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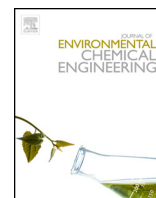
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## Adsorption and optimization studies of lead from aqueous solution using $\gamma$ -Alumina



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### ABSTRACT

In the present study, removal of Pb(II) ions using  $\gamma$ -Alumina was investigated.  $\gamma$ -Alumina used in the present study was prepared by gel combustion method. The XRD revealed that the synthesized particle was in amorphous phase and the SEM image showed highly porous surface which is a characteristic property of a good adsorbent. The pore size and surface area of the  $\gamma$ -Alumina were determined and found to be 243 m<sup>2</sup>/g and 41 Å, respectively. The effects of pH, initial lead concentration, adsorbent dosage on the extent of adsorption and time of contact were studied. Atomic absorption spectrometer (AAS) was used to determine the concentration of lead after adsorption. The Pb(II) removal capacity of  $\gamma$ -Alumina was found to be maximum at pH 7. From the Langmuir isotherm the maximum adsorption capacity of  $\gamma$ -Alumina toward Pb(II) was determined ( $Q_0 = 65.67$  mg/g). Compared to other metal oxides  $\gamma$ -Alumina showed a significantly higher adsorption capacity. Although Pb(II) adsorption occurred in the first 35 min of contact time, at least 90 min to attain equilibrium. The kinetics of adsorption can be described by first order rate equation. Statistically based experimental model such as Box–Behnken Method (BBM) was used to study the effect of variables on adsorption. Regeneration studies of the adsorbent were carried out and it was found that the adsorbent can be effectively regenerated upto 3 times with significant level of adsorption. The results suggest that  $\gamma$ -Alumina is effective adsorbent for the removal of lead.

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### Introduction

Human activities have led to generation of various bi-products and waste materials. Some of these waste materials have the potential to contaminate the environment. Substances like heavy metals, organic solvents, petroleum products, coal play a major role in polluting the environment. Among the heavy metals lead is one of the major pollution concerns of the present age; hence it has been attracting a wide scale of attraction from environmentalists. Activities such as battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing ceramic and glass industries, printing, painting, dyeing and other industries, radiation shielding, construction industries, insect controls are some of lead applications and major sources of lead into the

environment [1,2]. Due to its readily accumulating nature in the living systems, lead further intensifies its negative effects. Lead has adverse effects on human health if present in significant amount in body. The daily intake of lead contents from all sources *i.e.*, automobile emissions, lead smelter, burning of coal and oil, lead arsenates, pesticides, smoking, mining and plumbing *etc.* is in the range of 200–300  $\mu$ g of which 10% is adsorbed in the body. Lead poisoning in humans results in gastrointestinal problems, damage to kidneys, nervous breakdown, liver and brain damage and behavioral disorders. According to Environmental Policy Agency (EPA) drinking water standards, the permissible amount of lead is 0.05 mg/l, but a level of 0.02 mg/l has been proposed and is under review. Exposure to lead beyond the permissible limits has been associated with problems such as abortion, stillbirths, sterility, neo-natal deaths and intellectual disability [3].

A number of methods such as, precipitation as hydroxides, coagulation–sedimentation, reverse osmosis, ion exchange, adsorption, cementation *etc.* have been used for the treatment of lead present in water in the recent years [4,5]. These conventional methods have certain limitations such as, high cost

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devices, toxic waste production, low efficiency and requirement of high energy and space. Among all these methods, adsorption is considered to be most effective and economical for the removal of heavy metals [6–12].

Fine particles of metal oxides increase the adsorption sites. As the surface area increases, the adsorption increases. Porous oxide materials which are synthesized by different methods show excellent adsorption behavior for heavy metals ions [13]. Adsorbents such as activated carbon, filamentous fungal biomass, natural condensed tannin, carbon nanotubes, nanometal oxides, nanozeolite components have been used for the adsorption of the lead present in water. But the availability and efficiency of these materials are comparatively lower when compared to  $\gamma$ -Alumina [14–18]. Adsorbents such as alumina, silica, and zirconia are well known for their high surface area, high mechanical properties and good resistivity to thermal degradation. In case of  $\gamma$ -Alumina, the octahedral aluminum sites are fully occupied while vacant sites are randomly distributed at the tetrahedral positions.  $\gamma$ -Alumina is also used as an electrical insulator, catalyst and base catalyst in many chemical reactions, membrane process and waste water purification.  $\gamma$ -Alumina, due to amphoteric property acts as a superior metal ion adsorbent. It can be synthesized with appropriate particle size and shape which offers maximum surface area. The surface area is in the range of 150–500 m<sup>2</sup>/g and pore radius is in the range of 15–60 Å.  $\gamma$ -Alumina is very stable through the pH range of 2–13, making this applicable for all the scenarios. Due to its high thermal stability, it can be applicable at very high temperatures [19–22].

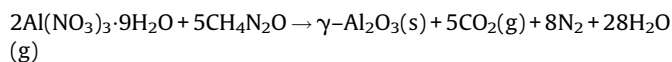
In the present work,  $\gamma$ -Alumina was prepared by gel combustion method and the synthesized nanoparticle was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The effects of adsorbent dosage, pH of the solution, initial Pb(II) ion concentration and contact time were studied. The adsorption was fit to different adsorption isotherms and also to kinetics of the adsorption was studied. After the adsorption, adsorbent was regenerated and its efficiency was tested. Parameters affecting the removal of Pb(II) ions from the aqueous solution was investigated and validated by using three factorial Box–Behnken Method (BBM).

## Materials and methods

### Synthesis of Al<sub>2</sub>O<sub>3</sub>

$\gamma$ -Alumina was synthesized by the gel combustion method. Aluminium nitrate (98.5%) was used as the aluminium precursor, and urea (99.5%) as the fuel for combustion. 20 g of aluminium nitrate and 3.3458 g urea were carefully weighed and dissolved in a

250 ml glass beaker containing 150 ml distilled water. A ratio of 0.35:1 between urea to nitrate was maintained. The beaker containing the reaction mixture was placed on a hot plate and heated. Nitrates were released during the process of heating. As the reaction progressed, the mixture turned into the form of a gelatinous material and finally the reaction was completed with a sudden self-ignition, leaving behind fine powder of  $\gamma$ -Alumina [23].



