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مجموعه مقالات چهارمین کنفرانس ملی مهندسی فرآیند، پالایش و پتروشیمی
۷ خرداد ۱۳۹۴، ایران، تهران، مرکز همایش‌های صدا و سیما
مجری: اهم اندیشان انرژی کیمیا ۸۸۶۷۱۶۷۶ – ۰۲۱
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Equilibrium studies of Pb(II) adsorption from aqueous solution using polythiophene nanocomposite

Sahar salehi[1], Mehdi parvini[2], Mohsen ghorbani[3*]
[1] semnan university, Iran, Ch.e.saharsalehi@gmail.com
[*] Babol Noshirvani University Of Technology, Babol, Iran, m.ghorbani@nit.ac.ir

Abstract

This study was carried out on the sorption of Pb^{2+} under ambient conditions from single component aqueous solution by polythiophene/clay nanocomposite(PTC) on using batch technique. In the work, the polythiophene/clay nanocomposite were synthesized by chemical oxidative polymerization method in the presence of anionic surfactant sodium dodecylbenzenesulfonate (DBSNa) and non-ionic surfactant Polyvinylpyrrolidone (PVP) as additive and hydrogen peroxide and ferric chloride as oxidant. Polythiphene/clay nanocomposite was characterized by technique Fourier Transform spectroscopy**.** The results of FTIR spectroscopy indicate that the surfactants interact with PTC**.**the adsorption of Pb^{2+} ions performed in batch system and langmuir and freundlich equations were used for studying sorption equations and the experimental datas fit to this equations. The sorption results fit well to the Langmuir and the Freundlich models. The results suggested that PTC is suitable as a sorbent material for recovery and adsorption of Pb^{2+} ions from aqueous solutions.

Keywords: adsorption, lead, polythiophene, clay, Langmuir, equilibrium, nanocomposite

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[1] M.Sc.Student Of Chemical Engineering, Semnan University, Semnan, Iran
[2] Faculty Of Chemical Engineering Semnan University, Semnan, Iran
[3] Faculty Of Chemical Engineering Babol Noshirvani University Of Technology, Babol, Iran

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1.Introduction

The pollution of water resources due to the indiscriminate disposal of metal ions has been causing worldwide concern. Wastewater from many industries such as metallurgical, tannery, chemical manufacturing, mining, battery manufacturing industries, etc. contains one or more toxic metal ions.[1] Lead in the natural environment arises from both natural and anthropogenic sources, and is detrimental to human and living things. Long-term drinking water containing high level of lead will cause serious disorders, such as anaemia, kidney disease and mental retardation. The enrichment and bioavailability of Pb(II) by plants and crops can transfer Pb(II) from natural environment to human. Metal ions are non-biodegradable, and therefore must be removed from water to eliminate the potential dangerous to human and environment. Many conventional methods have been used to remove metal ions from aqueous solutions including oxidation, reduction, precipitation, membrane filtration, ion exchange and sorption. Among the above methods, the promising process for the removal of metal ions from water and wastewater is sorption. Therefore, investigations of new promising adsorbents with high adsorption capacities and efficiencies have been the aims of many researchers.[2] Adsorption is the concentration of a substance at the surface. The adsorption at a surface or interface is largely as a result of binding forces between atom, molecules, and ions of the adsorbate on the surface.[3] Chen et al, a multiwall carbon nanotube/iron oxide magnetic composites was used for adsorption of Ni^{2+} and Pb^{2+} .[4] tritom et al, the adsorption was curried out by using chitosan- clay composite for removal Ni^{2+} and Cd^{2+}.[5] wang et al, a titanate nanotubes was employed for adsorption of Pb^{2+} , Cd^{2+} and Cr^{3+} .[6] xiong et al, a titanate nanotubes prepared via hydrothermal method was using for adsorption of Pb^{2+} and Cd^{2+}.[7]

in this work, the removal of lead by PTC ambient conditions will be investigated and polythiophene/clay nanocomposite will be synthesized. The purposes of this work are: (1) to synthesize the polythiophene/clay nanocomposite in the presence of two type of surfactant (2)to characterize the PTC by FTIR (3) to investigate equilibrium adsorbption.

