adsorption was selected due to its simplicity.

2.4.1 Effect of pH on adsorption of Pb (II) ions

The adsorption studies were carried out using thin film of p (o-cresol) of weight 0.008g, prepared electrochemically by cyclic voltammetry, and 50 mL aqueous solution of 50 mg/L Pb ions at serial pH values (3-6). The prepared samples were shaken with mechanical shaker for 6 h. The concentration of the Pb (II) ions before and after adsorption was determined using atomic absorption mass spectrometry (Thermo electron Ltd., solar House Cambridge. UK, Solar M₆A.A.spectrometer). The adsorbed amount of metal ions onto the polymer film was calculated according to the following "equation 1":

$$q = (C_o - C_t) / C_o \times 100 \quad (1)$$

Where q is the adsorptivity (%), C_o and C_t are the concentration of metal ions before and after adsorption in mg.

2.4.2 Effect of contact time on adsorption of Pb (II)

Typically, series of polymer thin films prepared at the same conditions were immersed into 50 mL of Pb (II) ion solution of 50 ppm and 6 pH for different lengths of time. The contact time was varied from 1 to 6 h under mechanical shaker to improve the distribution of the diffused lead ions. The residual Pb (II) ions concentration was determined by atomic absorption spectrophotometer.

2.4.3 Effect of initial metal ion concentration on adsorption of Pb (II) ions and adsorption isotherm

Typically, series of polymer thin films prepared at the same conditions were immersed into 50 mL of Pb (II) ions solution of pH 6 with various initial metal ion concentrations (from 50 to 250 mg/L). All the flasks were shaken with mechanical shaker. At the end of the equilibrium period, the thin film was removed from the solution. The residual Pb (II) ions concentration was determined by atomic absorption spectrophotometer. The amount of adsorbed Pb (II) ions at equilibrium, q_e (mg/g), was calculated from the following equation "equation 2":

$$q_e = V(C_o - C_e) / W \quad (2)$$

where q_e is the equilibrium adsorption capacity of adsorbent in mg (metal)/g (adsorbent), C_o is the concentration of metal ions before adsorption in mg/L, C_e is the equilibrium concentration of metal ions in mg/L, V is the volume of metal ions solution in liter scale, and W is the weight of the adsorbent in gram scale.

2.4.4 Adsorption kinetics experiment

Kinetic experimental procedures were identical to the equilibrium tests. The amounts of adsorbed Pb(II) ions (q_t) on the adsorbent materials at any contact time, t , were calculated as a function of the pb (II) concentrations before and after the adsorption. The amount of adsorbed Pb(II) ions in mg/g was calculated from the mass balance equation “equation 3” as follows:

$$q_t = V (C_0 - C_t) / W \quad (3)$$

Where C_0 is the concentration of metal ions before adsorption in mg/L, C_t is the concentration of metal ions after adsorption in mg/L, V is the volume of metal ions solution in liter scale, and W is the weight of the adsorbent in gram scale.

III. Result and discussion

3.1. Electropolymerization of o-cresol

The voltammograms of electropolymerization of o-cresol on platinum electrode is represented in” Fig.1”. The voltammogram exhibits two oxidation peaks (I and II) at -200 and 850 mV, respectively, and one reduction peak (I') at 223mV (vs.SCE). The first oxidation peak (I) is a result of hydrogen adsorption on Pt electrode. While the second oxidation peak (II) which corresponds to oxidation of monomer to give phenoxy radical which adsorbed on Pt-electrode [15]. These adsorbed radicals are considered as initiator radicals to form the polymer and the cathodic peak (I') is attributed to the reduction of o-cresol polymer.

