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Equilibrium and kinetics of Pb^{2+} adsorption from aqueous solution by dendrimer/titania composites

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ABSTRACT

The presence of lead in wastewater is dangerous to aquatic life even in relatively low concentration. In recent years, adsorption becomes an effective and economical alternative technique for removing heavy metals from aqueous solutions. In the current study, the removal of Pb^{2+} ions from aqueous solution onto generation 4 polyamidoamine (PAMAM) dendrimers adsorbent was investigated. Batch mode experiments were conducted to study the effects of different variables including pH, contact time, initial lead ions concentration, and adsorbent dose on the removal process. It has been found that a maximum lead adsorption was found at pH 7. The maximum adsorption almost reached after shaking for slightly more than 30 min. The adsorption potential and Pb^{2+} removal started to decrease after initial Pb^{2+} concentration of 400 ppm. The experimental data fitted well into the Langmuir isotherm. The kinetic showed that the process of adsorption of Pb^{2+} on PAMAM dendrimers conforming to second-order kinetics. The current study showed that PAMAM dendrimers is a promising adsorbent for removing lead ions from contaminated aqueous solutions.

Keywords: Pb^{2+}; Adsorption; Kinetics; Dendrimers composite; Aqueous solution

1. Introduction

Toxic metal contamination is a serious problem [1] threatening human health. Heavy metal ions are toxic and carcinogenic at even relatively low concentrations [2]. They are not biodegradable and can accumulate in living organisms [3]. Therefore, these heavy metals can be considered as one of the most important pollutants for waters and wastewaters [4]. Lead is an important pollutant introduced into natural waters. It is mainly discharged from exhaust gases of automobile to environment. Moreover, it diffuses to the water and environment through effluents from lead smelters, battery manufacturers, paper and pulp industries, and ammunition industries [5]. Major lead pollution has been through in the manufacture of storage batteries, painting pigments, ammunition, solder, plumbing fixtures, automobiles, cable coverings, radioactivity shields, caulking, and bearings [6,7]. The

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presence of lead in wastewater is dangerous to aquatic flora and fauna even in relatively low concentration and stringent environmental regulation attracts the attention of environmental scientists for its control. The removal of heavy metals is an important problem especially in industrial effluents. Various removal methods such as membrane processes (dialysis, electrodialysis, and reverse osmosis), neutralization-precipitation, extraction and ion exchange are useful [8–12]. However, in recent years, adsorption becomes an effective and economical alternative technique, since the other methods may have some limitations [8,13,14]. Adsorption is very popular due to its simplicity, low cost, [15–17] and potential for overcoming the environmental problems [17]. It may be considered as preferable in many cases due to its economical advantages, high efficiency, and applicability [8].

Although commercial activated carbon, with high surface area, microporous character, and high adsorption capacity, has made its potential adsorbent for the removal of heavy metals from industrial wastewater, it is expensive and has relatively high operation costs. Thus, low-cost adsorbents are becoming the focus of many investigations on the removal of heavy metals from aqueous solutions. In recent years, a wide variety of materials such as chitosan [18] granular red mud [19], sugar beet pulp [20], Lignite [21], rice husk [22–24], Zeolite [25], sawdust [26,27], leaves [28], and nut walnut shells [29], and eucalyptus camaldulenis tree leaves [30] are examples of low-cost materials used in the removal of heavy metal ions from aqueous solution. Dendrimers are a new class of polymeric materials. They are highly branched, mono disperse macromolecules. The structure of these materials has a great impact on their physical and chemical properties. As a result of their unique behavior, dendrimers are suitable for a wide range of biomedical and industrial applications. Dendrimers, hyperbranched molecules composed of monomers that radiate from a central core, are emerging as an important class of polymers targeting applications in environmental remediation, nanoparticle synthesis, and nanomedicine [31–33]. Perhaps, the most popularly studied dendrimers are polyamidoamine (PAMAM) dendrimers. PAMAM dendrimers are among the least toxic dendrimers and are made from inexpensive, readily available materials [34,35]. Initial efforts in the application of PAMAM dendrimers focused on generations [31–33], which have flat ellipsoidal shapes. However, higher generation dendrimers (4 and up), which are starburst shaped, were logical extensions and are particularly appealing for modern applications [31,36]. PAMAM dendrimers key property is their ability to chelate metal ions from solutions. This attribute has primarily been exploited in the synthesis of metal-nanoparticles [32,33,37,38]; however, recently, dendrimer-based chelation has gained interest. For example, metal-intoxication is a serious environmental concern as toxic metals are increasingly deposited into water, soil, and, inevitably, air and food. Hydroxyl and amine-terminated PAMAM dendrimers are, perhaps, the most popularly studied for metal complexation applications. PAMAM with OH-terminal groups are especially nontoxic due to a lack of surface amine [39]. Encapsulation of metal ions by generation 4 hydroxyl-terminated PAMAM (G4-OH) involves coordinating each metal ion with one of the dendrimer's 62 tertiary amine sites [40].