### Methods

The chemicals and reagents used for the experiments and analysis were of analytical grade. A stock solution of 1000 ppm Pb (II) were prepared from Pb(NO<sub>3</sub>)<sub>2</sub> (99.0%) in deionized water. As per the requirement various spiked solutions of 10, 20, 30, 40, 50, 100, 150, 200 ppm were prepared by taking a known amount of stock solution and by diluting it. Atomic Absorption Spectrometer (AAS) made -GBC 932 plus was used to measure concentrations of Pb(II) after adsorption.

## Results and discussion

### SEM analysis

SEM analysis was carried out using JOEL, JSM 6380-LA, U.S.A. to study the surface morphology of the  $\gamma$ -Alumina nano-particle. Fig. 1(a) shows the SEM image of the synthesized  $\gamma$ -Alumina which was calcinated at 900 °C. We can notice that, synthesized  $\gamma$ -Alumina shows a flake like morphology having a large void surface, which is a characteristic property of a good adsorbent. One gram of synthesized  $\gamma$ -Alumina was added to 100 ml of 1000 ppm lead solution taken in a 250 ml conical flask and the solution was subjected to shaking for 4 h.  $\gamma$ -Alumina adsorbent was then filtered and dried at 150 °C. The dried powder was characterized by SEM. The large flakes of Pb(II) ions adsorbed on  $\gamma$ -Alumina can be observed in Fig. 1(b).

### XRD analysis

The structure of synthesized particles is investigated by X-ray diffraction (JEOL JPX8, USA) at  $2\theta$ , 10–82° with a step size of 0.01 s. Fig. 2 shows the XRD patterns of  $\gamma$ -Alumina particles synthesized by gel combustion method. The observed peaks in Fig. 2 could be indexed based on pure Al and  $\gamma$ -Alumina phase in Joint Committee on Powder Diffraction Standard – International Centre for

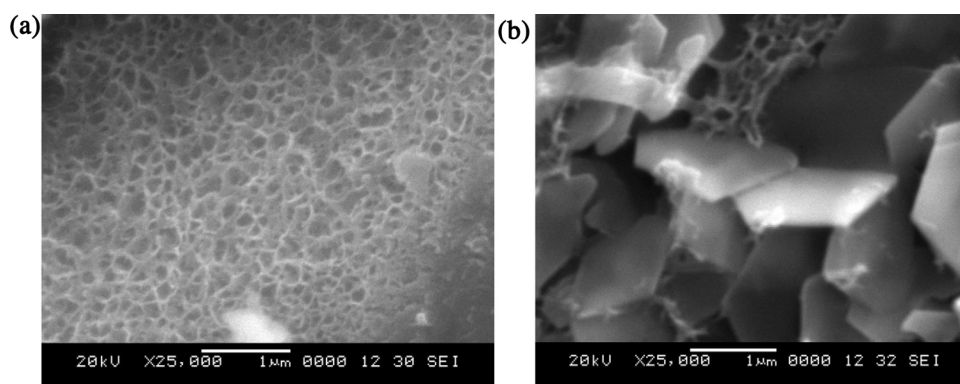


Fig. 1. SEM image with 25000× magnification (a) synthesized  $\gamma$ -Alumina before adsorption and (b) Pb(II) adsorbed  $\gamma$ -Alumina.

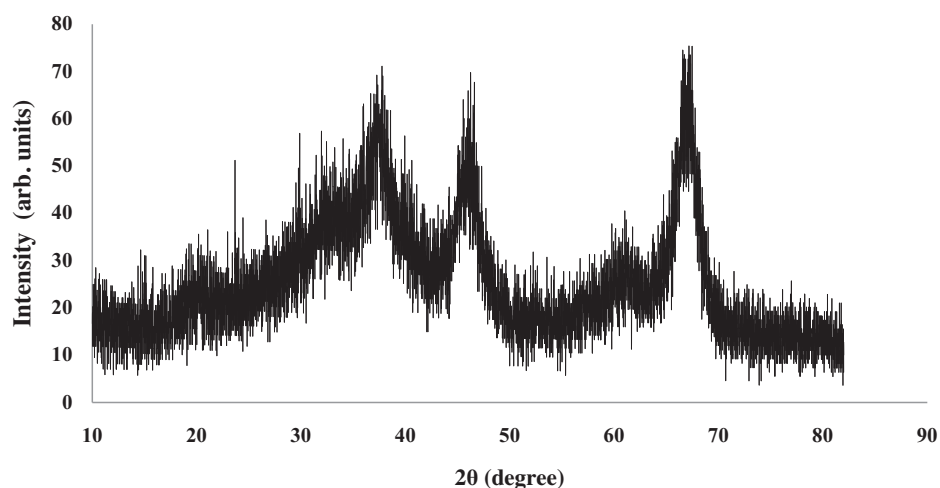


Fig. 2. X-ray diffraction of synthesized  $\gamma$ -Alumina.

Diffraction Data (JCPDS–ICDD) card nos. 85-1327 and 29-0063, respectively. The XRD pattern depicts that the synthesized  $\gamma$ -Alumina is amorphous in nature and the broad peaks indicate that the synthesized  $\gamma$ -Alumina particles are of nanosize.

In order to study the adsorption of lead on  $\gamma$ -Alumina from aqueous solution and optimize it, different parameters such as effect of adsorbent dosage, effect of initial concentration, pH of initial solution and effect of contact time were studied in a batch experiment. The effects of each parameter on adsorption is explained below.

#### Determination of surface area and pore size

The surface area of the calcinated  $\gamma$ -Alumina was determined by nitrogen physisorption using Micrometrics Flowsorb 2300. Before each measurement the calcinated sample was degassed at 400 °C for 2 h. To measure the nitrogen adsorption/desorption isotherms, Quantachrome NOVA 2000 was used. BJH model was used to determine the pore-size distribution.