2. Experimental

2.1. Material

Thiophene (Merck) was purified by distillation. The oxidant, hydrogen peroxide35%(H_2O_2, Merck), ferric chloride ($FeCl_3$, Merck) and surfactant sodium dodecylbenzenesulfonate (DBSNa, ACROS), Polyvinylpyrrolidone (PVP, Merck) were used as received. A lead nitrate ($Pb(NO_3)_2$, merck) was used for supplying the lead solution. Clay is for merck company.

2.2. Synthesis of polythiophene/clay nanocomposite

25 mmol (2 ml) of thiophene was mixed with 30 ml of deionized water in a reaction vessel containing a magnetic stirring bar.18.5 mmol of $FeCl_3$ was dissolved in 30 ml of deionized water.20ml of deionized water including 0.2 grmol clay was ultrasonically stirred for 10 min and then the ferric chloride solution and the clay solution added to the stirred

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monomer solution then supplemented dropwise 5ml H_2O_2. Polymerization was carried out for 5 h at room temperature. The resulting precipitate was collected by centrifugation for 15 min. It was washed by deionized water and ethanol to remove the residual oxidant and then dried in binder drier. The dark brown powder was polythiophene/clay nanocomposite.

For synthesis of polythiophene/clay nanocomposite in the presence of surfactants, The 0.1 grmol of surfactant(0.285 mmol DBSNa and 0.0025 mmol PVP) was added in the monomer solution. The sythesis process, purification, and drying process were the same as for PTC preparation.

2.3. Preparation of Pb(II) solution

lead nitrate was employed to prepare a stock solution , which was further diluted with deionized water to the required Pb(II) concentrations in the adsorption experiments.

2.4. Batch experimental

The adsorption experiments were performed in the glass test tubes under ambient conditions by using batch technique. The 0.1gr polythiophene/clay nonacomposite adsorbent added to10ml lead solution. the samples were gently shaken at 300rpm for 2 h to achieve sorption equilibration and centrifuged at 6000 rpm for 15 min. then the extant solution was filtered by purity paper.

The concentration of Pb^{2+} was analyzed by flame emission spectrometry using an atomic absorption spectrometer.

3. Results and Discussion

3.1. Adsorbent characterization

3.1.1. FT-IR study

The Fourier transform spectrum of polythiophene/clay nanocomposite with and without surfactant is appeared in figure 1. The FT-IR by with tensor27 model (BRUKER, Germany) using KBr pellets were recorded in the range of 400–4,000 cm^{-1}. At 1087 and 780 in PTC, the in plane and out of plane C-H aromatic bending stretching vibration substituted thiophene ring are situated.[8,12] The band at 83cm^{-1}may be allocated to C–S stretching vibration.[8,9] Band at 610 cm^{-1} depicts the ring deformation of C–S–C in PTC.[8,11] The spectrum showed the C=C vibrating band at the 1679 cm^{-1}.[10] The band assignments of spectra in the range from 4000 to 400 cm−1for surfactant-free PTC and in PTCs synthesized in the presence of surfactants are listed in Table2.PTCs synthesized in the presence of surfactants present in some cases bands slightly shifted compared to those of surfactant-free PTC. extra new bands belonging to surfactant seem in the FTIR spectrum of PTC readied in the presence of surfactant. Small peaks ranging from 2800 to 3000 cm^{-1}, which are allocated to the aliphatic C–H stretching modes, connected to the long alkyl tail of DBSNa and PVP,[8] were detected in the spectra of PTC–DBSNa and PT-PVP. the Peaks 1131 and 1042 cm^{-1} belonging to DBSNa in the spectrum of PT-

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DBSNa.[8] A slight shift of these peaks relative to their positions in the spectrum of neat surfactant demonstrates a more intimate interaction between the PTC and DBSNa.

