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ORIGINAL PAPER

Equilibrium studies on removal of lead (II) ions from aqueous solution by adsorption using modified red mud

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Abstract In the present experimental study, solid waste was used as an adsorbent and the effectiveness of the adsorbent was increased by novel treatment methods. Red mud, acid-treated activated red mud and iron oxide-coated acid-treated activated red mud were used for the removal of lead (II). The structural and functional groups were identified to confirm the removal of lead (II) by powder X-ray diffraction and Fourier transform infrared spectroscopy analyses. The enhancement of surface area was confirmed by Brunauer–Emmett–Teller analysis. Batch adsorption experiment was also conducted, and various parameters such as the effect of adsorbent dosage, pH, contact time and initial ion concentration were analyzed and reported. Adsorption equilibrium data were investigated using Langmuir, Freundlich and Dubinin–Radushkevich isotherm models with three parameters, and the rate of reaction was examined through kinetic models. The results indicate that in particular a novel modified form of red mud, namely iron oxide-coated acid-treated activated red mud was well fitted in lead (II) removal compared with reported adsorbents. The Langmuir isotherm shows that the maximum adsorption of adsorbate per gram was greater than other adsorbents (27.02 mg/g). In Freundlich isotherm, the Freundlich constant *n* values lie between 1 and 10 indicate the favorable adsorption. The calculated *n* values for normal red mud, acid-treated activated red mud and iron oxide-coated acid-treated activated red mud were found to be 1.9, 2.1 and 2.0 respectively. The correlation coefficient value was higher and the rate of reaction follows the pseudo-second-order kinetic model.

Keywords Batch studies · Heavy metal · Isotherm · Iron oxide · Kinetic models

Introduction

Metals having density more than 5 g/cc are called as heavy metals (Beetseh and Ocheje 2013). Heavy metals are highly toxic in nature due to their high density, and it highly pollutes the environment which affects the human life, flora and fauna. By using these heavy metals, a variety of products are manufactured in many industries (Tchounwou et al. 2012). Among the heavy metals, lead is one of the highly toxic metals with density 11.33 g/cc, which is used as a raw material for manufacturing various products like batteries, pigments and printing process. This can easily spread to the environment at the time of manufacturing. Inhale and intake of lead affect the human kidneys, liver and brain (Singha and Guleria 2014). The permissible level of lead presence in drinking water suggested by Indian Standard Institution is 0.05 mg/l and in land surface water 0.1 mg/l (Gupta et al. 2001). Letting out of the effluent with heavy metals without proper treatment creates bad impact on the environment. Hence, proper treatment is essential to change the existing issues. Chemical precipitation, membrane systems and ion

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exchange are some of the methods and used commercially to remove the heavy metals from the industrial wastewater. However, these methods have some disadvantages which include the high expense in cost, energy requirements and lengthy operation and hence, there is a need to identify a new method to remove the heavy metals (Yi et al. 2015). Adsorption is a promising inexpensive method which can be used to remove the heavy metals, and also the operation process of adsorption is simple and handy. Different adsorbents like activated carbon, fruit pell, fly ash and bentonite were already used to remove various heavy metals. Similarly, for the removal of lead ions, a number of natural adsorbents such as ficus carcia leaves, peat, sand, eriobotrya japonica leaves and agro waste like rice husk, maize cobs and coconut coir have been generally used by many researchers (Sun et al. 2004; Abdel-Ghani et al. 2007; Eisazadeh et al. 2013; Awwad and Salem 2013; Farhan et al. 2013; Yusoff et al. 2014). The maximum adsorption capacity of some other adsorbents like chicken feather, nano-silversol-coated activated carbon and silica was also found to be poor for the removal of lead ions. Waste materials generated from various industries and unfriendly material to the environment which are the potential candidate for the adsorption process can also be used as the adsorbent to convert the waste materials as useful and constructive one (Kumar et al. 2009; Egwuatu et al. 2014; Chen et al. 2015).