The surface area of the  $\gamma$ -Alumina after calcination to 900 °C was found to be 243 m<sup>2</sup>/g. The mean pore diameter was found to be 41 Å.

#### Effect of adsorbent dosage

To determine the effect of dosage of  $\gamma$ -Alumina on adsorption of Pb(II) ions a batch study was set up. The initial dosage amount of adsorbent was varied from 0.1 to 0.5 g in steps of 0.1 g.  $\gamma$ -Alumina

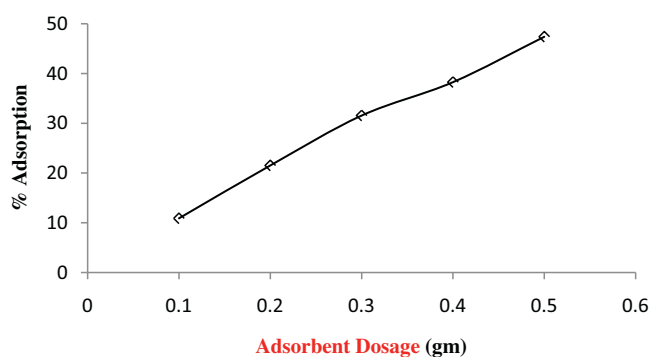


Fig. 3. Effect of adsorbent dosage on lead adsorption for 100 ppm lead concentration at pH 5.

was added to 100 ml of 100 ppm lead solution in different conical flasks. The pH of all the systems was maintained constant at 5.0. The mixture was subjected to adsorption in wrist-action shaker for 90 min. After adsorption, the mixture was filtered, centrifuged and analyzed for lead concentration using AAS. It can be seen from Fig. 3 that the percentage adsorption increases with increase in the adsorbent dosage. The percentage adsorption is varying almost linearly with increase in concentration. The percentage adsorption varied from 10.89 to 47.38% with the increase in the adsorbent dosage from 0.1 to 0.5 g.

It was found that, at higher dosage of adsorbent the adsorption of Pb(II) was significant. As the adsorbent dosage increases, the competition between molecules for binding sites decreases. The increase in the dosage of adsorbent increases the amount of metal ion adsorbed onto the surface of the adsorbent since there will be more sites for the adsorption [24]. Several other investigators have also reported the same trend of adsorbent dosage on Pb(II) adsorption [25–28]. For a given concentration of Pb(II) further increase in the adsorbent dosage practically does not have any effect on adsorption rate.

#### Effect of initial lead concentration

Batch adsorption studies were carried out for various Pb(II) concentrations ranging from 10 to 100 ppm using  $\gamma$ -Alumina to study the effect of initial Pb(II) ion concentration on adsorption. 100 ml of 10–100 ppm lead nitrate solution was taken in 5 different conical flasks. 0.5 g of  $\gamma$ -Alumina was added to each flask. The pH of

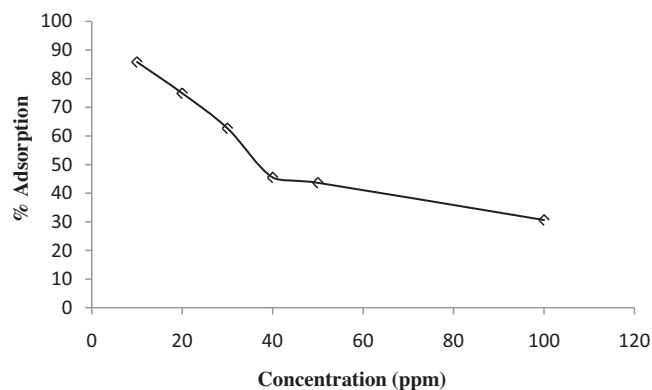


Fig. 4. Effect of lead concentration on adsorption at constant adsorbent dosage 0.5 g/100 ml solution at pH 5.

all the systems was maintained constant at 5.0. The adsorption mixture was subjected to adsorption in wrist-action shaker for 90 min at room temperature ( $25 \pm 3^\circ\text{C}$ ). The adsorption mixture was then filtered, centrifuged and analyzed for Pb(II) AAS. With the increase in metal concentration, the percentage adsorption decreased (Fig. 4). It was observed that the percentage adsorption decreased from 85.82 to 30.631% with the increase in the concentration from 10 to 100 ppm of Pb(II) ion in the solution. The increase in the initial lead concentration results in increase in number of available molecules per adsorption site. For a fixed amount of adsorbent, the percentage adsorption decreases [29].

The percentage adsorption was higher at lower concentrations. At 10 ppm, the adsorption capacity was nearly 86%. Only 30% adsorption was observed at 100 ppm initial Pb(II) concentration. Several other investigators have also reported the same trend of initial concentration on Pb(II) adsorption [27,30,31].

#### Effect of pH on adsorption

The solubility of metal ions, concentration of counterions on the functional groups of adsorbent and the degree of ionization of the adsorbate during the reactions are affected by the range of pH of the system. The effect of initial pH of the solution on adsorption of Pb(II) using 0.5 g of  $\text{Al}_2\text{O}_3$  was studied at different pH ranges ranging from acidic to basic medium. pH of lead standards were adjusted to 2–10 for 100 ppm lead solutions using NaOH and HCl. Fig. 5 shows the variation of percentage adsorption with change in the initial pH of the solution. There was an increase in the percentage adsorption from 27 to 99% when the pH of the solution varied from 2 to 7 (acidic to neutral); further increase in pH (basic medium) resulted in gradual decrease in the adsorption. The removal of Pb(II) from water by  $\gamma$ -Alumina was found to be highly dependent on the solution pH value which affects the characteristics of the adsorbent and adsorbate. pH 7 was found to be optimum for Pb(II) adsorption using  $\gamma$ -Alumina. Due to the competition of  $\text{H}_3\text{O}^+$  and metal ions, at pH 2 the extent of adsorption was significantly low [2,32,33]. The increase of pH leads to hydrolysis of Pb(II) species with known equilibrium constant [34].