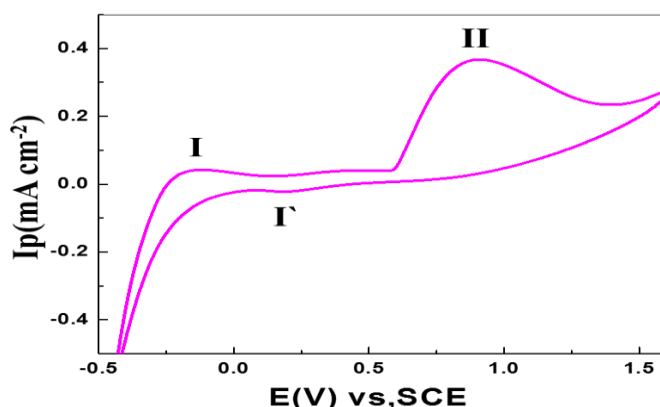


Figure. 1. Cyclic voltammograms of solution containing 0.04 M of o-cresol and 0.6 M of H₂SO₄ at 303K with scan rate 30mVs⁻¹.

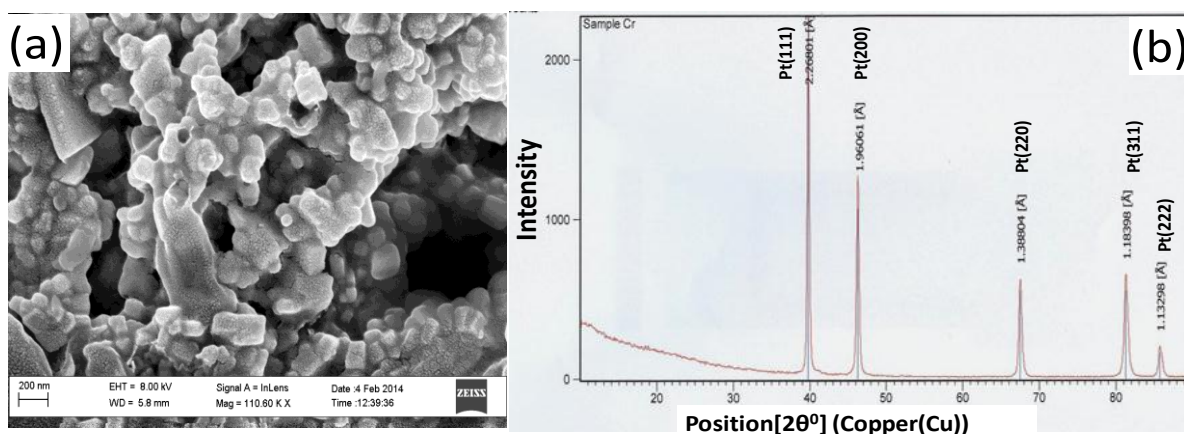


Figure.2. (a) Top-view FE-SEM image and (b) XRD of p (o-cresol) on Pt substrate prepared at the optimum conditions.

3.2. Characterization of the p(o-cresol):

The surface morphology of the polymer obtained at the optimum conditions was examined by scanning electron microscopy. “Fig” .2 shows top- view FE-SEM image of the electropolymerized film on Pt electrode. As shown in this figure, random aggregations of small nano granules are grown on the surface of Pt electrode. In order to check the chemical composition of the fabricated p (o-cresol), the sample was analyzed by XRD as shown in “Fig”.2 (b). In this XRD pattern, no peaks are appeared before $2\theta = 35^\circ$ indicating that the P (o-cresol) is amorphous structure. While the peaks above $2\theta = 35^\circ$ are assigned to Pt substrate.

3.3. Adsorption studies of Pb(II) ion on p(o-cresol)

3.3.1. Effect of initial pH

The pH of solution has been identified as one of the most important variable governing heavy metal ions adsorption. The effect of pH in the range from 3 to 6 was studied by evaluating the adsorption of Pb(II) ions on the p(o-cresol) thin film. This pH range was chosen to avoid precipitation of Pb in the form of metal chloride and metal hydroxides. The effect of pH on the adsorption efficiency is shown in “Fig. 3”. From this figure, removal of Pb(II) ions increases linearly with increasing the pH values from 3 to 6. Similar behavior had been reported by many authors [16,17] for the uptake of metal ions on various adsorbents. At low pH, there is strong competition between the large numbers of protons with metal cations to occupy the adsorption sites. Also according to Low *et al.*[18], at low pH value, the surface of the adsorbent would be closely associated with hydronium ions (H_3O^+) and hold mainly protonated sites. As a result, the surface maintains a net positive charge. So it hinders the access of the metal ions to the surface functional group. Consequently, the percentage removal of metal ions decreases as the pH values decreased.