Alumina is produced from the ore bauxite by using Bayer process. During the process, red mud (RM) is generated as residue. The generation of residue RM depends on the content of aluminum in the bauxite (Wang et al. 2008). RM is one of the solid wastes which contain Al_2O_3, Fe_2O_3, SiO_2 and TiO_2. The reason for the red color may be due to the presence of an iron compound in the mud (Ghorbhani et al. 2008). Disposal of RM is a challenging issue because around one to two tons of RM will be produced during the production of one ton of alumina. Totally, around 90 million tons of RM will be generated per year worldwide. Due to the remarkable production of RM from the industries, a large space is needed to dispose. Basically, RM belongs to alkaline in nature and the generated RM is deposited in huge pits excavated in the large space. The leachate generated from the RM pits pollutes the surface water and can penetrate to the ground water. In spite of disposal, the problem can be reduced by using the RM as an adsorbent (Liu et al. 2011).

In the present study, three different adsorbents such as red mud (RM), acid-treated activated red mud (ATARM) and iron oxide-coated acid-treated activated red mud (IOCATARM) were utilized for analysis. The modified adsorbent increases the removal efficiency of RM, adsorption capacity and surface area of RM. The aim of the present study is to remove the lead (II) from aqueous solution using RM and increase the adsorption capacity of RM by the novel modification process. The batch experimental studies on removal of lead (II) were carried out by using adsorbent RM and modified form of RM. The adsorbent was characterized by powder XRD, FTIR, BET and SEM analyses. The optimum pH, dosage, time and initial concentration were also analyzed and reported. Three mathematical models, namely Langmuir, Freundlich and Dubinin–Radushkevich, with three parameters were employed to find the adsorption capacity of RM and modified RM in the lead (II) removal, and also the adsorption equilibrium data were analyzed. Kinetic models were used to determine the rate of reaction that takes place in lead (II) adsorption. The present experimental study was carried out from November 03, 2015–October 20, 2016, at the Department of Civil Engineering, Bharathidasan Institute of Technology (BIT) Campus, Anna University, Tiruchirappalli, Tamilnadu, India.

Materials and methods

Preparation of RM adsorbent

The solid waste RM was sieved in 90 microns which is collected from aluminum industry, located in Salem, India. The sample was prepared and used for the further studies.

Preparation of ATARM adsorbent

The sieved RM with 90 microns was treated with HCl of 0.5 M consequently and then rinsed with distilled water. As a result, sodalite was diminished due to the acid leaching which is confirmed by PXRD analysis which is shown in Fig. 1a. Then, the product was heated with the help of hot air oven at 105 °C for 2 h. The surface area of RM was enhanced by the thermal process, and it was investigated by BET analysis. The resultant adsorbent was used for the further research work.

Preparation of IOCATARM adsorbent

100 ml of 0.02 mol/l of $FeSO_4{\cdot}7H_2O$ was taken in a conical flask in which 0.2 N of sodium hydroxide was added dropwise with continuous stirring. The pH of the solution was adjusted between 10 and 11. Due to the continuous stirring, a black precipitate was observed after 10 min which confirms the formation of iron oxide. Then, the product was centrifuged for 10–15 min and then iron oxide was separated and mixed with ATARM and it was placed in hot air oven for 1 h at 105 °C (Lai et al. 1994; Shalaby et al. 2014). The PXRD analysis confirmed the synthesis of iron oxide and IOCATARM as shown in Fig. 1b. The