Surfaces naturally charge to form a double layer. When the surface charge-determining ions are  $\text{H}^+/\text{OH}^-$ , the net surface charge is affected by the pH of the liquid in which the solid is submerged.

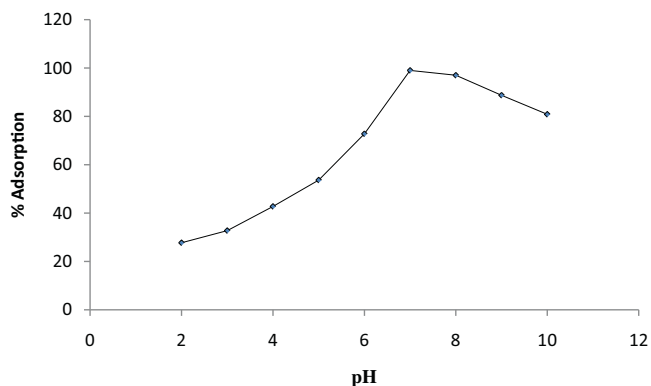


Fig. 5. Effect of initial pH on percentage adsorption at adsorbent dosage 0.5 g/100 ml.

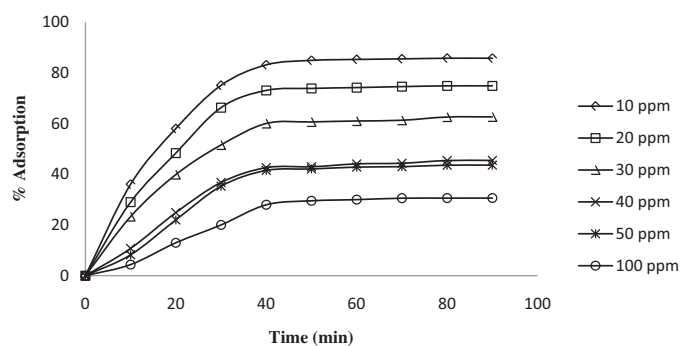


Fig. 6. Effect of contact time on rate of adsorption of Pb(II) ion with varying concentration onto  $\text{Al}_2\text{O}_3$ , pH 5.0, adsorbent dosage 0.5 g/100 ml.

As pH of the solution increases, the concentration of  $\text{H}^+$  ions decreases, forcing the reaction to right hand side. The adsorption of bivalent metal ions on alumina can be showed by the following equation [35].



At pH 7, the concentration of  $\text{H}^+$  is the least hence including the maximum adsorption of Pb(II) onto the surface of  $\text{Al}_2\text{O}_3$ . At pH 7.0, adsorption capacity increases remarkably.

#### Effect of contact time

Two different batch studies were conducted to study the effect of contact time. One of the batch consisted of a constant adsorbent dosage of 0.5 g/100 ml and the pH of the solution was maintained at 5.0, with varying initial Pb(II) concentration. Fig. 6 shows the adsorption rate of lead. At the beginning, the rapid adsorption rate of Pb(II) ions was observed up to 40 min of contact time. Thereafter, the adsorption rate became practically constant.

Second batch consisted of constant initial Pb(II) concentration (100 ppm) and pH (5.0). The adsorbent dosage was varied by 0.1 g/100 ml. Fig. 7 shows the adsorption rate of Pb(II). It was observed that, the initial rate of adsorption was rapid and after 35 min, the rate of adsorption was practically constant.

The variation in the extent of adsorption is due to the fact that, at the beginning all the sites on the surface of the adsorbent were vacant and the solute concentration gradient was relatively high. With the passage of time, the adsorbent sites were occupied and there was a drop in the concentration gradient of Pb(II) ion. This resulted in a drop of rate of adsorption. The results obtained in both the batch studies are in accordance with several other experimental studies conducted on adsorption of Pb(II) [36,37].

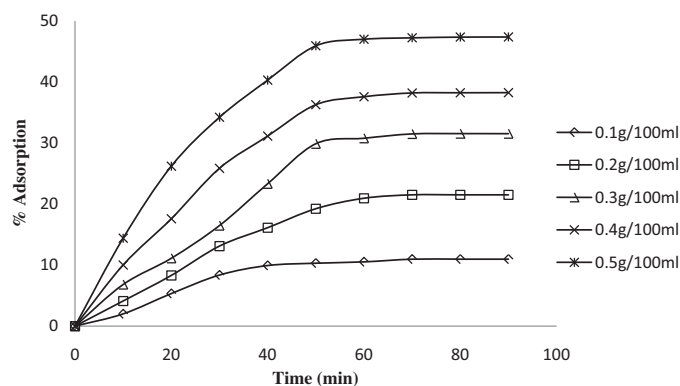


Fig. 7. Effect of contact time on rate of adsorption of Pb(II) ion with varying adsorbent dosage onto  $\text{Al}_2\text{O}_3$ , pH 5.0, adsorbent dosage 0.5 g/100 ml.

### Pb(II) equilibrium adsorption isotherms

Adsorption isotherms help in optimizing the use of  $\gamma$ -Alumina as an adsorbent. Empirical equations play a major role in data interpretation and predictions. In the present work, batch adsorption tests were carried out to validate Langmuir and Freundlich adsorption isotherms. The equilibrium metal adsorption capacity was calculated using the following expression.

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (4)$$

where  $q_e$  is the  $\gamma$ -Alumina's adsorption capacity (mg/g),  $V$  is the volume of the sample (l),  $C_0$  is the Pb(II) concentration (mg/l),  $C_e$  is the equilibrium Pb(II) concentration (mg/l), and  $m$  is the weight of the  $\gamma$ -Alumina used (g).

Langmuir isotherm is given by Eq. (5).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (5)$$

where  $C_e$  is the equilibrium concentration of Pb(II) (mg/l),  $q_e$  is the amount of metal uptake (mg/g),  $Q_0$  (mg/g) and  $b$  (l/mg) are Langmuir constants.

Freundlich Isotherm is given by Eq. (6).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

where  $C_e$  is the equilibrium concentration of Pb(II) (mg/l),  $q_e$  is the amount of metal uptake (mg/g) and  $K_f$  and  $n$  are the Freundlich constants.

