Exploring the adsorption and desorption characteristics of lead(II) ions from synthetically contaminated wastewater by anionic surfactant modified neutral alumina

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In our previous studies, it has been shown that anionic surfactant (AS) can be removed from water media by neutral alumina through adsorption and subsequent bilayer formation. In this study, it has been shown that after the AS adsorption, the spent sludge can be used for Pb(II) removal from water. The modified alumina upon surfactant loading (which can be regarded as a waste material) is utilized to remove another waste. The effects of several parameters important for the operation, like dose of adsorbent, initial level of concentration of Pb(II), shaking speed, temperature, and also pH are studied. The maximal adsorption capacity has been reported to be 30.3 mg/g under optimized condition. The experimental data follows the reaction kinetics of pseudo-second order model. The investigation to establish isotherm shows a better correlation with Freundlich isotherm model in contrast to Langmuir model. The process can be inferred as favorable, spontaneous, and exothermic by the obtained values of thermodynamic parameters.

Keywords: Adsorption, sodium dodecyl sulfate (SDS), SDS treated alumina, lead(II) removal, desorption.

Introduction

The poisonous effect of lead, a heavy metal, is of great concern, globally, for its bioaccumulation, biomagnification and non-biodegradable property. Lead has been in trend of multipurpose use in many industries, for example, the acid battery of car, gasoline production, ceramic, and glass manufacturing[1]. It is highly toxic and its discharge in the environment may result its entry into the food chain. Here, in this study, we have shown a study where alumina after adsorption of SDS (an anionic surfactant) in high concentration has been utilized for lead removal from aqueous media. Hence the recycling of surfactant bearing alumina can be practiced to treat wastewater containing Pb(II) at a significantly high concentration.

Materials and methods

Neutral alumina and disodium salt of ethylenediaminetetraacetic acid was procured from Sisco Research Laboratories Pvt. Ltd. (SRL), India. Sodium dodecyl sulphate, lead nitrate, toluene, acetone, glacial acetic acid, sodium hydroxide, nitric acid, hydrochloric acid, Cu(II) sulphate pentahydrate, sodium dihydrogen phosphate dihydrate, calcium chloride, nickel(II) sulphate heptahydrate, sodium chloride, sodium sulphate, and sodium nitrate were procured from Merck, India. Double distilled water (pH 6.7–7.0) was used for the study. Pb(II) determination was accomplished using a fast sequential flame atomic-absorption-spectrometry, in short AAS (Model No: Varian AA240FS, Made in Australia) at 217 nm. An incubator shaker (By REMI Instruments, India) was arranged to agitate the samples in a conical flask for a specified contact period. The preparation, in laboratory, of surfactant modified alumina (SMA) had been executed following our earlier published method[2].

Results and discussion

Comparison of alumina and SMA for Pb(II) removal :

A study was accomplished in order to contrast the competence of Pb(II) removal by SMA with alumina under identical experimental conditions with Pb(II) solution in distilled water, maintained concentration was 100 mg/L, while the applied dose of SMA or alumina was 4 g/L. The pH of Pb(II) solutions were 4.5 and the solutions were agitated for 30 min at a rotational speed of 150 rpm at 30°C. The observa-

tion showed that only 26% of Pb(II) could be removed by alumina, whereas the SMA was effective to remove 69% of Pb(II) in the same controlled conditions (Fig. 1).
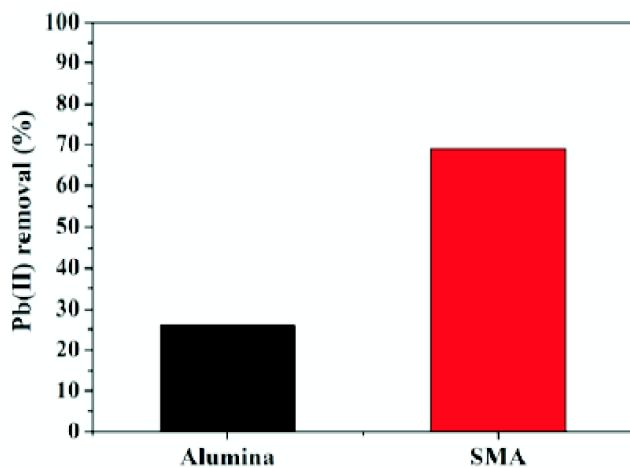

Fig. 1. Comparison of Pb(II) removal efficiency of SMA and alumina (Experimental condition: contact time = 30 min, Pb(II) concentration = 100 mg/L, adsorbent dose = 4 g/L, pH = 4.5±0.2, speed of agitation = 150 rpm, temperature = 30±2°C).

