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Synthesis and application of composite terpolymer for the removal of lead from aqueous solution

V Sangu* & K Kannan

Department of Chemistry, Shivani College of Engineering and Technology, Trichy 620 009, India.
Department of Chemistry, Government College of Engineering, Salem 636 011, India
E-mail: venkatasangu@gmail.com

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A new composite GO-4-HBDTOF is prepared by coating 4-HBDTOF terpolymer on graphene oxide. The terpolymer and composite has been characterized by Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy analysis. Batch experiments have been carried out to evaluate efficiency of the sorbents 4-HBDTOF and GO-4-HBDTOF composite for the removal of Pb(II) ion from aqueous solutions. The effects of contact time, *p*H and initial concentration of Pb(II) on the adsorption process have been investigated. The equilibrium data is fitted to Langmuir and Freundlich isotherm model. The Langmuir isotherm gives a better representation of data than Freundlich isotherm. From Langmuir adsorption isotherm model, the calculated value of monolayer adsorption capacity for composite is found to be higher than that of terpolymer. Thus, the newly synthesized terpolymer composite can be used as a better adsorbent for the removal of Pb(II) from aqueous solution.

Keywords: Terpolymer, Composite, Adsorption, Lead, Langmuir isotherm and Freundlich isotherm

Lead has many industrial applications, such as metal plating, metallurgy, alloying, mining, ceramics, batteries, paints, pigments, petrol, cables, steels, plastics, and glass industries. However, Pb(II) ion is more toxic and carcinogenic. Lead poisoning in human beings cause severe damage to the nervous system, reproductive system, liver, kidney, as well as the brain and sometimes causes death. According to WHO, the maximum permissible limit (MPL) of lead in drinking water is 0.1 mg/L. Hence, the selection of an appropriate treatment method for industrial effluent, which reduces Pb(II) ions in an aqueous system, is very important[1]. There are several conventional technologies, such as membrane separation, ion-exchange precipitation, and filtration for the removal of heavy metal ions from wastewater. However, adsorption is the maximum common, effective removal method, for many pollutants even at low concentration[2]. Uses of agricultural waste, activated carbon and polymeric resin for removal of heavy metal including Pb(II) have been reported in many study[3]. Chelating ion exchange polymeric resins have been widely used as adsorbent in effluent treatment for the removal of organic and inorganic pollutants[4].

In this present work, a novel terpolymer composite 4-HBDTOF (4-hydroxybenzoicacid-dithiooxamide-formaldehyde) sorbent was successfully synthesized by coating 4-HBDTOF terpolymer onto grapheneoxide. The terpolymer and composite were characterized by FTIR and scanning electron microscopy studies. Batch equilibrium experiments were conducted to optimize contact time, *p*H, and sorbent dosage for efficient removal of Pb(II) from aqueous solution. The equilibrium data were fitted to Langmuir and Freundlichisotherm models to determine the nature of adsorption process and to evaluate the amount metal adsorbed per unit mass of adsorbent and to know the nature of adsorption process.

Experimental Section

Synthesis of 4-HBDTOF terpolymer

Terpolymeric resin 4-HBDTOF was synthesized by condensation of 4-hydroxybenzoicacid and dithiooxamide with formaldehyde at 2:3:5 molar ratios in the presence of 100 mL of 2 M H_2SO_4 as acatalyst at 120°C±2°C for 4 h[5]. The resulting mixture was poured into ice cold water with constant stirring and kept overnight as such. The pale yellow terpolymer resin obtained was washed with water and ether, and then dried in air. Terpolymer was further purified by dissolving in 10% NaOH and regenerated in 1:1 (v/v) HCl. In the same way, the resin was repeatedly purified for two or three times to remove unreacted monomers. The purified terpolymer was washed repeatedly with distilled hot water and dried in oven.

Preparation of graphene oxide (GO)

Graphene oxide was synthesized as in literature by Hummers method[6]. 4 g of graphite flakes were added to 120 mL con. H_2SO_4 in round-bottom flask and stirred well for one hour. While being stirring of the above mixture at each interval of 20 min, 3 g of $KMnO_4$ is added to this mixture. The mixture was heated at 40°C over the period of 5 h to oxidize graphite. Consequently, 150 mL of distilled water was added to this mixture. Later, 15 mL of hydrogen peroxide solution was added with constant stirring for 30 min and kept as such overnight. The mixture was centrifuged, washed several times with distilled water and dried in oven at 45°C for 24 h[6].