Fig. 8 shows the linearized Langmuir adsorption isotherm model with  $Q_0 = 65.66$  mg/g,  $b = 4.694$  l/mg, having a regression coefficient of  $R^2 = 0.9538$ . The value obtained in the current experiment is in accordance with the reported literature [38,39].

Fig. 9 shows the Freundlich adsorption isotherm model. The Freundlich constants obtained are  $n = 0.3164$  and  $K_f = 0.231$  mg/g with  $R^2 = 0.9481$ . The value obtained in the current experiment is in accordance with literature [38,39]. The  $R^2$  value for Langmuir isotherm (0.9583) is higher than that for Freundlich isotherm (0.9481). Thus it can be concluded that, Langmuir isotherm provides a better fit to the data than Freundlich isotherm. This indicates a monolayer adsorption.

### Adsorption kinetics and mechanism of Pb(II) ions on $\gamma$ -Alumina

Adsorption kinetics is one of the major characteristics which represent the efficiency of the adsorbent. It helps in determining

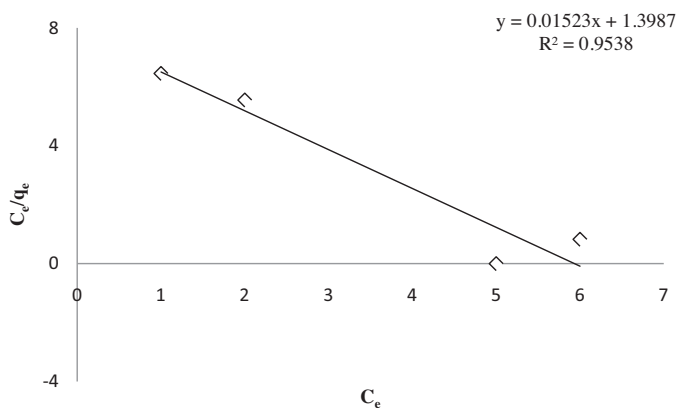


Fig. 8. Linearized Langmuir isotherm for adsorption of Pb(II) with variation in initial concentration of Pb(II) (pH 5.0, adsorbent dosage 0.5 g/100 ml and contact time 90 min).

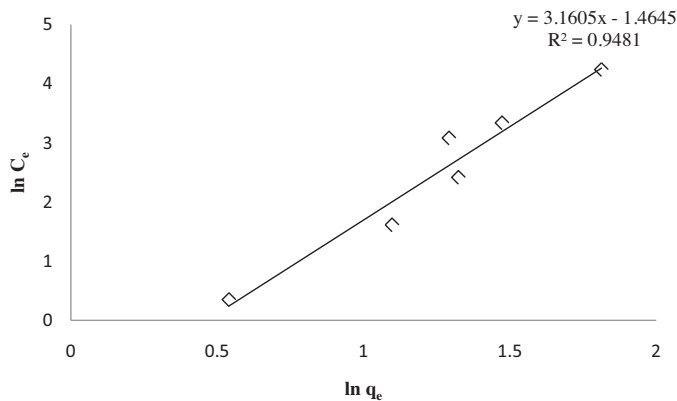


Fig. 9. Linearized Freundlich isotherm for adsorption of Pb(II) with variation in initial concentration of Pb(II) (pH 5.0, adsorbent dosage 0.5 g/100 ml and contact time 90 min).

the potential applications of the adsorbent. Fig. 10 shows the kinetic adsorption of Pb(II) onto  $\gamma$ -Alumina. From Figs. 6 and 7, it is known that during the first 35 min of contact time, there is a significant increase in the Pb(II) removal by  $\gamma$ -Alumina. As the void sites fill up with time, gradually the rate of removal decreased after 35 min. It can be inferred that, the removal of Pb(II) takes place in two distinct steps: a relatively fast step followed by a slower one. The necessary time to reach equilibrium is approximately 90 min.

The kinetics of heavy metal adsorption can be modeled by the first order equation and the pseudo-second order equation [40], shown by Eqs. (7) and (8) respectively.

$$\ln \frac{q_e - q_t}{q_e} = -K_L t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{2K'q_e^2} + \frac{t}{q_e} \quad (8)$$

where  $K_L$  is the Lagergen rate constant of adsorption (1/min);  $K'$  the pseudo-second order rate constant of adsorption (g/mg min);  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed (mg/g) at equilibrium and time  $t$  respectively.

Linear plots of  $\ln (q_e - q_t)/q_t$  versus  $t$ ; and  $t/q_t$  versus  $t$ ; are shown in Fig. 10(a) and (b) respectively. The  $K_L$  and  $K'$  values from the slopes and intercepts are shown in Table 1. The first order rate model describes the adsorption of lead with high correlation coefficient ( $R^2 = 0.9923$ ). The results obtained in the current experiment matches the values obtained by Kannan and Veemaraj [38,39].

During adsorption, adsorbed ions that retain their hydration sphere are termed as "outer sphere" complexes and ions that lose a part or all their hydration spheres and bonded directly to the oxide is termed as "inner sphere" complexes. Uptake of Pb(II) occurs in the presence of a positively charged alumina surface. This adsorption behavior is consistent with the formation of inner sphere complexes. Pb(II) bonds to only one oxygen of the oxide surface [41]. NMR and infrared spectroscopic electrical conductivity [42] and potentiometric studies of oxide surface immersed in water provide evidence that the oxide surface is populated with hydroxide functional group and these surface hydroxide groups behave as weak acids and bases which react with solution species to form surface complexes, depicted as follows:



$\gamma$ -Alumina is a defect spinel structure and thus the  $\gamma$ -Alumina may consist of hydroxides bound to octahedrally or tetrahedrally coordinated Al atoms.