This type of enhancement by SMA was reported, by the previous researchers, as a result of the formation of surfactant admicelle on the surface of alumina. As the surface charge of alumina at pH less than 9.16 is positive, Pb(II) ions are eventually repelled by alumina surface causing very less removal. But after the AS removal by alumina when surfactant admicelle is formed on alumina surface, the surface charge becomes negative and due to this negative charge Pb(II) ions are attracted by admicelle or surfactant bilayer.

Effect of various parameters on removal efficiency of Pb(II) by SMA:

Effect of variation of contact time:

The investigation was executed to find out the consequence of variation of contact duration on the efficiency of Pb(II) removal at starting level of concentrations 10, 30, and 50 mg/L. The change in efficiency of Pb(II) removal, expressed in percentage, with variation of time of contact, has been shown in Fig. 2.

It is conspicuous that the process is quick, and the rate of removal reaches at constant value after 30 min. This is a very unique property of SMA. Such a quick removal is advantageous for column study. Subsequently, it was decided
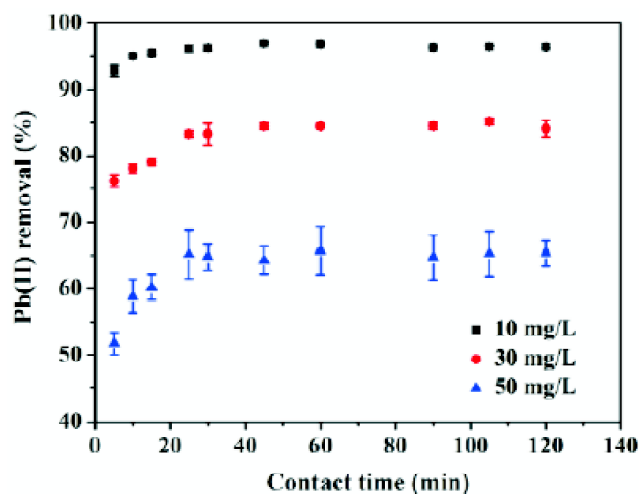

Fig. 2. Effect of contact time on % removal of Pb(II) by SMA (Experimental condition: adsorbent dose = 2 g/L, pH = 4.5±0.2, speed of agitation = 150 rpm, temperature = 30±2°C).

that the time required to attain equilibrium was 30 min and used for other studies. The achieved efficiency of removal, in 30 min, was 93%, 83%, and 65% for those concentrations which were initially 10, 30 and 50 mg/L, respectively.

Effect of variation of adsorbent dose:

The Pb(II) removal depends on the dose of SMA to a great extent. A study was executed to look over the end result of variation of SMA dosage on the overall process of Pb(II) removal. The study was accomplished by three Pb(II) concentrations which were initially 10, 50 and 100 mg/L. The graphical representation of the removal of Pb(II), expressed in percentage vs SMA dose is illustrated in Fig. 3 for three different initial Pb(II) concentrations (10, 50 and 100 mg/L).

It unveils the intensified process of Pb(II) removal as the applied dose of SMA increases. This is because of the presence of additional interactive sites at a higher level of SMA dose, in contrast to a lower dose of SMA, for a specific concentration, initially, of Pb(II).