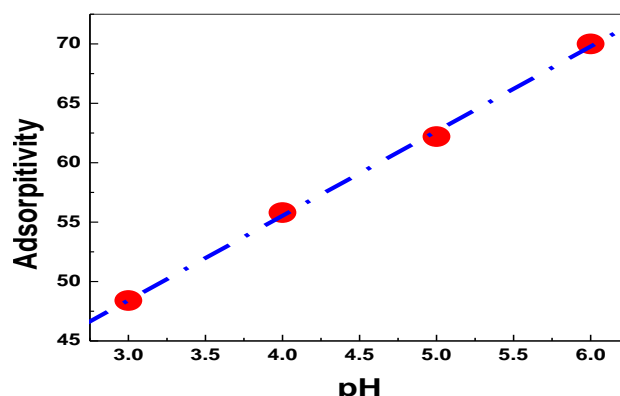


Figure.3. The effect of pH on the percentage removal of Pb(II) in a solution containing thin film of P(o-cresol) weighted 0.008 g adsorbent, 50 ml of 50 mg/l of Pb(II) ions and contact time of 6 h.

3.3.2. Effect of contact time on adsorption rate

The effect of contact time on the adsorption of Pb (II) ions at initial metal ion concentration of 50 mg/L is shown in “Fig. 4”. During the experiment, the contact time was varied from 1 to 5 h. The analysis of batch adsorption of metal ions was carried out in 30 min steps and the concentration of each sample was measured by atomic absorption spectroscopy after 6 h agitation time. This figure shows nonlinear increase in the adsorptivity of Pb (II) ions with the increase in contact time. There is increase in adsorption with the increasing of contact time and maximum adsorption takes place at 4 h and again after 4 h contact time there was no further adsorption. This may be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the lead uptake rate by adsorbent was decreased significantly due to the decrease in number of adsorption sites. Therefore, the optimum contact time for adsorption of the heavy metals was considered to be 4 h.

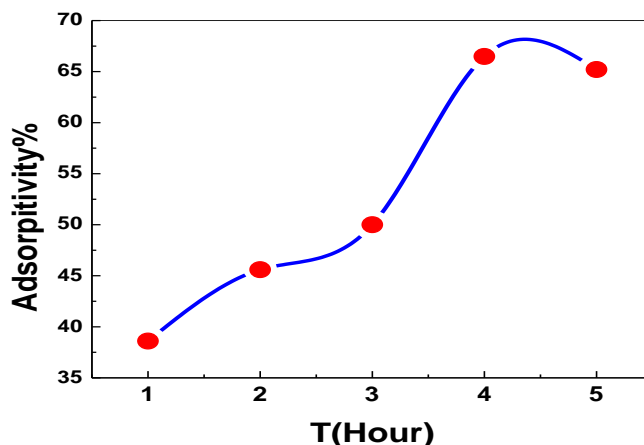


Figure 4. The effect of contact time on the percentage removal of Pb (II) ions in a solution containing thin film of P (o-cresol) weighted 0.008 g adsorbent, 50 ml of 50 mg/l of Pb (II) ions.

3.3.3. Effect of initial Pb(II) ions concentration

The adsorption of Pb (II) ions on the p(o-cresol) thin film was evaluated as a function of the initial Pb(II) ion concentrations from 50 to 250 mg/l at a pH value of 6. The adsorption time was fixed at 24 h to achieve an equilibrium state. As illustrated in “Fig. 5”, the Pb (II) ions adsorptivity decreases with the increasing of initial lead concentration. This may be ascribed to the increase in the driving force from the concentration gradient, and hence the Pb (II) ions at low concentrations could bind to the abundant adsorption sites on the surface of the film leading to the distinctively increased adsorptivity. But at high Pb (II) ions concentrations, more metal ions are left un-adsorbed in the solution due to the saturation of the binding sites. This indicates that energetically less favorable sites become involved with increasing ion concentration in aqueous solution so the adsorptivity decreased.