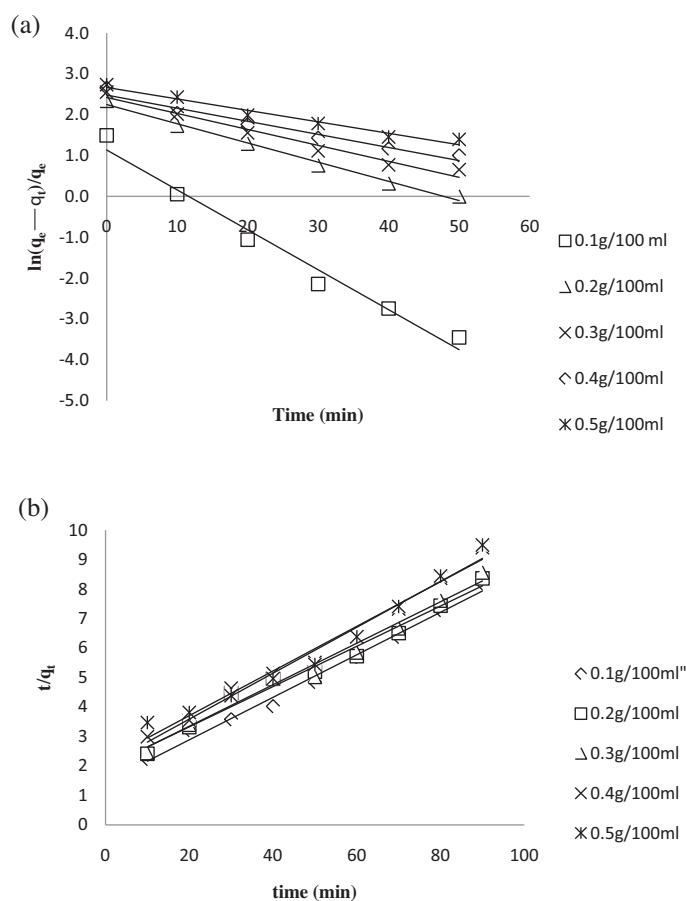


Fig. 10. Linearization of Pb(II) adsorption kinetics on  $\gamma$ -Alumina (a) first-order rate and (b) pseudo-second-order rate kinetic plots.

Table 1

List of values of correlation factor and rate constants of first order and pseudo- second order rate equation.

Adsorbent dosage (g/100 ml)	$R^2$ values of first order kinetics	$R^2$ values of pseudo-second order kinetics	$K_L$ values for first-order kinetics ( $\text{min}^{-1}$ )	$K'$ value for pseudo-second order kinetics (g/mg min)
0.1	0.9761	0.9893	0.0978	0.0019
0.2	0.9923	0.9789	0.047	0.0011
0.3	0.969	0.9744	0.0391	0.0013
0.4	0.9598	0.9851	0.0321	0.0015
0.5	0.966	0.9703	0.0281	0.0013

#### Box–Behnken method (BBM)

Statistical based experimental designs are more efficient in adsorption studies as compared to traditional approach. The effects of all the three variables (pH, initial concentration of lead and adsorbent dosage) on adsorption are studied using Box–Behnken Method (BBM). Box–Behnken designs are a class of rotatable or nearly rotatable second order designs based on three level factorial designs [43]. In order to investigate and validate the parameters affecting the removal of Pb(II) ions from the aqueous solution. In the present work three factorial BBM experimental design was used. Table 2 gives the detailed list of levels for BBM.

Based on the BBM factor method, the following analysis was made and the percentage adsorption was calculated experimentally. Table 2 gives the BBM experimental design plan of the optimization design with experimental and predicted values of adsorption. Table 3 evidently shows that the maximum adsorption

was attained at pH 7, 1 g/100 ml weight of adsorbent and 200 ppm initial Pb(II) concentration.

Fig. 11 depicts the effect of pH and adsorbent dosage on the adsorption of Pb(II) ions onto the surface of  $\gamma$ -Alumina. With the increase in loading of  $\gamma$ -Alumina and pH of the solution the percentage adsorption increases. The increase in the adsorbent dosage provides more surface area for adsorption and the increase in the pH reduces competition from the  $\text{H}_3\text{O}^+$  ions. But as the

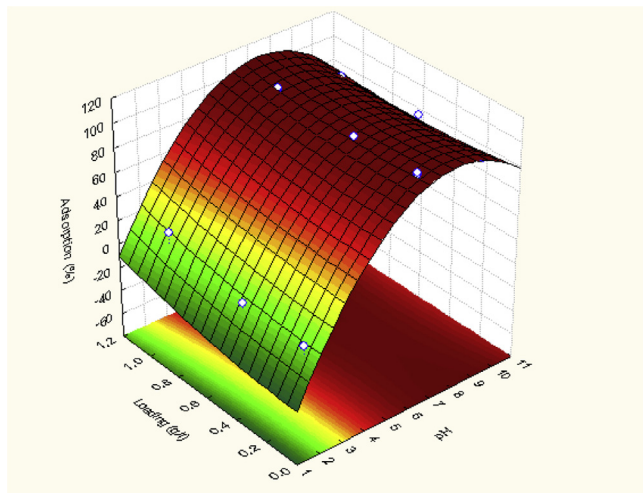
Table 2

List of variables and their levels considered for BBM.

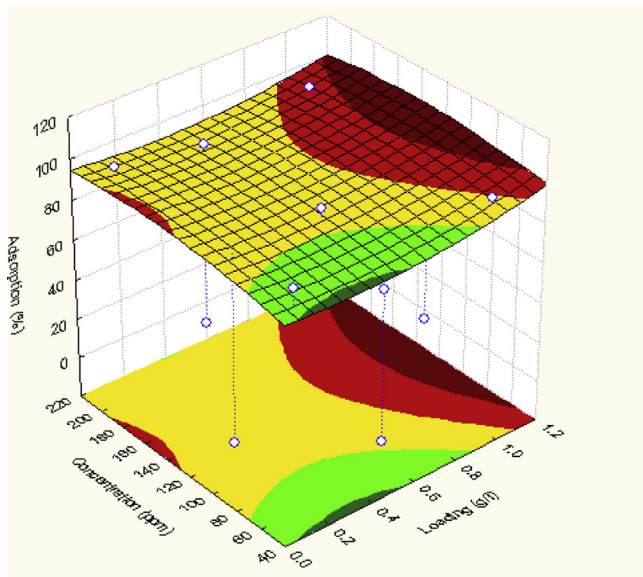
Variable	Factor	-1	0	1
$X_1$	pH	2.0	7.0	10.0
$X_2$	Initial concentration (ppm)	50	100	200
$X_3$	Adsorbent dosage (g/100 ml)	0.1	0.5	1.0