In the current study, generation 4 PAMAM dendrimers were immobilized over titanium(IV) oxide (titania) for the removal of Pb^{2+} from synthetic solutions as models for the wastewater that produced from industries. The influence of several operating parameters for the adsorption of Pb^{2+}, such as pH, contact time, metal ion concentration, and dosages of PAMAM dendrimers have been investigated. The adsorption process by PAMAM dendrimers have also been studied through a kinetic study. The Langmuir isotherm model was used to describe the equilibrium adsorption characteristics.

2. Materials and methods

2.1. Materials

All the chemicals used in this study were of analytic grade. Lead nitrate $Pb(NO_3)_2$ used in adsorption experiments in extra pure grade and was purchased through Merck. The stock solution of Pb^{2+} was prepared by dissolving $Pb(NO_3)_2$ in deionized water obtained from Millipore system, France. A series of Pb^{2+} solutions used in these experiments were made by diluting the stock solution to the desired concentrations ranging from 50 to 500 mg/L. Before mixing these solutions with the adsorbent, pH adjustments were carried on using 0.1 N hydrochloric acid (HCl) and 0.1 N sodium hydroxide (NaOH). pH meter 3510 (Jenway) was used to measure the pH values of the solutions. The concentrations of Pb^{2+} were determined by ICP-OES (Varian 720-ES), and average values of three replicates were taken for each determination. The surface morphology of the PAMAM adsorbent was characterized by scanning electron microscope (SEM).

2.2. Adsorbent preparation

The adsorbent used in the current study was prepared, as recorded by Barakat et al. [41], by adding 1 g of G4-OH (generation 4 PAMAM) dendrimers with ethylenediamine core) to a large excess of deionized water. A mass of 99 gm of titanium (IV) oxide was slowly added to the dendrimers containing aqueous solution. Once all of the titania were added, mild sonication ensued for 2 h. Following sonication, the composite materials were dried with mild heating on a hot plate (temperature 60˚C) to remove the solvent and then in a drying oven (Temperature 90˚C) to remove all excess moisture.

2.3. Batch adsorption experiments

Adsorption experiments were carried out at various pH (3–9). For each batch experiment, 500 ml solution containing adsorbent dose (1 g/L) and initial Pb^{2+} concentration (50 mg/L) was used. After setting pH, the mixture was agitated on mechanical shaker at a speed of 150 rpm for a contact time (120 min) at 25˚C. After each 30 min, a small amount of the mixture was taken and filtered to separate the adsorbent from supernatant. The residual concentration of lead in supernatant was determined by ICP to determine the optimum pH for Pb^{2+} removal. After pH adjustment, 500 ml solutions containing various initial lead concentrations (50–500 mg/L), and adsorbent dose (0.1–1 g) at contact time (120 min) at the optimum pH were investigated to determine the best conditions on Pb^{2+} removal. All experiments were carried out in triplicate. The removal (adsorption) percentage (*R*%) of lead was calculated for each run as follows:

$$\text{Adsorption } \% = [(C_i - C_f/(C_i)] \times 100 \quad (1)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively.

The adsorption capacity of an adsorbent, which is obtained from the mass balance on the adsorbate in a system with solution volume *V*, is often used to study the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of Pb^{2+} ions at equilibrium were calculated using Eq. (2).

$$q(\text{mg/g}) \ \% = [(C_i - C_f)/(M)] \times V \quad (2)$$

where C_i and C_e were the initial and final concentration of lead ions in the solution, respectively (mg/L). *V* is the volume of solution (L) and *M* is the mass of adsorbent (g).

3. Results and discussion

3.1. Adsorbent characterization

SEM is used to investigate the morphological features of the adsorbent (dendrimer/titania composites). Fig. 1 shows the observation of scanning electron micrograph of PAMAM dendrimers. It indicates the presence of many pores and a rough structure on the surface of PAMAM dendrimers, which is favorable for adsorption. Different characterization analysis for the adsorbent such as FTIR, XRD, pore properties, and specific surface areas of the titania before and after dendrimer immobilization, was done in the previous article [41]. The BET surface areas were 2.7 m^2/g. The pore diameters and volumes were 2.8 nm and 8×10^{-3} cm^3/g, respectively. The structure of titania was also confirmed with a diffraction pattern of the rutile phase obtained. The (110), (101), (200), (111), (211), (220), and (310). Miller indices were observed [41].