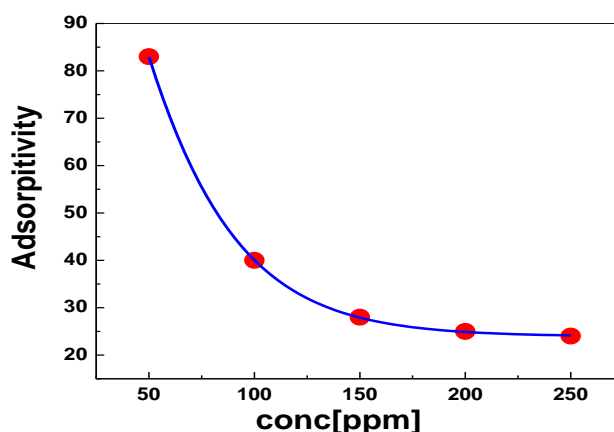


Figure 5. The effect of adsorbate concentrations on the percentage removal of Pb (II) ions using P(o-cresol) thin film weighted 0.008 g adsorbent, 50 ml of 50 mg/l of Pb (II) ions, agitation time of 24 h.

3.3.4. Adsorption isotherm

Adsorption isotherms describe the relationship between the amount of the adsorbed substance per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution. They are used for describing adsorption equilibrium for waste water treatments. The equilibrium adsorption isotherms are important to determine the adsorption capacity of Pb (II) ions and diagnose the nature of adsorption onto the polymer film.

The equilibrium adsorption capacity of adsorbent was calculated by equation (2), where C_e was measured for initial concentration (C_0) ranged from 50 to 250 mg/l after equilibrium time. The adsorption isotherms of Pb (II) ions on p(o-cresol) are shown in ‘Fig. 6’. In this figure, the equilibrium uptake increased with Pb (II) ions concentration. This is a result of the increase in the driving force from the concentration gradient. at the same conditions, if the concentration of Pb (II) metal ions is higher, the active sites of p(o-cresol) are surrounded by many more Pb(II) ions and the process of adsorption would occur. Since 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.

3.3.4. 1. Langmuir adsorption isotherm

The Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. The Langmuir adsorption isotherm applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and given by “equation 4” as follows [19]:

$$C_e/q_e = 1/(q_0 K_L) + (1/q_0)C_e \quad (4)$$

Where C_e (mg/l) is the equilibrium concentration, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbate, and q_0 and K_L are the Langmuir constants related to the adsorption capacity and the rate of adsorption, respectively. When C_e/q_e was plotted against C_e , a straight line with a slope of $1/q_0$ was obtained ‘Fig 7 (a)’. The Langmuir constants K_L and q_0 were calculated from this isotherm and their values are listed in “Table 1”. Another important parameter, R_L , called the separation factor or the equilibrium parameter, is evaluated in this study and determined from the following relation R_L , can be determined from “equation 5” [20].

$$R_L = 1/[1 + K_L C_0] \quad (5)$$

Here, K_L is the Langmuir constant (l/mg) and C_0 (mg/l) is the highest Pb (II) metal ions concentration.

3.3.4.2. The Freundlich adsorption isotherm

The Freundlich adsorption isotherm is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor, n . The linear form of Freundlich adsorption isotherm takes the following form “equation 6”:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{6}$$

Where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of Pb(II) ions. K_F and n are Freundlich constants, where K_F [(mg/g)/(mg/L)^{1/n}] is the adsorption capacity of the adsorbent and n giving an indication of how favorable the adsorption process. The slope of the linear relation in “equation 6” is $1/n$ and its value ranging from 0 to 1. This slope is a measure of adsorption intensity or surface heterogeneity, where the surface becomes more heterogeneous as its value gets closer to 0.