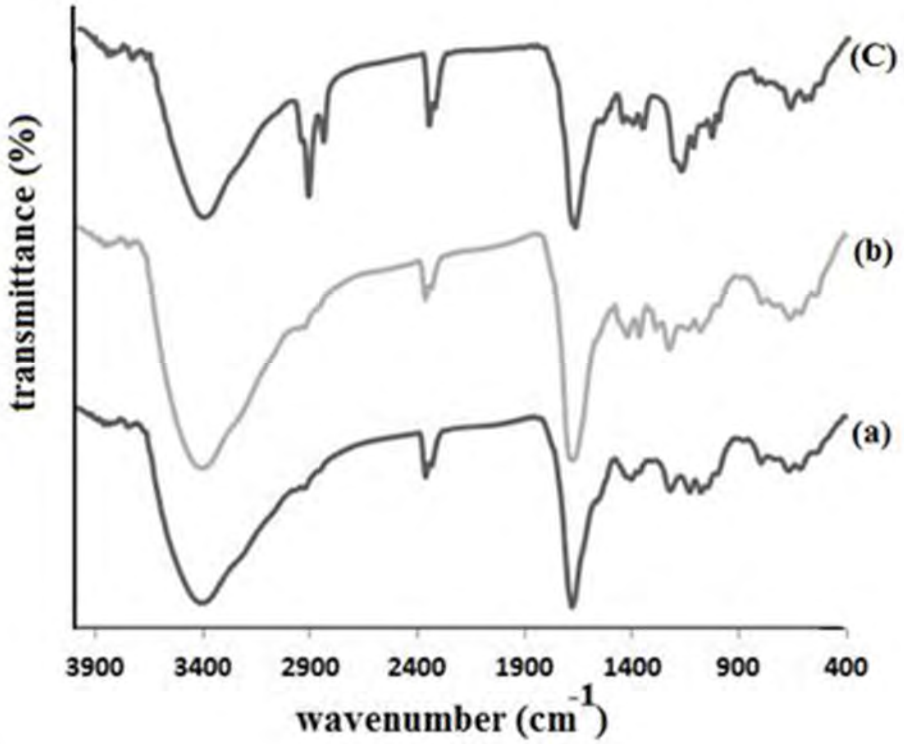

Fig.1. FT-IR spectra of (a) PTC, (b)PTC-PVP, (c) PTC-DBSNa

Table 1
assignments of FT-IR bands of PTCs

Wavenumbers cm^{-1}			Assignments
PTC-DBSNa	PTC-PVP	PTC	
3423	3424	3429	O-H stretching of water in KBr [8]
831	831	831	C-S stretching
2924	2926	2925	C-H stretching (aromatics)
1401	1429	1401	[5,3,10] C=C stretching [9]
1681	1678	1679	C=C vibrating
779	779	779	C-H out of plane stretching vibration
1011	1010	1010	C-H in plane deformation
615	615	615	C-S-C ring deformation
1186	1227	1223	C-C [9]

3.2. Equilibrium isotherms

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The equilibrium adsorption isotherms are of fundamental importance in determining the adsorption capacity of Pb^{2+} onto polythiophene/clay nanocomposite. As general anticipated, a change in the inlet metal ion concentration of the feed influences the adsorption. The effect of metal ion concentration on Pb^{2+} Adsorption was investigated over the concentration ranges 50 - 400 mg/l, at room temperature. In order to discover the adsorption, data were fitted to several equations applicable to adsorption from solution processes such as Langmuir and Freundlich models have been applied. The equilibrium adsorption isotherm obtained at constant temperature are shown in Fig.2. From this, it is observed that the adsorption capacity (qe) increases as a function of metal concentration.