Preparation of composite sorbent (GO-4-HBDTOF)

Terpolymer gel was prepared by adding 50g of terpolymer 4-HBDTOF in 1L of 10% of oxalic acid with constant stirring. The mixture was stirred well using magnetic stirrer for 2-3 h for proper mixing. 250 g of graphene oxide was added to the terpolymer gel and stirred for 24 h. The contents were allowed to settle and the clear liquid was filtered out under vacuum with whatmann no.41 filter paper. The composite terpolymer sorbent was washed twice with distilled water and dried in the oven at 318 K for 24 h. The coating process was then repeated for maximum coating of terpolymer on graphene oxide[7].

The amount of 4-HBDTOF terpolymer loaded on the graphene oxide was determined by measuring the weight loss of sorbent at high temperature pyrolysis. Dried composite sorbent was accurately weighed into a crucible and placed in muffle furnace. The sorbent was muffled for 6 h at 1000 K. Afterwords, the furnace was cooled in dry air and weight loss of the sorbent was obtained. Control experiments with empty crucible, pure as well as acid treated graphene oxide, pure 4-HBTOF terpolymer, and composite terpolymer sorbent were also carried out. All the experiments were repeated to confirm the reproducible results. The composite sorbent was characterized by scanning electron microscope and FTIR analysis.

Preparation of Pb(II) solution

A Pb(II) stock solution having 1000 mg/L concentration was prepared by dissolving 1.599 g of $Pb(NO_3)_2$ in 1000 mL of distilled water.Standard solutions of lead at required concentration was prepared by appropriate dilution of stock solution. The *p*H of the solutions was adjusted by using acetic acid/sodium acetate buffer.

Batch adsorption experiments

Adsorption studies were carried out by batch technique to determine adsorption capacity of GO-4-HBDTOF composite and 4-HBDTOF terpolymer sorbent. 100 mg of sorbent was added into the flask containing 100 mL of 10 mg/L Pb(II) solution equilibrated for predetermined period. At the end of equilibrium time, the sorbent was filtered using whatman filter paper no. 41. The filtrate was analysed for lead concentration using Atomic adsorption spectrometer at 193.7 nm by acetylene air flame method[2].

The amount of lead adsorbed from aqueous by composite and terpolymer sorbents were calculated as follows:

$$\text{amount of Pb(II) adsorbed } (q_t) = \frac{(C_{int} - C_{fin})}{m} \text{ mg/g}$$

$C_{int}$is initial concentration of Pb(II) in mg/Land C_{fin} is final concentration of Pb (II) mg/L.

Results and Discussion

Characterization of Composite 4-HBDTOF terpolymer sorbent

FTIR spectrum of 4-HBDTOFF terpolymer is shown in Fig. 1. The broad band observed at 3388 cm^{-1} indicates presences of stretching vibration of phenolic hydroxyl (–OH) group[8]. The peak at 2927 cm^{-1}, can identify the ethylene bridges associated with 4-hydroxybenzoic acid[7]. The adsorption peak at 1660 cm^{-1} indicate –C=O carbonyl stretching[7]. The peaks appeared at 1193 and 770 cm^{-1} are due to methylene bridges coupled with aromatic ring[9].The tetra substitution in the benzene ring is established by the presence of medium band at 881 cm^{-1} that is attributed to (C-H) bending vibration[7]. A peak at 1478 cm^{-1} may be ascribed to -N-H bending of secondary amide group[7]. The peak at 915 cm^{-1}

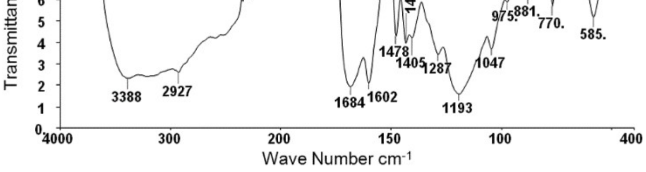

Fig. 1 — FTIR Spectrum of 4-HBDTOF terpolymer

indicates –C=S stretching vibration[8]. The shift in adsorption band passion in GO-4-HBDTOF composite (Fig. 2), indicates the interaction between graphene oxide and the terpolymer during composite formation.

Scanning electron micrograph of 4-HBDTOF terpolymer and GO-4-HBDTOF composite are shown in Figs 3 and 4. Fractured surfaces were observed for both terpolymer and GO-4-HBDTOF composite by SEM photograph. The SEM images show roughing of GO-4-HBDTOF composite surface, which led to increased surface area and favourable situation for the composite material if it is used as an adsorbent[6].