The plot of $\ln q_e$ versus $\ln C_e$ “Fig.7 (b)” gives straight lines with slope $1/n$. This figure shows that the adsorption of Pb(II) ions follows the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated and listed in “Table 1”.

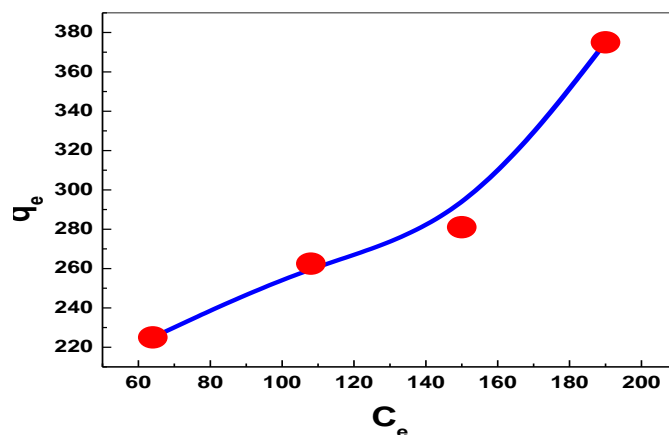


Figure. 6. Adsorption isotherms of Pb (II) ions on the p(o-cresol) film.

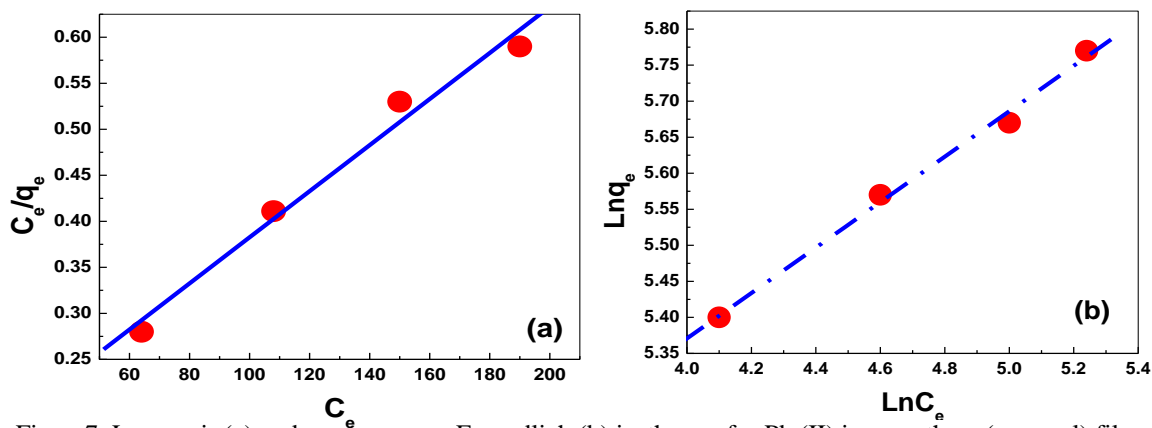


Figure7. Langmuir (a) and Freundlich (b) isotherms for Pb (II) ions on the p (o-cresol) film.

Table 1. Isotherm parameters for removal of Pb (II) ions by p(o-cresol) film.

| Isotherms | Parameters | film of P(o-cresol) |
|------------|--------------|---------------------|
| Langmuir | q_0 (mg/g) | 400 |
| | K_L (l/mg) | 0.019 |
| | R_L | 0.172 |
| | R^2 | 0.99 |
| Freundlich | K_F | 1.349 |
| | $1/n$ | 0.3 |
| | n | 9.17 |
| | R^2 | 0.997 |

3.3.5. Kinetics analyses

The study of adsorption kinetics describes the solute removal rate and evidently this rate controls the residence time of adsorbate removal at the solid–solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process [21]. Also kinetic analysis of adsorption process is very important for the design of adsorbents because the kinetics provide essential information on the adsorption mechanism and the metal ion uptake rate. The process of Pb (II) ions removal from an aqueous phase by adsorbent can be explained by using kinetic models and examining the rate-controlling mechanism of the adsorption process such as chemical reaction, diffusion control and mass transfer. The kinetic parameters are useful in predicting the adsorption rate which can be used in designing and modeling of the adsorption process. The kinetics of metal ions removal is explicitly explained in the literature using pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models.