Effect of variation of the initial concentration of Pb(II):

The consequence of variable initial Pb(II) level on the percentage removal of Pb(II) by SMA was executed in a wide range of concentration (5–100 mg/L). Three different adsorbent doses (1 g/L, 2 g/L and 4 g/L), temperature 30±2°C, and pH 4.5±0.2 were chosen. The results of the experiment (Fig. 4) showed that possible removal was in the range of 90–97% for the lower initial Pb(II) concentrations with an ap-
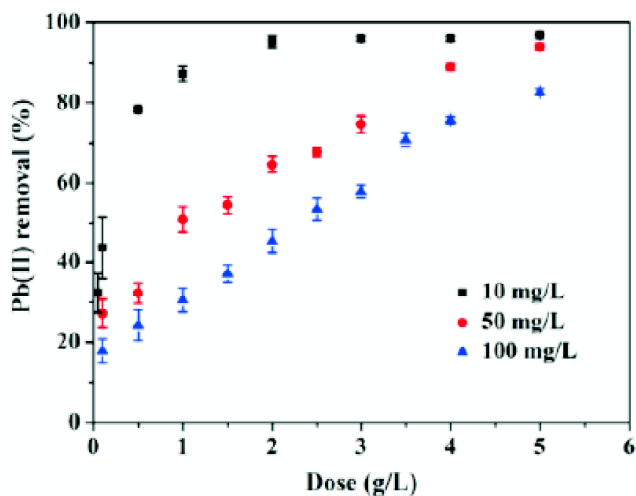
Fig. 3. Effect of SMA dose on % removal of Pb(II) (Experimental condition: adsorbent dose = 0.1–5 g/L, contact time = 30 min, pH = 4.5±0.2, speed of agitation = 150 rpm, temperature = 30±2°C).

plied SMA dose of 2 g/L.

However, only 70% removal was achieved for the higher Pb(II) concentration which was initially 100 mg/L by applying a 4 g/L SMA dose. The maximum relative standard deviation for these experimental results was 8.82% Pb(II) concentration which was initially 50 mg/L and, at the same time, the applied SMA dose was 1 g/L.
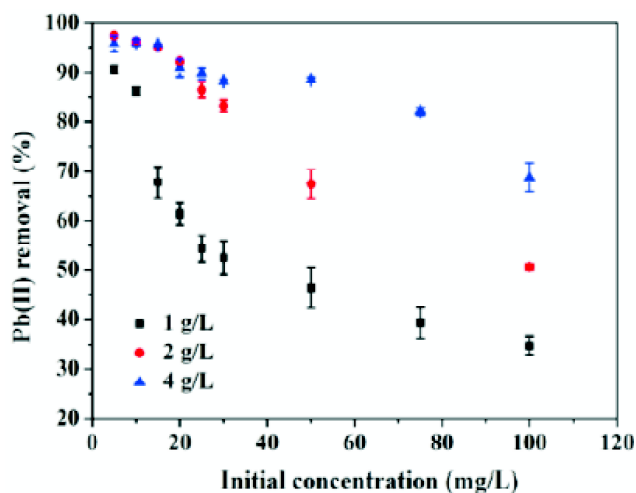

Fig. 4. Effect of initial concentration on % removal of Pb(II) (Experimental condition: initial concentration of Pb(II) = 5–100 mg/L, contact time = 30 min, pH = 4.5±0.2, speed of agitation = 150 rpm, temperature = 30±2°C).

Effect of variation of pH:

One of the critical parameters in adsorption is the solution pH. The solubility of the heavy metals, and the chemical properties as well, depends on solution pH[3]. The reaction of taking Pb(II) away from solution, using the process of adsorption, by SMA was investigated in a controlled and predetermined pH range of 1.0 to 5.5. The solution pH was kept in the aforementioned range by 1 N NaOH and 0.15 N HNO$_3$. The data obtained by the investigation are plotted in Fig. 5.
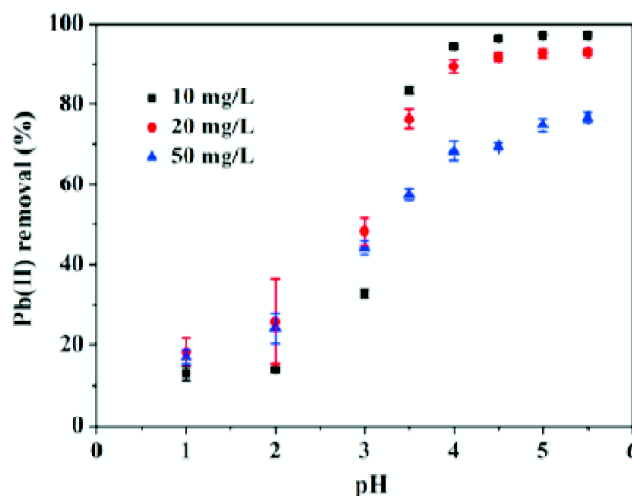

Fig. 5. Effect of pH on removal of Pb(II) by SMA (Experimental condition: dose of SMA = 2 g/L, contact time = 30 min, pH = 4.5±0.2, speed of agitation = 150 rpm, temperature = 30±2°C).