**Table 3**  
Box–Behnken method experimental plan for adsorption of Pb(II) on  $\gamma$ -Alumina.

Run No.	Factor 1 $X_1$ : pH	Factor 2 $X_2$ : lead concentration (ppm)	Factor 3 $X_3$ : weight of adsorbent (g/100 ml)	Adsorption (experimental) (%)	Adsorption (predicted) (%)
1	2.00	100	0.1	1.080	1.334
2	10.00	100	0.1	86.788	89.064
3	2.00	100	1	18.110	16.605
4	10.00	100	1	87.066	86.040
5	2.00	50	0.5	1.364	3.542
6	10.00	50	0.5	76.928	78.335
7	2.00	200	0.5	1.092	0.164
8	10.00	200	0.5	92.032	89.375
9	7.00	50	0.1	96.678	92.999
10	7.00	50	1	97.568	97.661
11	7.00	200	0.1	98.584	99.732
12	7.00	200	1	99.483	101.919
13	7.00	100	0.5	96.873	96.873



**Fig. 11.** Effect of pH and adsorbent dosage on percentage adsorption by BBM approach.



**Fig. 12.** Effect of concentration and adsorbent dosage on percentage adsorption by BBM approach.

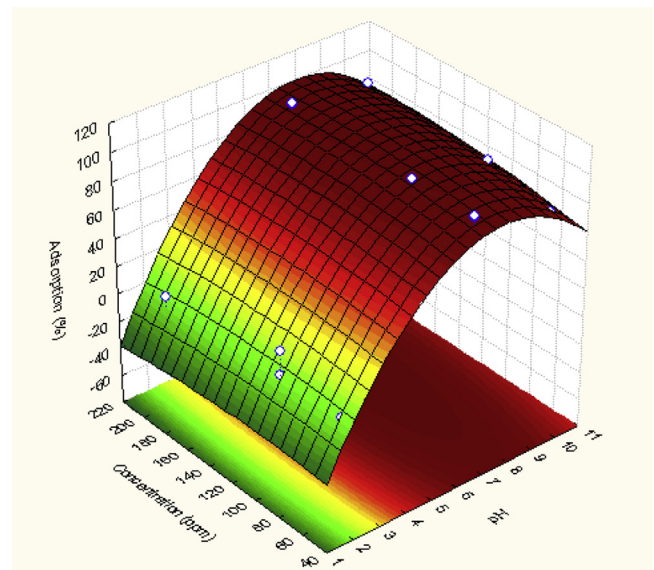
solution becomes more alkaline, the hydrolysis of Pb(II) ions takes place and hence decreases the percentage adsorption.

With the increase in the adsorbent dosage the number of binding sites increase, but with the increase in the initial concentration of Pb(II) ions, the availability of free binding sites decreases. Hence with the increase in the adsorbent dosage and initial concentration of the solution, the percentage adsorption shows a slight increase. Fig. 12 depicts the effect of initial concentration and adsorbent dosage on the percentage adsorption.

The increase in the initial concentration of the Pb(II) ions decreases the free sites available for adsorption. Hence, it can be seen from Fig. 13 that as pH and initial concentration increase the percentage adsorption also increases. It can be inferred from Figs. 11–13 that at neutral pH, low loading of adsorbent and low initial concentration of Pb(II), the percentage adsorption is maximum.

Petro chart presented in Fig. 14 implies the importance of different parameters which contribute to adsorption of Pb(II) ions onto the surface of  $\gamma$ -Alumina. From Fig. 14, it is evident that the influence of pH is very high when compared to adsorbent dosage and initial concentration.

The predicted and experimental (observed) values are compared and plotted in Fig. 15. It can be observed that the



**Fig. 13.** Effect of concentration and pH on percentage adsorption by BBM approach.



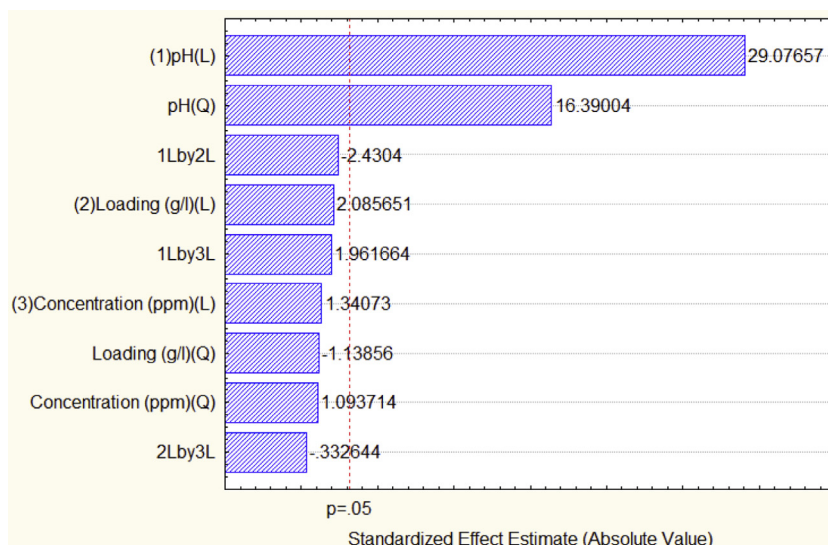


Fig. 14. Chart of standardized effects/ the values of BBM.