In order to investigate the mechanisms of metal adsorption process, the linear equations of pseudo- first-order, pseudo- second- order and intraparticle diffusion kinetic models were applied and the results were shown in “Fig. 8”. The pseudo-first-order kinetic model assumes that the binding is originated from physical adsorption and given by “equation 7” as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (7)$$

Where q_e and q_t are the amounts of Pb(II) ions adsorbed on the p(o-cresol) in mg(adsorbate)/g(adsorbent) at equilibrium and at time t , respectively. k_1 is the rate constant of the pseudo first-order model for the adsorption (min^{-1}) [22]. The values of q_e and k_1 can be determined from the intercept and the slope of the linear plot of $\ln(q_e - q_t)$ versus t .

The pseudo second-order model is based on chemical adsorption (chemisorption) and given by “equation 8” as:

$$(t/q_t) = 1/(k_2 q_e^2) + (t/q_e) \quad (8)$$

Where q_e and q_t follow the same definition as the pseudo first-order model and k_2 is the rate constant of the pseudo second-order model for adsorption (g/mg min). The slope and intercept of the linear plot of t/q_t against t yielded the values of q_e and k_2 . In addition, the initial adsorption rate h (mg/g min) can be determined from $h = k_2 q_e^2$.

In addition, the kinetic results will be analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism. This model is expressed in “equation 9”as:

$$q_t = k_i t^{1/2} + C \quad (9)$$

Where C is the intercept and k_i is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$), which can be evaluated from the slope of the linear plot of q versus $t^{1/2}$ [23].

The results of “Fig. 8” are fitted using pseudo-first- and second-order models and intraparticle diffusion model. The fit of these models was checked by each linear plot of $\ln(q_e - q_t)$ versus t , (t/q_t) versus t , and q_t versus $t^{1/2}$, respectively, as shown in Fig.8. Table 2 presented the coefficients of the pseudo-first and second-order adsorption kinetic models and the intraparticle diffusion model.

By comparing the regression coefficients for each expression, first order rate expression and intraparticle diffusion model is not fully valid for the present system due to low correlation coefficients. A good agreement of the experimental data with the second order kinetic model was observed for the adsorbate which is presented in “Fig. 8(b)”. Correlation coefficients for the linear plots using the pseudo-second order model are superior (in most cases >0.99), and theoretical and experimental q_e values show excellent agreement. Therefore, this clarify that the sorption of Pb (II) ions by p (o-cresol) is kinetically controlled by the second order reaction rather than the first order process.