The outcome of the experiment confirmed that the increase in pH results in intensification of removal efficiency and the peak removal was 97.2% at pH 5.5 for the Pb(II) concentration which was initially of 10 mg/L and dose of SMA 2 g/L. The maximum relative standard deviation for these experimental results was 18% for the solution which had concentration level of 20 mg/L initially, while the added dose of SMA was maintained at 2 g/L at pH 1.0. When the pH of the solution was 6.0, the Pb(II) is precipitated as lead hydroxide (Pb(OH)$_2$). But at a lower concentration of lead, the precipitation was not visible. Hence, pH 4.5±0.2 was selected for further studies. At lower pH (< 3.0) the active sites of SMA get protonated and the metal ion Pb(II) removal was very less, almost insignificant, in pH range 1–3 because the surface was occupied by H$^+$ ions. There is a competition between Pb(II) ions and H$^+$ ions at lower pH to interact with

the SMA. On the other hand, a substantial amount of OH⁻ ions at higher pH enhances the Pb(II) removal efficiency by making the surface negative[4].

Effect of foreign ions:

This experiment was accomplished to find out the interference of foreign ions, both anions and cations, which exist together with Pb(II). The results are illustrated in Figs. 6 and 7.
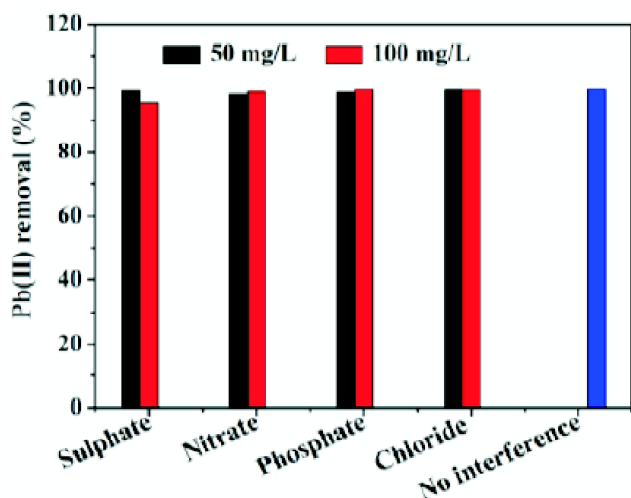

Fig. 6. Effect of anions on Pb(II) removal by SMA (Experimental condition: Pb(II) = 50 mg/L, dose of SMA = 5 g/L, contact time = 30 min, pH = 4.5±0.2, speed of agitation = 150 rpm).

Fig. 7. Effect of cations on Pb(II) removal by SMA (Experimental condition: Pb(II) = 50 mg/L, dose of SMA = 5 g/L, contact time = 30 min, pH = 4.5±0.2, speed of agitation = 150 rpm).
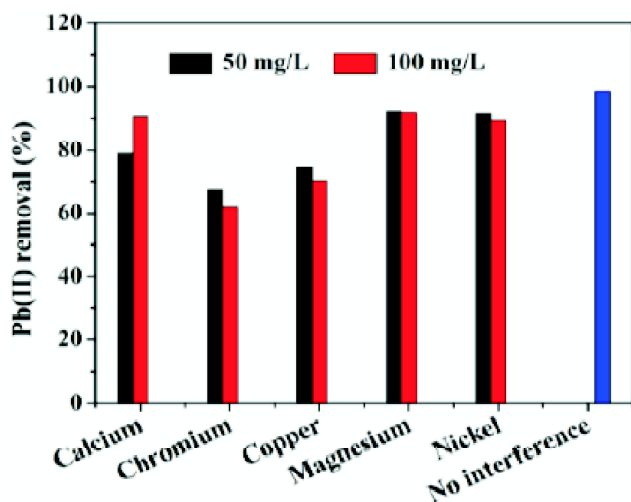
The presence of anion showed no significant interference. But the presence of cations coexisting with Pb(II) showed a considerable decrease in overall removal percentage of Pb(II). The maximum interference (37% reduction) is shown by chromium ion (Cr^{3+}) of 100 mg/L initial concentration in solution.