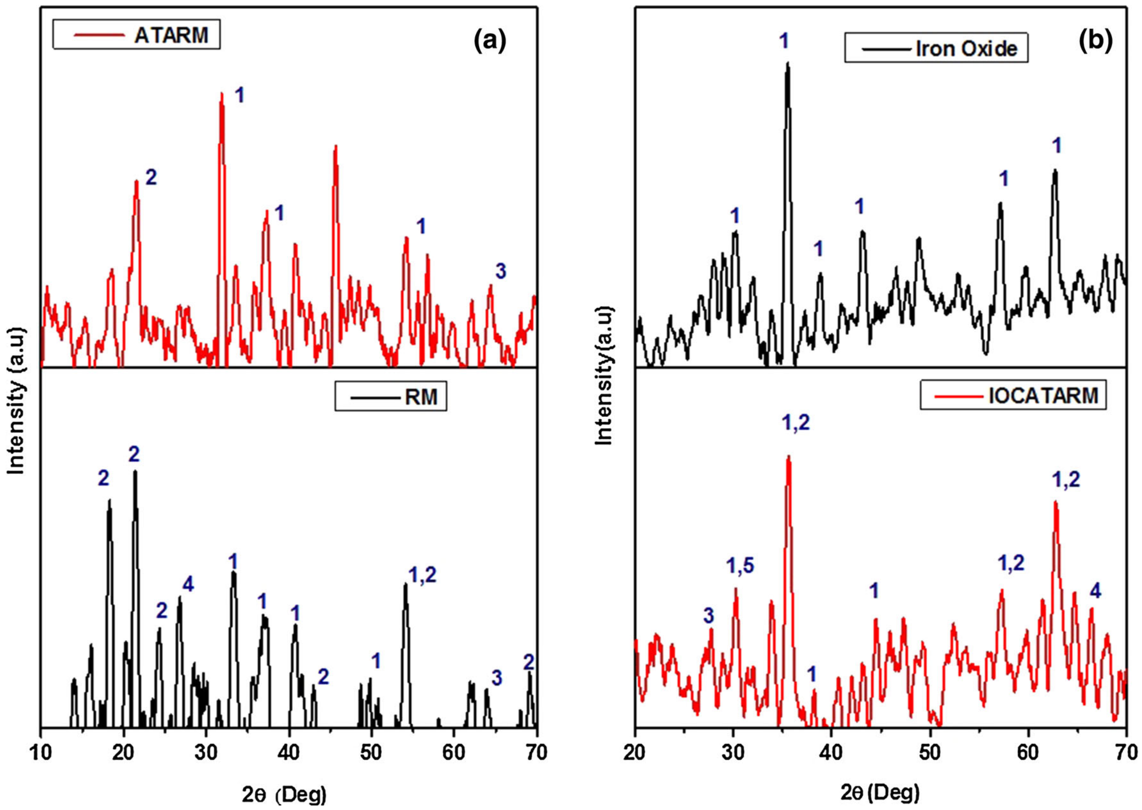

Fig. 1 **a** XRD analysis for red mud and acid-treated activated red mud *1* hematite, *2* quartz, *3* anatase and *4* sodalite, **b** XRD analysis for iron oxide and iron oxide-coated acid-treated activated red mud *1* iron oxide *2* hematite, *3* quartz, *4* anatase and *5* sodalite

prepared adsorbent was stored in a container box for further studies.

Preparation of stock solution

The stock solution of 1000 mg/l of Pb (II) was prepared by dissolving 1.598 g of lead nitrate in 1000 ml of deionized water. The stock was diluted several times to make the required concentration.

Lead (II) analysis

In the present study, the concentrations of Pb (II) ions before and after the adsorption were determined by using UV–Vis spectrophotometer. Standard solutions of Pb (II) ions (10–100 mg/l) were prepared by diluting the stock solution. The baseline was set using distilled water and then calibration curve was plotted by placing various concentrations of Pb (II) ions equipped from stock solutions. The aqueous solution was transparent and the maximum absorbance was obtained at 283.6 nm. Then, the samples were placed and the corresponding concentration was determined.