The average amount of weight loss of 4-HBDTOF terpolymer coated on graphene oxide was obtained by high temperature pyrolysis method. The results show that the pure graphene oxide losses about 2.2% weight. Graphene oxide treated with oxalic acid lost 6.2% of weight and single coating chitosan on graphene oxide lost 8.1%. Net wt loss of 4-HBDTOF terpolymer on twice coated sorbent was 28.5%. Pure 4–HBDTOF terpolymer leaves residue of about 0.6% after pyrolysis at 1050 K, which is negligible.

Effect of contact time on sorption of Pb(II) ion

Metal ion solutions of 100 mg/L Pb(II) concentration at *p*H 6.0 were kept in contact with the absorbents 4-HBDTOF terpolymer and GO-4-HBDTOF composite for 24 h. The solutions were checked for Pb(II) concentration at constant interval of time. Results are shown in Fig. 5. The rate of Pb(II) adsorption by adsorbents was greater in the initial stages then gradually increases and remains almost constant near 80 min, beyond this time both terpolymer and composite adsorbent showed no significant changes in adsorption capacity for Pb(II) ion.

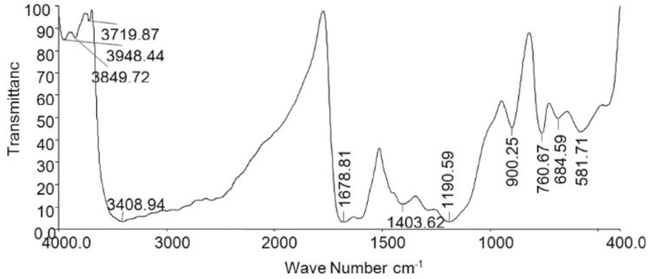

Fig. 2 — FTIR Spectrum of GO-4-HBDTOF composite

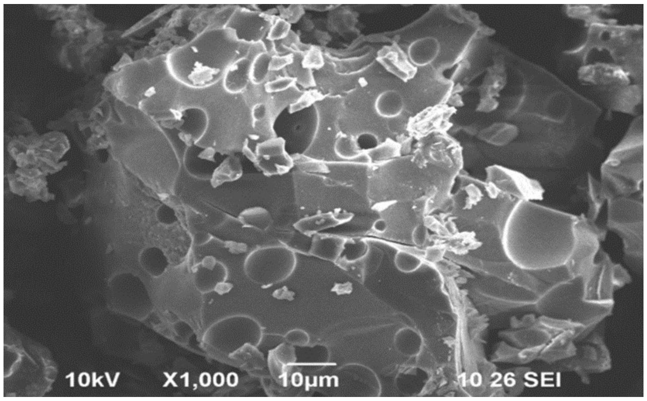

Fig. 3 — SEM image of 4-HBDTOF terpolymer

Effect of *p*H on adsorption

Effect of *p*H on Pb(II) adsorption using 4-HBDTOF and GO-4-HBDTOF composite as an adsorbent have been studied in the *p*H range 2 to10 and presented in Fig. 6. It was observed that amount of Pb(II) adsorbed on the terpolymer and composite sorbents were appreciable in the *p*H range 4-6. It is noticed that solution *p*H plays a very important role in the adsorption of Pb(II). The percentage removal increases steadily when the *p*H is in the range 2 to 6 and gradually decreases as *p*H increases.This phenomenon can be explained by the surface charge of the adsorbent

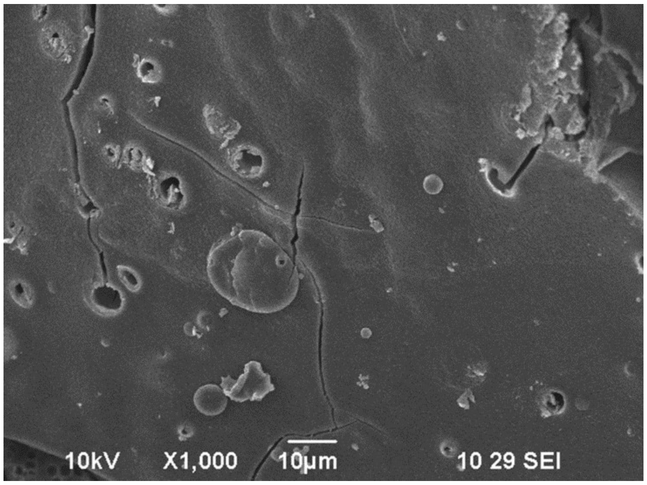

Fig. 4 — SEM image of GO-4-HBDTOF composite

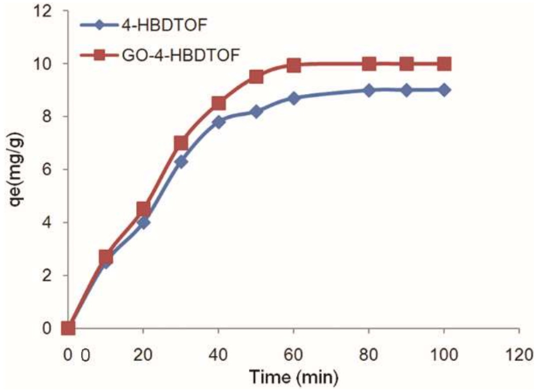

Fig. 5 — Effect of contact time on adsorption of Pb(II) 4-HBDTOF terpolymer andGO-4-HBDTOF