Adsorption isotherm:

Many theoretical models can be used for isotherm study. Two models are used very often by researchers in adsorption field, first one is Freundlich isotherm model and the other one is Langmuir isotherm model. The Langmuir model postulates that adsorption takes place in a single layer on the homogeneous surface. In contrast, the empirical theory of Freundlich isotherm model postulates that adsorption is to be taken place on the heterogeneous surface. The constants of isotherm models were derived from the slope with x-axis and intercept of the y-axis of the obtained straight lines, by the plotted data of the study, and presented in Table 1. The results clearly indicate that Freundlich isotherm is better followed compared to the Langmuir isotherm. The obtained value $0.1 < 1/n < 1$ for Freundlich isotherm indicates a favorable adsorption[5].

Table 1. Isotherm constants for removal of Pb(II) on SMA

Freundlich isotherm			
$1/n$	K_F (mg/g (L/g)$^{1/n}$)	R^2	χ^2
0.317	6.62	0.990	0.04
Langmuir isotherm			
q_m (mg/g)	K_L (L/mg)	R^2	χ^2
30.3	0.07	0.959	0.17

Adsorption kinetics study:

The time-dependent adsorption datapoint for Pb(II) removal by SMA, at three Pb(II) concentrations which were initially 10, 30 and 50 mg/L, was fitted to pseudo-first order model (PFOM) and simultaneously, it fitted to pseudo-second order model (PSOM) also. The comparison showed that the magnitude of R^2 of PFOM kinetic (Fig. 8) was much less than that of PSOM kinetic (Fig. 9) for all the initial concentrations.

It was reported in previous studies that, when reaction followed the PSOM kinetic model, then the rate-limiting or rate-determining step was adsorption but not the mass transfer[6].
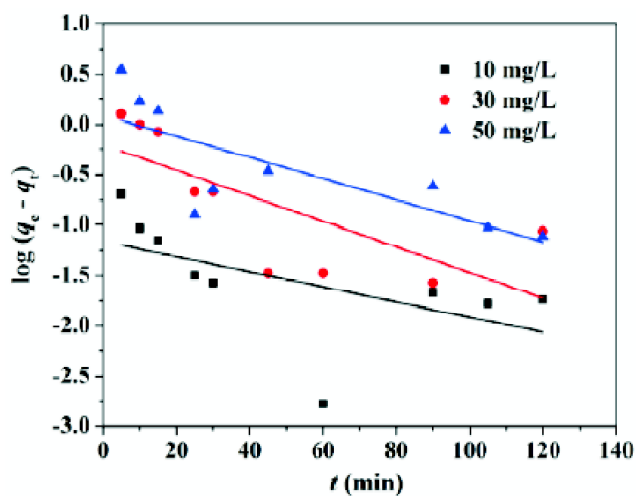
Fig. 8. Pseudo-first order (Experimental condition: adsorbent dose = 2 g/L, contact time = 5–120 min, pH = 4.5±0.2, speed of agitation = 150 rpm, temperature = 30±2°C).
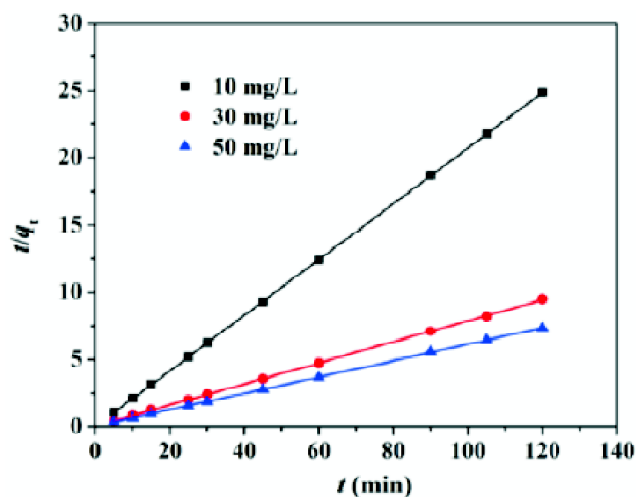

Fig. 9. Pseudo-second order (Experimental condition: adsorbent dose = 2 g/L, contact time = 5–120 min, pH = 4.5±0.2, speed of agitation = 150 rpm, temperature = 30±2°C).