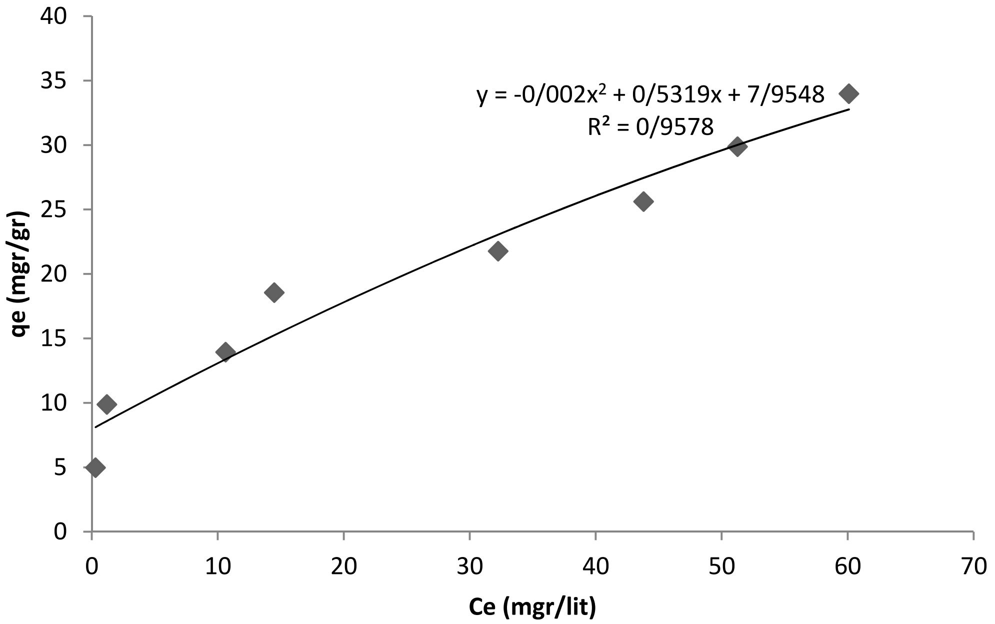

fig.2. equilibrium isotherm of Pb^{2+} ion by polythiophene/clay nanocomposite (m=0.1gr, pH=6, V=10ml, t=120min at room temperature)

3.2.1. Sorption isotherms

Equations frequently used to describe the experimental isotherm data are those developed by Freundlich, by Langmuir. The Freundlich and Langmuir isotherms are employed most usually to describe the adsorption characteristics of adsorbent employed in water and wastewater treatment.

3.2.1.1. Langmuir isotherm

The Langmuir theory was first used to describe the adsorption of gas molecules onto metal surfaces.[13] However, this model has supplied successful application in many other sorption processes. The basic assumption of the Langmuir model is that the amount of metal ions adsorbed can be expressed by

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$$q_e = \frac{x}{m} = \frac{Q_0 b C_e}{1 + bC_e} \tag{1}$$

where X is the initial concentration of solute minus the final concentration of solute in solution at equilibrium (mg/l) and m is the concentration of adsorbent (g/l).

A linear form of this equation is

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{2}$$

where C_e is the equilibrium concentration of metal in solution q_e is the amount of metal ions sorbed onto adsorbent and Q_0 and b are Langmuir constants related to sorption capacity and sorption energy, respectively. The langmuir isotherm indicates a monolayer adsorption. Maximum sorption capacity (Q_0) indicates monolayer coverage of sorbent with sorbate and b indicates enthalpy of sorption and should vary with temperature. The equilibrium data for metal cation over the concentration range from 50 to 400 mg/l at room temperature has been mutually related with the Langmuir isotherm (Fig.3). The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Table 2.

Table2
langmuir parameters

metal sample	Langmuir parameters		
	Q_0 (mgr/gr)	b (lit/mgr)	R^2
Pb^{2+}	34.0136	3.80807	0.9192

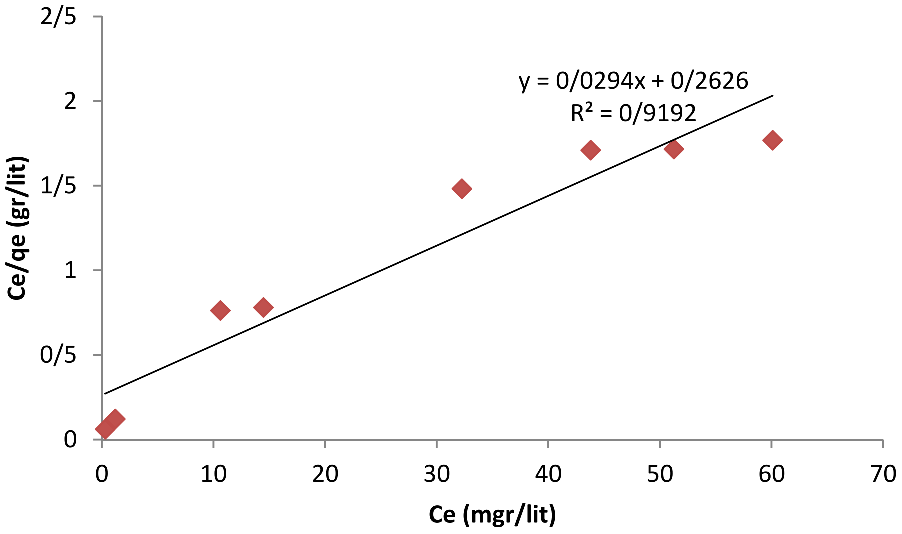

Fig.3. Langmuir sorption isotherm of Pb^{2+} on polythiophene/caly nanocomposite (m=0.1gr, pH=6, V=10ml, t=120min at room temperature)