and the H^+ ions present in the solution. At low *p*H, the cations compete with the H^+ ions in the solution for the active sites and therefore lower adsorption. The *p*H range was chosen as 2-6 in order to avoid the formation of metal hydroxides, which has been estimated to occur at *p*H > 6.5 for $Pb(OH)_2$[10].

Effect of the initial concentration of Pb(II) in solution

Adsorption studies were carried out with varying initial concentration of Pb(II) ion in aqueous solution in the range of 10 to 100 mg/L at *p*H 6.The results areshown in Fig. 7. This has been attributed to the increasing driving force of metal ion towards the adsorbent surface. The results indicate that there are higher attractive forces between Pb(II) ion and 4-HBDTOF terpolymer and GO–4-HBDTOF composite adsorbents.

Adsorption isotherm

Adsorption isotherm studies were carried out to determine the amount of solute adsorbed per unit weight of adsorbent. Adsorption isotherm data were useful to understand mechanism and characteristics of adsorption process. In this present study, sorption data were fitted into Langmuir equation.

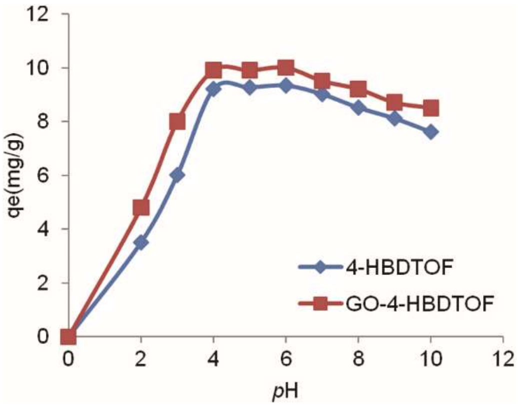

Fig. 6 — Effect of *p*H on adsorption of Pb(II) by4-HBDTOF terpolymer and GO-4-HBDTOF composite

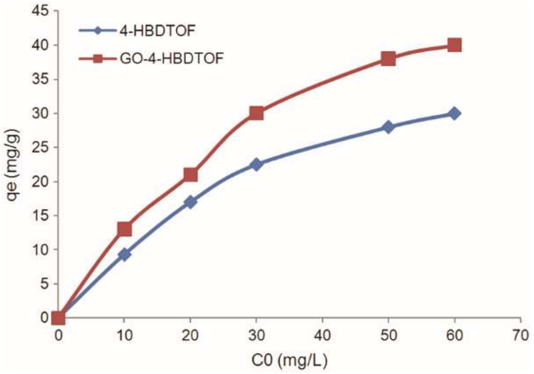

Fig. 7 — Effect of Initial Pb (II) ion concentrations on adsorption capacity of 4-HBDTOF terpolymer and GO-4-HBDTOF composite

Langmuir adsorption isotherm

The basic assumption of the Langmuir adsorption process is the formation of a monolayer of the adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place[11]. The Langmuir is expressed as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad \ldots(1)$$

The isotherm data have been linearized using Langmuir equation and was plotted between C_e/q_e versus C_e (Fig. 8). The Langmuir parameterQ_0 (mg/g) and b (mg/L) were calculated from the slop and intercept and were given in the Table 1. Monolayer adsorption capacity, Q_0values were found to be as 33.33 mg/g for 4-HBDTOF terpolymer and 45.45 mg/g for GO–4-HBDTOF composite. The Langmuir constant b (L/mg) denotes energy of adsorption process. The calculated values of b were found to be 3.75 and 5.5 L/mg for 4-HBDTOF terpolymer and GO–4-HBDTOF composite respectively. The high values of correlation coefficient (R^2) indicate good agreement between the experimental values and isotherm parameters and confirm the monolayer adsorption of Pb (II) on 4-HBDTOF terpolymer and GO–4-HBDTOF composite[12].