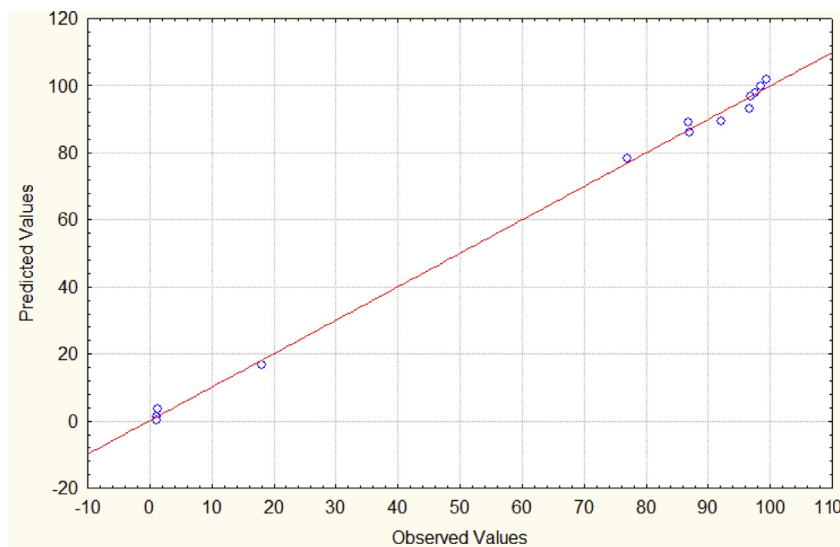


Fig. 15. Plot of predicted values to the observed (experimental) values of BBM.

experimental values which have been obtained almost balances as the predicted values in the experiment. The regression equation for the Box–Behnken is given below:

$$Y = -81.9120 + 43.533X_1 + 7.9848X_2 + 0.1033X_3 - 2.7929X_1^2 + 14.4533X_2^2 - 0.0006X_3^2 - 2.549X_1X_2 - 0.0183X_2X_3 + 0.0120X_1X_3$$

#### Competition among metal ions

In the practical scenario, wastewater would contain a number of metal ions. An experiment was conducted to determine the binding of each metal ion in the presence of other metals. 100 ppm solutions of Pb(II), Ni(II) and Cd(II) were prepared using  $Pb(NO_3)_2$ ,  $Ni(NO_3)_2$  and  $Cd(NO_3)_2$ , respectively. 0.5 g of  $\gamma$ -Alumina was added and placed in wrist-action shaker for 90 min. The solution was filtered and analyzed for metal ion concentration using AAS. The

same was repeated for different metal ion combinations. It was found that  $\gamma$ -Alumina can effectively bind a number of heavy metal ions, but with varying efficiency. Table 4 shows the percentage adsorption of each ion in the presence of other ions. The general binding affinity of  $\gamma$ -Alumina for the materials studied, in the order of decreasing affinity was  $Pb(II) > Cd(II) > Ni(II)$ .

It is clear that some of the metal ions compete with one another for binding sites, but it is evident from the table that the binding of

**Table 4**  
Percentage adsorption of Ni(II), Cd(II) and Pb(II) in the presence of each other.

Heavy metal ion mixture	% Adsorption		
	Ni(II)	Cd(II)	Pb(II)
Ni(II)–Cd(II)	20.32	43.41	–
Ni(II)–Pb(II)	27.57	–	69.32
Cd(II)–Pb(II)	–	38.40	55.69
Ni(II)/Cd(II)/Pb(II)	21.31	53.86	26.32

Pb(II) is relatively unaffected by other metals [44]. The difference in adsorption behavior of Pb(II), Cd(II) and Ni(II) can be explained by the different affinity of metal ions for the donor atoms present in the structure of  $\gamma$ -Alumina.

#### Regeneration studies of $\gamma$ -Alumina

To determine the regeneration capacity of  $\gamma$ -Alumina batch adsorption studies were run in succession with the adsorbent being regenerated between every adsorption cycle. 0.5 g of adsorbent was added to a 100 ppm Pb(II) solution at pH 7 and adsorption was carried out for 90 min. The solution was then filtered to separate the adsorbent and the solution. The solution was analyzed for Pb(II) concentration using AAS and the percentage adsorption was found to be 99%. The adsorbent was washed, regenerated by treating it with 0.1 N ammonium hydroxide for 60 min in a wrist-action shaker and dried at 120 °C for 60 min. The regenerated adsorbent was used to run another adsorption cycle. The solution and adsorbent were separated again by filtration. While the solution was analyzed for Pb(II) concentration the  $\gamma$ -Alumina was regenerated. The percentage adsorption of Pb(II) ions in the second run was found to be 82%. On successive regeneration of the adsorbent, the percentage adsorption decreased to 65% and 60% on the second and third regeneration, respectively. After third iteration, the amount of adsorbent available was significantly low. Thus, the regeneration was limited to three cycles. The results of regeneration study indicate that  $\gamma$ -Alumina can be used efficiently after regeneration.

#### Conclusion

In the present study,  $\gamma$ -Alumina was synthesized by gel combustion method and was used as an adsorbent for removal of lead from the aqueous solution. The synthesized  $\gamma$ -Alumina was found to be amorphous and of nanosize. Adsorption was confirmed by SEM images of both unadsorbed and adsorbed  $\gamma$ -Alumina. High percentage adsorption of lead occurred at pH 7 and 0.5 g of adsorbent. The adsorption data were fit to Langmuir and Freundlich isotherms. It was found that monolayer adsorption takes place in the batch study. First order and pseudo second order rate constants were found out using first order and pseudo second order rate equation. In order to study the effect of variables statistical techniques such as Box–Behnken Method (BBM) was employed. It was confirmed that pH effects significantly on adsorption of Pb(II) ions onto the surface of  $\gamma$ -Alumina. 99% adsorption was observed for 200 ppm solution at pH 7 for 1 g/100 ml dosage of  $\gamma$ -Alumina. From the results, it is evident that very high concentrations of Pb(II) ions can be removed using small quantity of adsorbent in neutral media. The predicted values (% adsorption) are in good agreement with experimental values for BBM. The regeneration studies of  $\gamma$ -Alumina were carried out using ammonium hydroxide. It was found that regeneration could be possible up to 4 times with a significant high level of adsorption upto 60%. Based on the above discussion, it can be concluded that  $\gamma$ -Alumina synthesized by gel combustion method could be used to remove Pb(II) ions from water.

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