3.2. Efficiency of dendrimer/titania composites for Pb^{2+} ion removal from wastewater

The dendrimer/titania composites were evaluated as adsorbents for Pb^{2+} ion removal from synthetic wastewater. The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the degree of ionization, surface charge of the adsorbent, and speciation of adsorbate [42,43]. To establish the effect of pH on the sorption of Pb^{2+}, a batch experiment containing Pb^{2+} concentration of

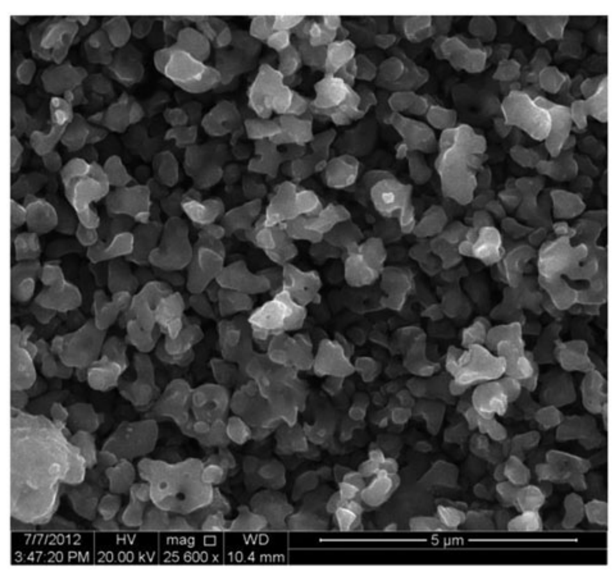

Fig. 1. Scanning electron micrograph of dendrimers on TiO_2 (Black matrix is TiO_2, white is dendrimers).

50 mg/L, stirring speed at 150 rpm, temperature at 25℃ at various pH values was carried out in the range of 3–9. PAMAM dendrimers adsorbent dose of 1 g was added. The pH of lead solution was adjusted after adding the adsorbent. Fig. 2 shows the adsorption percentage of Pb^{2+} ions on PAMAM dendrimers. It is clear that the adsorption decreased with increase in pH. It is noted that at low pH values, solution is strongly acidic and the surface of the sorbent is surrounded by hydrogen ions, which prevent the metal ions from approaching the binding sites on the sorbent. Due to this reason, it is thought that sorption capacity increases with increase in pH. With increasing in pH (above pH Point Zero Charge), the acidity starts to decrease allowing the metal ions to bind on the PAMAM dendrimer sites. At pH value of 7, metal ions can easily compete hydrogen ions and bind active sites of adsorbent. Due to this reason, sorption capacity was high at pH 7. At higher pH, sorption capacity decreased and this can be attributed to the fact that at higher pH number of hydroxyl ions is more and chances of formation of metal hydroxides are also more that result in precipitation. This precipitation caused a decrease in sorption capacity with accumulation of metal ions [44–46]. Therefore, in subsequent equilibrium experiments, pH value of 7 was used.

The effect of contact time on the Pb^{2+} ions by adsorption on PAMAM dendrimers was investigated over time intervals from 0 up to 120 min. Table 1 shows the removal yield by adsorption as a function of contact time. It can be shown that the removal reached more than 95% at 30 min and the maximum adsorption of 99.9% was reached at 60 min.

Initial concentrations of Pb^{2+} ions between 50 and 500 mg/L at constant values of pH 7, PAMAM dendrimers of 1 g/L, and contact time of 60 min have been used to investigate their effect on Pb^{2+} removal (Table 2). It has been found that Pb^{2+} removal has not been affected by increasing the initial Pb^{2+} concentration up to 400 mg/L. Then, the adsorption potential and Pb uptake started to decrease. This could be attributed to the saturation of the active sites on the adsorbent.

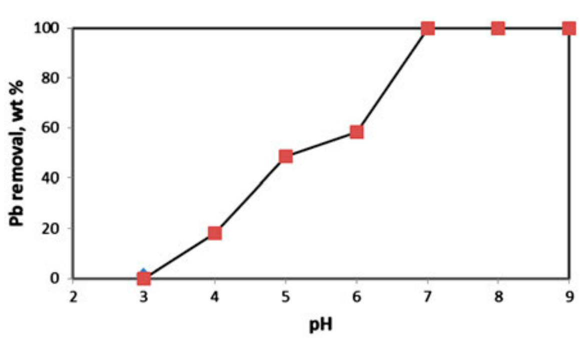

Fig. 2. Effect of pH on removal of pb^{2+} by adsorption on PAMAM dendrimers (Conditions: 1 g/L PAMAM dendrimers, contact time 60 min, 50 ppm Pb^{2+}).