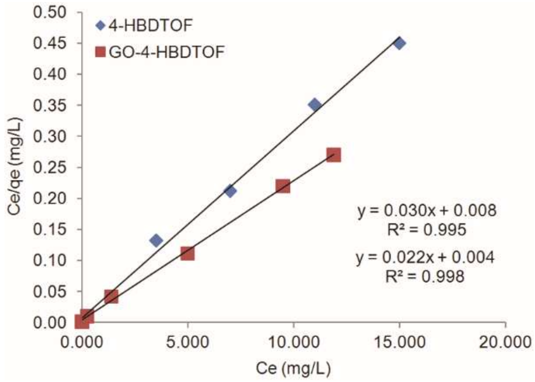

Fig. 8 — Langmuir isotherms for the adsorption of Pb (II) ion from aqueous solution

Table 1 — Langmuir and Freundlich isotherm parameter at 30°C

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	Q_0(mg/g)	b(L/mg)	R^2	K_f(mg/g)	1/n(mg/L)	R^2
4-HBDTOF	33.33	3.75	0.995	25.06	0.175	0.932
GO-4-HBDTOF	45.45	5.50	0.998	28.12	0159	0.972

Table 2 — R_L values for the adsorption of Pb(II) ion

S.NO	Concentration of Pb(II) ion in mg/L	R_L values for 4-HBDTOF terpolymer	R_L values for GO-4-HBDTOF composite
1	10	0.0260	0.0179
2	20	0.0132	0.0090
3	30	0.0088	0.0060
4	40	0.0066	0.0045
5	50	0.0053	0.0036
6	60	0.0044	0.0030

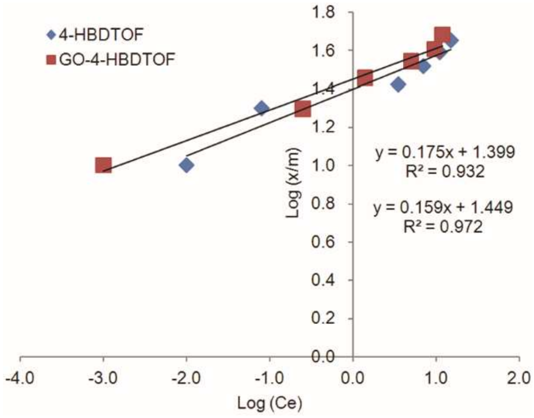

Fig. 9 — Freundlich adsorption isotherm for the adsorption of Pb(II) ionfrom aqueous solution

R_L is a dimensionless parameter, it is the measure of favorability of adsorption process. The calculated values R_L at different concentration for adsorption Pb(II) onto 4-HBDTOF terpolymer and GO–4-HBDTOF composite are presented in the Table 2. R_L values are in the range of $0< R_L< 1$ which confirms the adsorption of Pb(II) on 4-HBDTOF terpolymer and GO–4-HBDTOF composite were favuorable process[12].

Freundlich isotherm model

Freundlich isotherm was used to describe adsorption pattern (Freundlich and Helle 1939). The model assumes multiple layers at the adsorbent surface and adsorption will increase as long as concentration increases. The Freundlich adsorption isotherm represents the relation between the amount of metal adsorbed per unit mass of the adsorbent x/m (mg/g) and the concentration of the metal in solution at equilibrium C_e (mg/L). The equation is expressed as

$$\log (x/m) = \log K_f + 1/n \log (C_e) \qquad \ldots (2)$$

Figure 9 illustrates the plot of Freundlich adsorption isotherm, this adsorption isotherm incorporate the adsorption capacity K_f and intensity of adsorption 1/n. Freundlich constants (K_f and 1/n) were obtained from the slop and intercept of the plot (Table 1) log C_e vs log (x/m). The results indicate adsorption capacity of composite was higher than that of terpolymer. The adsorption data were fitted well with Langmuir isotherm equation than Freundlich isotherm with good correlation coefficient[12].

Conclusion

- The terpolymer 4-HBDTOF is successfully synthesized with good yield by condensation of monomers 4-hydroxybenzoic acid, dithiooxamide and formaldehyde in 2:3:5 molar ratios.
- The terpolymer is successfully coated on graphene oxide to prepare GO-4-HBDTOF composite.
- Terpolymer and composites have been characterized by FTIR and SEM photographs. SEM image shows roughing of GO-4-HBDTOF composite surface, which increases surface area and favourable situation for adsorption of metal ions on the composite adsorbent. The composite material is proved to be a better adsorbent than terpolymer for the removal of Pb(II) from aqueous solution and more active sites are exposed on composite surface.
- The study could be extended to the newly synthesized GO-4-HBDTOF composite to remove toxic metals from industrial effluent. Study can also be extended for the fabrication of column using the composite for water purification.

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