Thermodynamic parameter study:

There are three vital thermodynamic parameters, enthalpy, entropy, and Gibbs free energy change which are very important for any chemical process. The slope with x-axis and intercept at y-axis of the plot of ln K_e vs $1/T$ (Fig. 10), known as van't Hoff plot, was determined to calculate ΔH and ΔS.
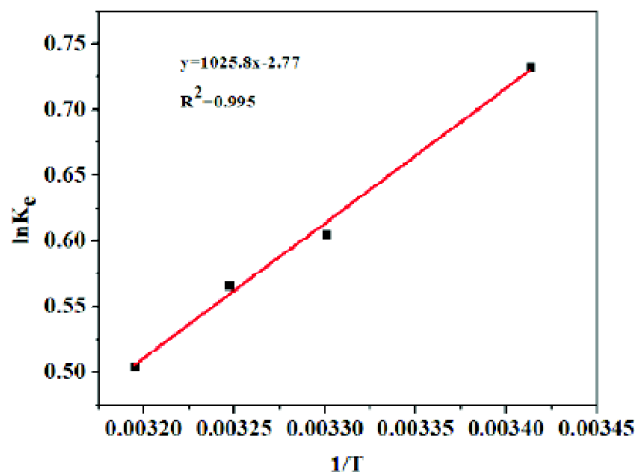

Fig. 10. van't Hoff plot of ln K_e vs $1/T$ for Pb(II) adsorption by SMA (Experimental condition: Pb(II) = 50 mg/L, dose of SMA = 2 g/L, contact time = 30 min, pH = 4.5±0.2, speed of agitation = 150 rpm).

The results are compiled in Table 2. The ΔG, determined from the study at the temperature range of 20–40°C, were negative, which indicates that the reaction Pb(II) removal by SMA is favorable. The maximum negative value of ΔG was attained at 20°C which implies that low temperature is favorable for the reaction. The negative value of ΔH implies that the reaction is exothermic, and so, low temperature is favorable. The ΔS yields negative value, which signifies the reduced randomness of the system after adsorption of Pb(II) by SMA.

Table 2. Thermodynamic parameters for Pb(II) removal by SMA

Initial concentration (mg/L)	Temp. (°C)	K_e	ΔG (J/mol)	ΔH (J/mol)	ΔS (J/mol/K)	R^2 (mg/L)
50	20	2.08	–1784.15	–8521.85	–23.04	0.995
	30	1.83	–1524.82			
	35	1.76	–1451.14			
	40	1.66	–1314.52			

Desorption study:

In any type of treatment process, sludge management is one of the most important steps. It is essential to check the desorption of Pb(II) adsorbed by SMA, which is already exhausted. In this study, first the SMA was exhausted by adsorption of Pb(II). A 100 mL solution of Pb(II), concentration of which was 30 mg/L initially, was taken for the study and 2 g/L of SMA dose was applied. The leftover Pb(II) in solution was 4.91 mg/L after 30 min. In the next step, the desorption was accomplished by an Na_2-EDTA solution (0.2 *M*). Then, the SMA (0.2 g), exhausted by adsorption of Pb(II), was agitated for 60 min at 150 revolutions per min with 100 mL Na_2-EDTA solution at 30°C. It was observed that 65% of adsorbed Pb(II) was recovered by this process. The regenerated SMA can be reused for Pb(II) removal, though the capacity of adsorption was very low.

Conclusion

The present study gives a detailed picture of the utilization of the neutral alumina for Pb(II) removal after adsorption of anionic surfactant at a high loading. After surfactant removal, the alumina is designated as surfactant modified alumina (SMA). Pb(II) removal by SMA is very fast. The outcome of variation of adsorbent dose, initial Pb(II) concentration, pH, contact time, interfering ions are discussed. The experimental data of study follows Freundlich isotherm and the best representation of reaction kinetics is the pseudo-second order kinetic model. The thermodynamic studies show that the process of adsorption is exothermic and favourable.

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