Adsorption studies

The prepared adsorbents were employed to remove the Pb (II) from aqueous solution. All the chemicals were purchased as analytical grade from Merck India Limited, Mumbai, India. The batch experiments were conducted using 250-ml Erlenmeyer flask with the known strength of 50 mg/l of 100 ml Pb (II) solutions for a period of 105 min and kept in Remi made rotary shaker at 120 rpm used to agitate the flask. The samples were filtered through Whatman filter paper (No. 41). The resultant filtrates were analyzed to find out the residual Pb (II) concentration using UV–Vis spectrophotometer (Lab India UV 3092) at the absorbance range of 283.6 nm. To reduce the experimental errors, each experiment was repeated for three times and the data were averaged. Error bars on the graphs represent the standard deviations of triplicate measurements. The error bars are not noticeable since the error is minor than the graph symbol. The percentage of removal and amount of adsorption Q (mg/l) were calculated by using Eqs. (1) and (2).

$$\text{The percentage of removal} = C_0 - C_e/C_0 \times 100 \quad (1)$$

$$\text{Adsorption capacity } Q = \{(C_0 - C_e)\,V\}/M \quad (2)$$

Table 1 Surface area of adsorbents

Adsorbents	BET surface area (m^2/g)
Red mud	24.74
Acid-treated activated red mud	27.57
Iron oxide-coated acid-treated activated red mud	49.44

where Q is the adsorption capacity (mg/g), C_0 and C_e are the concentration of metal ion in the initial and final solutions (mg/l), respectively and M is the mass of adsorbent (g) used (EL-Shishtawy and Soltan 2002; Ghaedi et al. 2013; Pushpa et al. 2015). Langmuir, Freundlich and Dubinin–Radushkevich isotherms were employed in the present study to determine the adsorption capacity of the adsorbent in the lead (II) removal and used to analyze the adsorption equilibrium data.

Results and discussion

Brunauer–Emmett–Teller (BET) analysis and composition of adsorbents

The specific surface area of adsorbent is a very important parameter for the adsorption process and the surface area for RM, ATARM and IOCATARM was analyzed by using Quanta chrome Nova-1000 instrument. The results are depicted in Table 1. From the table, it is revealed that the surface area of ATARM and IOCATARM is higher than the RM which shows the effect of the thermal process on the RM for the removal of lead (II). The composition of three adsorbent was exhibited by using "X-ray analytical microscope." The result shows that RM is composed of iron oxides—50.11%, aluminum oxides—16.85%, titanium oxides—14.21%, quartz—13.75% and sodium oxides—1.38%. The compositions of ATARM are iron oxides—54.71%, aluminum oxides—20.74%, titanium oxides—2.99% and quartz—1.76%. Similarly, iron oxides—73.66%, aluminum oxides—25.47%, titanium oxides—1.62% and quartz—1.12%, are the chemical compounds present in IOCATARM.

Powder X-ray diffraction (PXRD) analysis

The PXRD analysis of as-prepared normal RM, ATARM and IOCATARM was performed using "X'Pert pro panalytical instrument" and is shown in Fig. 1a, b, respectively. The major constituent of RM is mentioned in Fig. 1a, and the components are 1. hematite, 2. quartz, 3. anatase and 4. sodalite. The presence of sodalite was declined (Sushil et al. 2012; Ma et al. 2014; Smiciklas et al. 2014) after treated with HCl and the reduction in sodalite peak is confirmed in Fig. 1a at the range of 20°–30°. The adsorption efficiency of RM was increased due to the diminution of sodalite and it was identified by other researchers (Bhatnagar et al. 2011). Similarly, the major components are identified in Fig. 1b which are 1. iron oxide, 2. hematite, 3. quartz, 4. anatase and 5. sodalite. The presence of iron oxide was indicated by the major peaks (1) and is well matched with reported values (Zhang et al. 2007; Moradinasab and Behzad 2014). The peaks of IOCATARM have obviously confirmed the presence of iron oxide, hematite, quartz, anatase and sodalite (Sushil et al. 2012; Smiciklas et al. 2014).

Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectral analysis of before and after adsorption is shown in Fig. 2a, b, respectively. All the samples were analyzed using PerkinElmer make—model spectrum RX1 for the range 4000–400 cm^{-1}. From both the figures, the observed peak indicates the presence of OH group from 3140 to 3185 cm^{-1}. The observed shift in the peaks of OH group from 3146, 3180 and 3180 cm^{-1}, respectively, to 3185, 3173 and 3181 cm^{-1} assigns the lead (II) adsorption. The shift in peak corresponds to the stretching vibration of a hydroxyl group which associates with the binding of metal Pb^{2+} with the hydroxyl groups present in the adsorbent. Hence, the interaction stimulates the changes in peaks and it indicates the role of the adsorption process. The same kind of changes during the adsorption process has been earlier reported (Lim and Lee 2015; Yang et al. 2016). The presence of carbonate is confirmed by the peak appeared around 1410–1645 cm^{-1} before adsorption. The functional group is slightly shifted from 1410 to 1412 and 1413 cm^{-1} and carbonate group is shifted from 1643, 1642 and 1645 to 1631 cm^{-1}, 1646 and 1634 cm^{-1} which clearly shows the adsorption of lead (II) (Suguna and Siva Kumar 2013; Jadav et al. 2015). The sharp peaks at 993 and 991 cm^{-1} may be due to the presence of Si–O group (Khan et al. 2015).

Scanning electron micrograph (SEM) analysis

The surface morphology of the adsorbents was examined and recorded using ZEISSEVO-18 instrument and the images are shown in Fig. 3a–c. Significantly, Fig. 3a shows before the modification process the surface of RM was smooth and less porous in structure. The surface of the adsorbents becomes more rough and high porous in the structure after treated with acid and then coated with iron oxide which is shown in Fig. 3b, c. This high porosity and roughness are one of the important factors for increasing

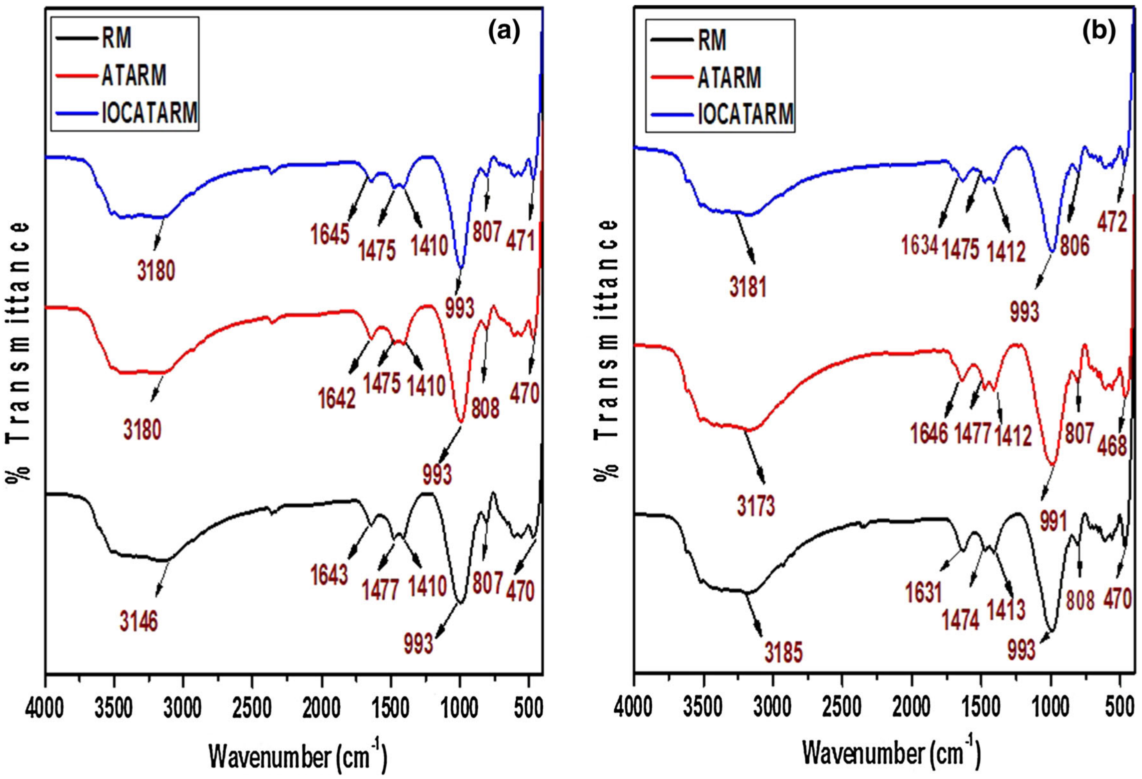

Fig. 2 **a** Analysis of FTIR for before adsorption and **b** analysis of FTIR for after adsorption