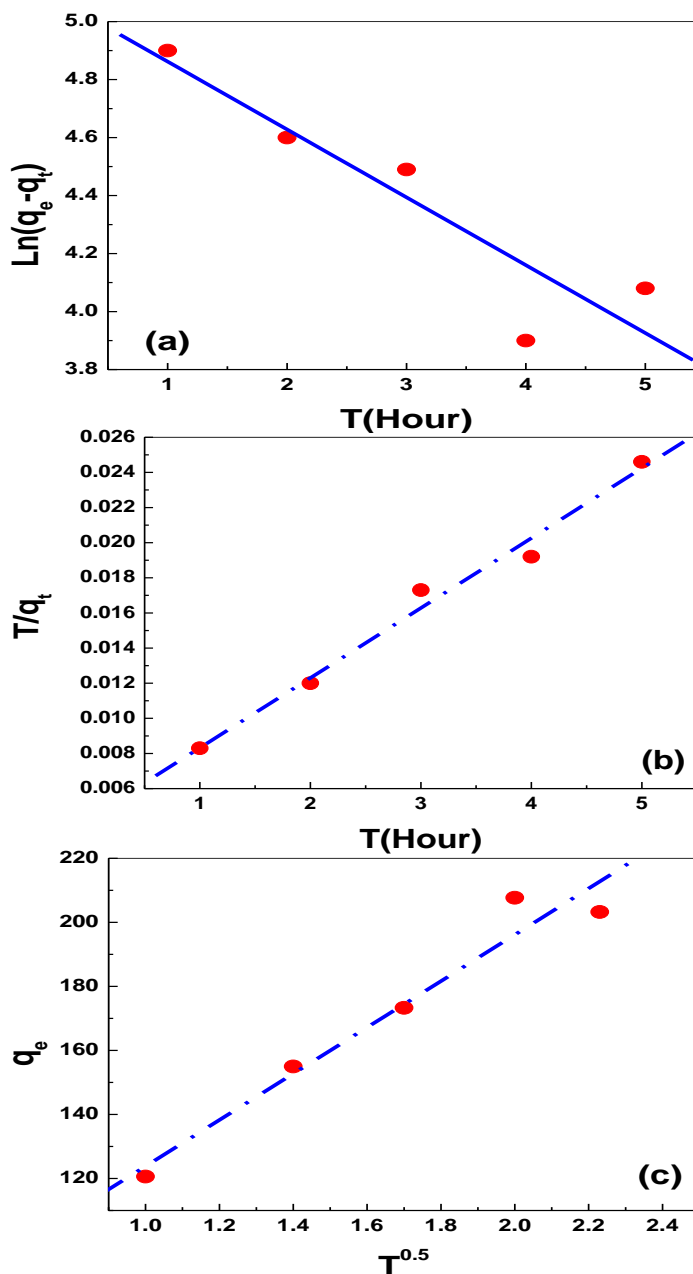


Figure.8. Regressions of kinetic plots for the thin film of p (o-cresol): (a) pseudo-first-order model, (b) pseudo-second-order model and (c) intraparticle diffusion model.

Table 2. Coefficients of pseudo-first and second order adsorption kinetic models and intraparticle diffusion model ((Pb (II) metal ions = 50 mg/l, p(o-cresol) film 0.008g).

| Orders models | Parameters | P(o-cresol) |
|-------------------------------|-----------------------------------|-----------------------|
| Pseudo first order | q_e Cal. (mg/g) | 148.4 |
| | q_e Exp. (mg/g) | 251 |
| | K_1 (min^{-1}) | -0.23 |
| | R^2 | 0.912 |
| Pseudo second order | q_e Cal. (mg/g) | 251.3 |
| | q_e Exp. (mg/g) | 251 |
| | K_2 (g/mg min) | 3.66×10^{-3} |
| | R^2 | 0.993 |
| Intraparticle diffusion model | k_i ($\text{mg/g min}^{0.5}$) | 72.3 |
| | C (mg/g) | 51.5 |
| | R^2 | 0.976 |

IV. Conclusion

P (o-cresol) was synthesized electrochemically by cyclic voltammetry technique. The fabricated Polycresol film has ability in the adsorption of pb (II) ions on its surface. The adsorption characteristics of Polycresol film have been examined at different pH values, contact time, and initial lead ions concentrations. The obtained results can be summarized as follows:

- The adsorption of Pb (II) ions by P (o-cresol) film is increased linearly with the increasing of the pH values from 3 to 6.
- The optimum contact time for adsorption of the heavy metal was found to be 4 h and after which there was no further adsorption.
- The adsorption experimental results of Pb (II) are in a good agreement with the Freundlich isotherm.
- The kinetics studies suggest that the adsorption of Pb (II) by P(o-cresol) film followed the second-order kinetics model, which relies on the assumption that chemical adsorption may be the rate-limiting step involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