Evaluation of PAMAM dendrimers adsorbent doses of 0.1–1 g/L at constant values of pH 7, pb^{2+} ions concentration of 50 ppm, and contact time of 60 min have been used to study their effect on Pb^{2+} removal (Fig. 3). The results show that the removal efficiency increased by increasing the adsorbent concentration. A dose of 0.5 g of adsorbent at the mentioned conditions was enough to remove 100% of the present Pb^{2+} ions concentration. Increase in the adsorption percentage with PAMAM dendrimers dose may be due to the increase in adsorbent surface area and availability of more adsorption sites [47]. Saturation of the available active sites on the surface functional groups may prevent further metal ion uptake. Fig. 4 shows the adsorption potential of the PAMAM dendrimers adsorbent to Pb^{2+} ions concentrations. The results show that the adsorption potential of PAMAM dendrimer increased by increasing the initial pb^{2+} ions concentrations. This can be due to the greater availability of the active sites. At higher concentration of Pb^{2+} ions concentration (above 400 mg/L), the linearity of the adsorption potential started to deviate. This deviation may be due to saturation of the available active sites on the surface functional groups. The mechanism of adsorption can be attributed to the electrostatic interaction between the positive charges on the metal ions with the negative charge on the terminal hydroxyl groups of the PAMAM dendrimers. This is also reported by Mousavi and Seyedi [48] who studied the efficiency of NA as adsorbent for removal of Pb^{2+}. Comparing the adsorption potential of PAMAM dendrimers to other adsorbents, it has been found that PAMAM dendrimers is more effective compared with fly ash (37 mg/g) [49], eichhornia activared carbon (16.6 mg/g [50], natural phosphate (115 mg/g) [51], sugarcane bagasse (333 mg/g) [52], and Ulmus carpinifolia (201.1 mg/g) [53]. However, it was lower than NA [48] (1000 mg/g).

3.3. Isotherm and kinetics studies

Langmuir isotherm model was used to study the sorption data obtained for the variation of metal ion concentrations.

Langmuir equation: $c_e/q_e = (1/k_L Q_m) + (c_e Q_m)$ (3)

Table 1
Effect of contact time on the removal of Pb^{2+} (1 g/L PAMAM dendrimers P, 50 ppm Pb^{2+}, pH 7, temperature 25℃)

Time, minute	Adsorption %
0	95.8
30	99.9
60	99.9
90	99.9
120	

Table 2
Effect of initial Pb^{2+} ions concentrations on their removal by PAMAM dendrimers (1 g/L PAMAM dendrimers P, pH 7, temperature 25℃, contact time 60 min)

Pb^{2+} initial concentration, mg/L	Adsorption %
50	95.9
100	99.8
200	99.6
300	99.1
400	98.1
500	83.9

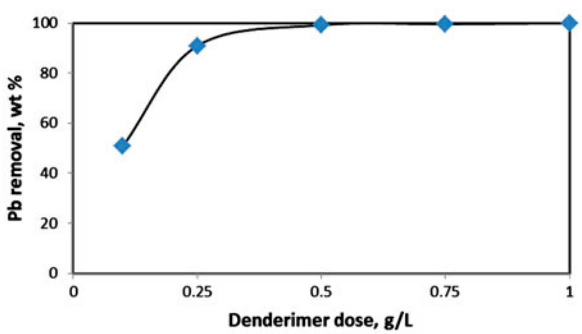

Fig. 3. Effect of PAMAM dendrimers adsorbent dosage on the removal of Pb^{2+} ions (Conditions: 0.1–1 g/L PAMAM dendrimers P, 50 ppm Pb^{2+}, pH 7, temperature 25℃, contact time 60 min).

where c_e is the equilibrium concentration of metal ions in solution (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), and Q_m (mg/g) is the measure of adsorption capacity under the experimental conditions and K_L is a constant related to the energy of adsorption (L/mg). It is shown from the results of Fig. 5 that the adsorption of Pb^{2+} onto PAMAM dendrimers follows the Langmuir isotherm. The essential characteristic of the Langmuir isotherm may be expressed in terms of dimensionless separation parameter R_L, which is indicative of the isotherm shape that predicts