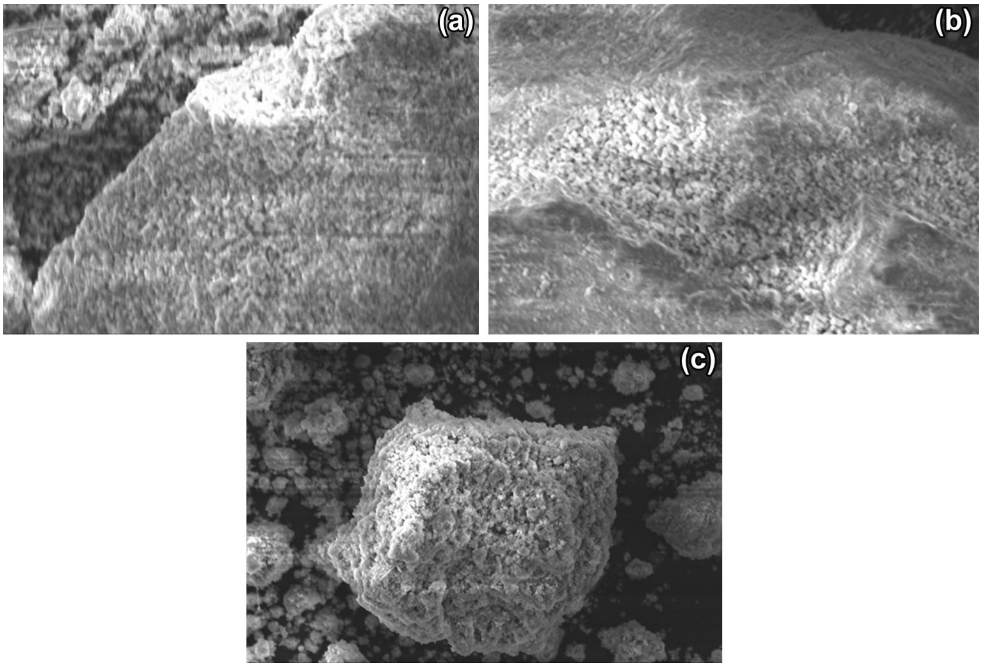

Fig. 3 **a–c** SEM analysis for red mud, acid-treated activated red mud and iron oxide-coated acid-treated activated red mud, respectively

the adsorption capacity of adsorbent. Similarly, the roughness increases the adsorption efficiency which has been reported and shown by various researchers (Boujelben et al. 2009).

Batch adsorption experiment

Adsorption at various pHs

The role of pH is a significant one to determine the uptake of lead (II) ions by the adsorbent. In the present experimental study, the effect of pH on the lead (II) removal was analyzed by varying the pH from 1 to 10. The pH was adjusted by adding some drops of HCl and NaOH. Digital pH meter (Hanna make) was used to measure the pH of the solution. The concentration of H^+ ions is high in the initial stage of pH 1 and 2. These H^+ ions compete with lead ions to occupy the adsorption site and hence, the adsorption of lead (II) ions in the adsorbent is reduced (Boujelben et al. 2009; Saka et al. 2011). At higher pH 8–10, the presence of OH^- ions is high which leads to the formation of precipitation and the lead ions become lead hydroxide and consequently reduction in the adsorption (Masoudi Soltani et al. 2015). A plot has been drawn between different pH and the percentage of adsorption and is shown in Fig. 4a. From the figure, it is observed that higher adsorption occurs at pH 5 for RM, pH 7 for ATARM and pH 6 for IOCATARM. The percentage of removal is found to be 79.64, 85.18 and 93.56, respectively. The respective pH values are maintained for the further investigation.