References

- [1] A .Sari, M.Tuzen , Biosorption of cadmium (II) from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies , *Journal of Hazardous Materials* ,157,2008, 448.
- [2] X. Liu, Q.Hu, Magnetic chitosan nanocomposites: a useful recyclable tool for heavy metal ion removal, *Journal of Langmuir*, 25, 2008, 3-8.
- [3] NSC,Lead poisoning, available at: <http://www.nsc.org /library/facts/lead.htm>,1.9.2007.
- [4] A .Afkhami, BE .Conway, Investigation of removal of Cr (VI), Mo (VI), W (VI), V (IV), and V (V) oxy-ions from industrial wastewaters by adsorption and electrosorption at high-area carbon cloth, *Journal of Colloid and Interface Science*, 251, 2002, 248-255.
- [5] A.Afkhami, T .Madrakian, Effect of the impregnation of carbon cloth with ethylenediaminetetra acetic acid on its adsorption capacity for the adsorption of several metal ions,*Journal of Hazardous Materials* ,150,2008,408-412.
- [6] G. Hota, BR, Kumar, Fabrication and characterization of a boehmite nanoparticle impregnated electrospun fiber membrane for removal of metal ions, *Journal of Materials Science*, 43 ,2008, 212-217.
- [7] J.Wang, C.Chen , Biosorbents for heavy metals removal and their future,*Journal of Biotechnology Advances*, 27,2009, 195-226.
- [8] S. Pacheco, J.Tapia, Cadmium ions adsorption in simulated wastewater using structured alumina-silica nanoparticles, *Journal of Non-crystalline Solids*,352,2006, 5475-5481.
- [9] JW .Wang, YM .Kuo, Preparation and adsorption properties of chitosan-poly (acrylic acid) nanoparticles for the removal of nickel ions. *Journal of Applied Polymer Science*, 107, 2008, 2333-2342.
- [10] MM .Rao, D. Ramana, Removal of some metal ions by activated carbon prepared from *Phaseolus aureus* hulls, *Journal of Hazardous Materials*, 166, 2009, 1006-1013.
- [11] JM. Dias, M. Alvim-Ferraz, Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review, *Journal of Environmental Management*, 85 ,2007,833-846.
- [12] M.Jiang, Q.Wang , Removal of Pb (II) from aqueous solution using modified and unmodified kaolinite clay, *Journal of Hazardous Materials* ,170 ,2009, 332-339.
- [13] VS.Munagapati, V.Yarramuthi , Biosorption of Cu (II), Cd (II) and Pb (II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics. *Journal of Chemical Engineering*, 157, 2010. 357-365.
- [14] CM .Li,W. Chen, X.Yang, CQ. Sun,C. Gao, ZX.Zheng, J.Sawyer, Impedance labelless detection-based polypyrrole protein biosensor,*Journal of Frontiers in Bioscience*, 10 ,2005, (Supplement), 2518-2526.
- [15] G. Arslan, B. Yazici, M. Erbil, The effect of pH, temperature and concentration on electrooxidation of phenol,*Journal of Hazardous Materials*, B124 ,2005, 37-43.
- [16] G .Zhang,Y. Dong , Effects and mechanisms of oxalate on Cd (II) sorption on goethite at different pH and electrolyte concentration. *Journal of Plant Nutrition and Fertilizer Science*, 7, 2001, 305-310.
- [17] M.Mohapatra, S. Anand , Studies on sorption of Cd (II) on Tata chromite mine overburden. *Journal of Hazardous Materials*, 148, 2007, 553-559.
- [18] K. Low, C.Lee , Removal of metals from electroplating wastes using banana pith. *Journal of Bioresource Technology*, 51, 1995, 227-231.
- [19] I .Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *Journal of the American Chemical Society*, 40, 1918, 1361-1403.
- [20] K. Hall, L. Eagleton, Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Journal of Industrial & Engineering Chemistry Fundamentals*, 5, 1966, 212-223.
- [21] Eddy, Metcalf, Inc., *Wastewater Engineering, Treatment and Reuse*, fourth edition (Tata McGraw–Hill Publishing Co., New Delhi, 2003)
- [22] E .Demirbas, N.Dizge, Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Journal of Chemical Engineering*, 148, 2009, 480-487.
- [23] W. Weber, J. Morris, Kinetics of adsorption on carbon from solution, *Journal of the Sanitary Engineering Division* 89, 1963, 31-60.