3.2.1.2. Freundlich isotherm

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The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with exponential distribution of active centres, characteristic of heterogeneous surfaces. The amount of solute adsorbed, X/m, is related to the concentration of solute in the solution, C_e, following

$$\frac{x}{m} = k^f C_e^{1/n} \qquad (3)$$

The constants in the Freundlich isotherm can be determined by plotting log X/m vs log C_e and making use of the above equation rewritten as

$$\log\frac{x}{m} = \log k_f + 1/n \log C_e \qquad (4)$$

Both K_f and n are empirical constants, being indicative of the extent of adsorption and the degree of nonlinearity between solution and concentration, respectively. Here the linear line obtained gives a slope that is the value of 1/n, and the y-intercept is log K_f (fig.4.) A relatively slight slope (and hence a high value of n) indicates that adsorption is good over the entire range of concentrations studied, while a steep slope (and hence small n) means that adsorption is good at high concentrations but much less at lower concentrations. A greater value of the intercept K_f indicates a higher capacity for adsorption than a smaller value.

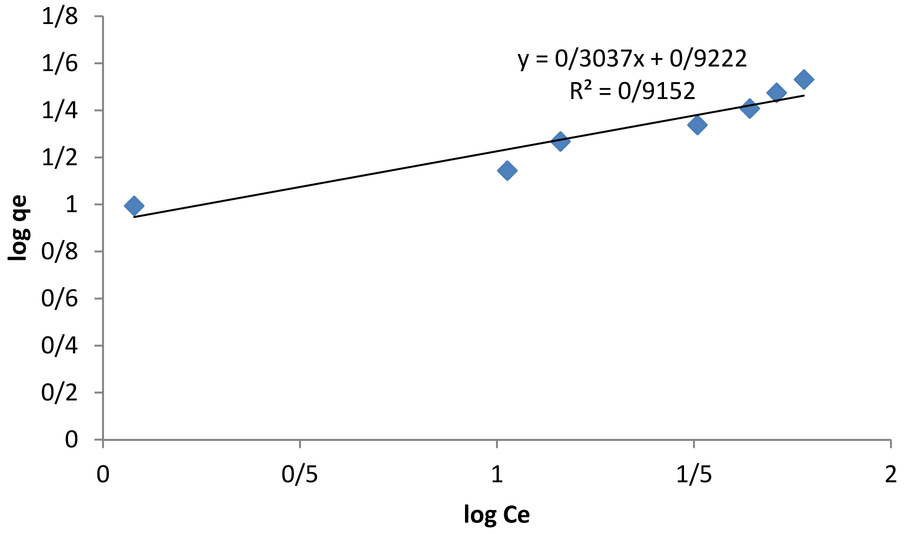

Fig.4. freundlich sorption isotherm of Pb^{2+} on polythiophene/caly nanocomposite (m=0.1gr, pH=6, V=10ml, t=120min at room temperature)

From the slope and intercept of straight portion of the plot the values of Freundlich parameters that given table 3.

Table3
freundlich parameters

Metal sample	Freundlich parameters		
	K_f	n	R^2

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Pb^{2+}	7.7911	3.0769	0.9152

Values of k_f and n signify the sorption intensity and sorption capacity, respectively. The numerical value of 1/n <1 indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentration. The Freundlich sorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm does not predict any saturation of the sorbent by the sorbate thus infinite surface coverage is predicted mathematically, indicating a multilayer sorption of the surface.[13]

Conculasion

Polythiophene/clay nanocomposite was prepared in the presence of two types of surfactants by chemical oxidative polymerization. The results of FTIR spectroscopy indicate that the surfactants interact with PTC. The morphologies of the resulting PTC are greatly influenced by the presence of the surfactant.

From the results of Pb(II) sorption on PTC under our experimental conditions, the following conclusions can be obtained:

- The experimental data of Pb(II) on PTC follows the Langmuir and Freundlich sorption isotherms. The sorption results fit well to the both isotherms.
- The results suggested that PTC is suitable as a sorbent material for recovery and adsorption of Pb^{2+} ions from aqueous solutions.

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