Effect of adsorbent dosage

The percentage of removal of lead (II) was studied by varying the dosage of adsorbent from 0.1 to 0.8 g and was added with 100 ml of 50 ppm metal lead (II) aqueous solution. The experiment was conducted with obtained optimum pH and, time and ion concentration were maintained as constant. The filtrate was analyzed after the adsorption using UV–Vis spectrum and is shown in Fig. 4b. The result shows that the maximum removal was obtained at 0.7 g for RM, 0.6 g for ATARM and 0.5 g for IOCATARM. Also, the figure confirms that the uptake of lead (II) increases with increasing dosage of adsorbent. This may be due to the enhanced active surface site of the adsorbent. After the addition of 7 g of dosage, the removal efficiency attains equilibrium and hence, no change in removal efficiency is observed. Further, the addition of adsorbent creates the interaction with the adsorption sites. As a result, the aggregation of adsorbent occurs and hence, the removal efficiency of adsorbent is slightly decreased (Majeed et al. 2014; Ren et al. 2014).

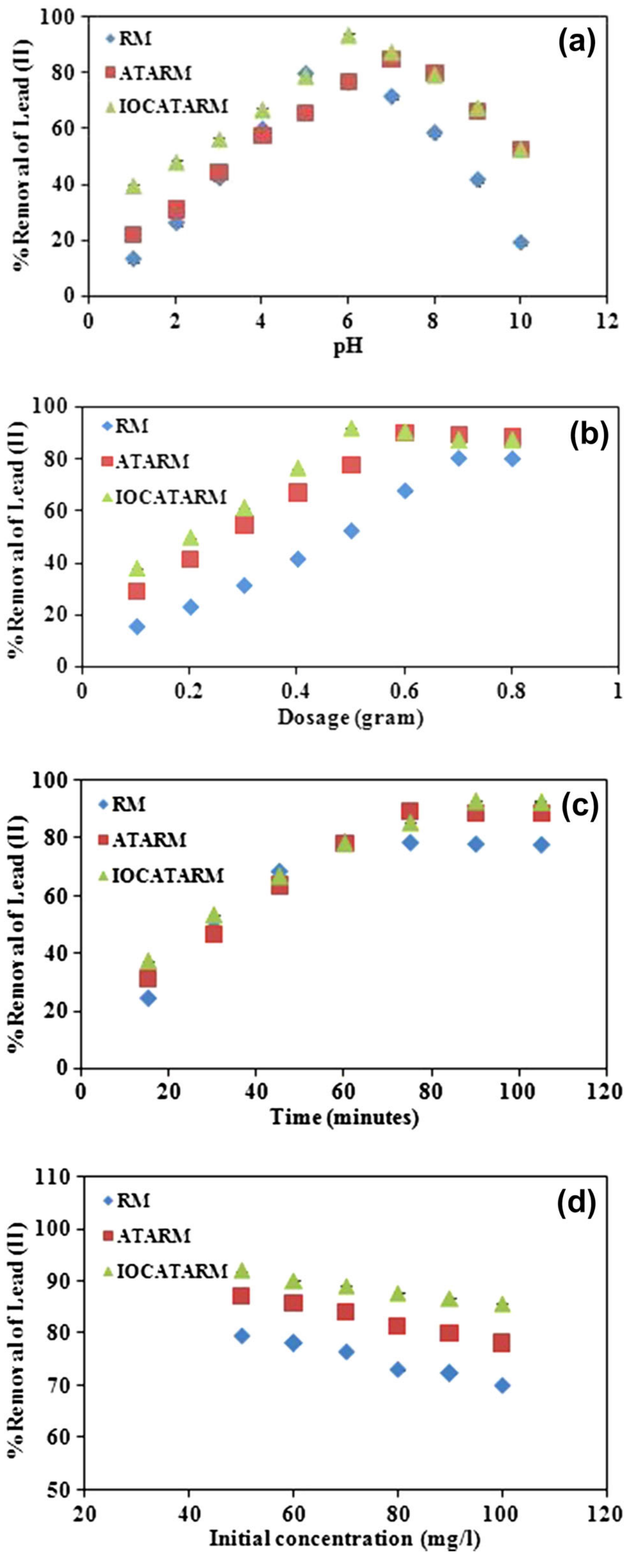

Fig. 4 **a** Effect of pH on adsorption of lead (II) (initial concentration: 50 mg l^{-1}, adsorbent dose: 0.5 g in 100 ml and contact time: 105 min), **b** effect of adsorbent dosage on adsorption of lead (II) (initial concentration: 50 mg l^{-1} and contact time: 105 min), **c** effect of contact time on adsorption of lead (II) (initial concentration: 50 mg l^{-1}), **d** effect of initial concentration on adsorption of lead (II)

Effect of contact time

The initial concentration of 50 ppm of lead was taken with optimized weight (0.7, 0.6 and 0.5 g) of adsorbent and optimum pH (5, 7 and 6) to find the effect of contact time. The concentration was maintained as constant and the time of contact was varied. Variation in adsorption with time was carried out for 15–105 min and is shown in Fig. 4c. The figure reveals that the efficiency of adsorbent in the removal of lead (II) is high at the initial stage of adsorption due to the unoccupied and free active sites. The adsorbent site becomes occupied by the adsorbate lead (II) and attains equilibrium when the time increases. Also, Fig. 4c shows that the percentage of removal of lead (II) is high and rapid at the beginning and reaches equilibrium as time increases (Ghimire et al. 2002; Bhatnagar et al. 2006). The appropriate time of lead (II) removal with adsorbent RM, ATARM and IOCATARM is found to be 60, 75 and 90 min, respectively and the corresponding percentage of removal is 79.12, 89.44 and 93.21. The subsequent experiments were conducted with this optimized time.