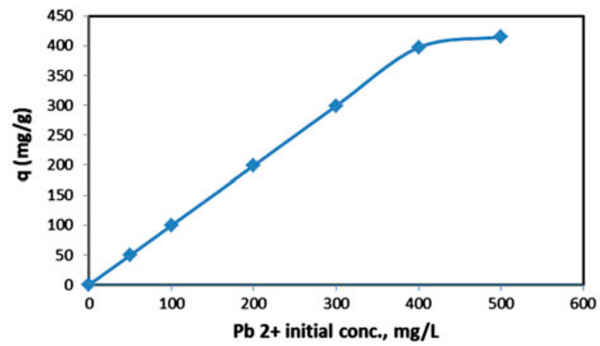

Fig. 4. Adsorption Potential of PAMAM dendrimers to Pb^{2+} ions concentrations (Conditions: 1 g/L PAMAM dendrimers P, 50 ppm Pb^{2+}, pH 7, temperature 25℃, contact time 60 min).

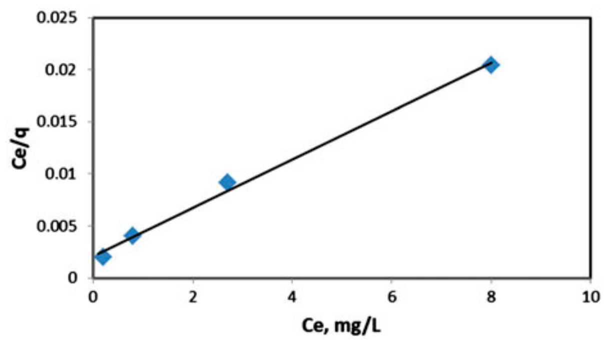

Fig. 5. Langmuir isotherm plot for the adsorption of lead onto PAMAM dendrimers.

whether an adsorption system is favorable or unfavorable. R_L is defined as follows:

$$R_L = 1/(1 + k_L c_e) \tag{4}$$

where k_L is the Langmuir constant and c_e is the Pb^{2+} ions concentrations. The R_L values calculated for the present experimental data fall between zero and one, which is an indication of the favorable adsorption of lead on the adsorbent.

The kinetics of Pb^{2+} adsorption was studied by plotting time vs. Pb^{2+} ions removal percentages curves. The rate kinetics of Pb^{2+} adsorption on the adsorbents was analyzed using the second-order kinetic model. A second-order equation [54] based on adsorption equilibrium capacity may be expressed in the form:

$$t/q_t = (1/k_2 q_e^2) + (t/q_e) \tag{5}$$

where k_2 is the second-order reaction rate equilibrium constant ($g\,mg^{-1}\,min^{-1}$). A plot of t/q_t against t

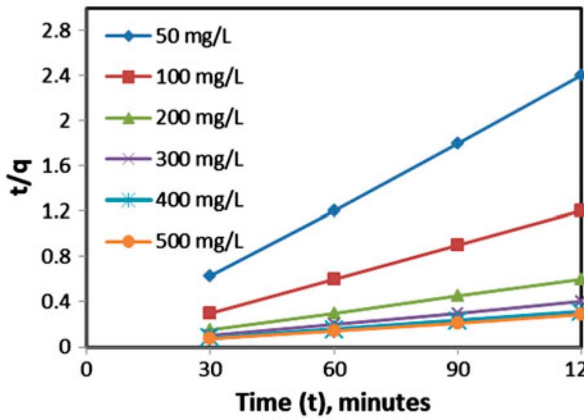

Fig. 6. Plot of the second-order model at different initial pb^{2+} concentrations (Conditions: 1 g/L PAMAM dendrimers P, 50–500 ppm Pb^{2+}, pH 7, temperature 25℃, contact time 60 min).

should give a linear relationship for the applicability of the second-order kinetic. The second-order model is shown in Fig. 6. It has been found that the determination coefficient (R^2) for the second-order kinetic model is nearly equal 1 (0.97, 1, 1, 0.9, 0.98, 0.94 for the initial pb^{2+} concentrations of 50, 100, 200, 300, 400, 500 g/L, respectively). Therefore, the kinetics of lead adsorption onto the adsorbent can be described well by second-order equation.

4. Conclusions

The current study proved that PAMAM dendrimers is an effective adsorbent for the removal of Pb^{2+} ions from contaminated aqueous solutions. The adsorption reached the equilibrium at a time of slightly more than 30 min. The adsorption was found to be greatly dependent on solution pH and the optimum pH for the removal of Pb^{2+} ions was 7. The maximum adsorption capacity of Pb^{2+} ions on PAMAM dendrimer was around 400 mg/g. The batch adsorption data for lead were successfully followed Langmuir model. The kinetic sorption data fitted well into the second-order kinetic model.

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