Effect of initial ion concentration

Lead (II) with 50–100 ppm concentration was used for the analysis of initial ion concentration by treated with the adsorbent RM, ATARM and IOCATARM. Optimum pH, constant dosage and time and the variable concentration were determined for the experiment. The respective optimum gram of adsorbent was treated with various concentrations of the ion. The variation in initial concentration with the percentage of removal of lead (II) is shown in Fig. 4d. The figure confirms that at lower initial concentration, the percentage of removal of ions is high and it is decreased in a higher concentration of ions. Because at the initial stage of time the adsorbent has free and fresh active sites and the concentration of ions is also low, hence increase in adsorption takes place. Further, increase in ions concentration the adsorbent-free sites become fewer and hence decrease in adsorption takes place (Nadaroglu and Kalkan 2012; Suhasini and Begum 2013).

Isotherm models

Adsorption isotherms generally describe the relationship between the quantity of metal ion adsorbed and its equilibrium concentration in the solution. The experimental data were applied to the three isotherm models of Langmuir, Freundlich and Dubinin–Radushkevich for the adsorption of lead (II) by RM, ATARM and IOCATARM which are shown in Table 2. The distribution of a metal ion between solid and liquid phases describes through the Langmuir, Freundlich and Dubinin–Radushkevich models. The nature of adsorption process and adsorption capacity was investigated using isotherm models with various initial ion concentrations from 50 to 100 mg/l. The Langmuir isotherm assumes monolayer of the adsorption that takes place with homogeneous adsorption sites and represents the equilibrium distribution of metal ions between the adsorbent and adsorbate. The linear form of Langmuir isotherm is expressed as

$$C_e/q_e = C_e/q_m + 1/k_L \cdot q_m$$

where k_L is the Langmuir constant related to the energy of adsorption (l/mg), q_m is the maximum adsorption of adsorbate per gram and C_e is the equilibrium concentration

Table 2 Langmuir, Freundlich and Dubinin–Radushkevich isotherm parameters for lead (II) ions adsorbed on the adsorbents

Isotherms	Red mud values	Acid-treated activated red mud values	Iron oxide-coated acid-treated activated red mud values
Langmuir isotherm parameters			
q_m (mg/g)	16.39	19.23	27.02
K_L (l/mg)	0.0525	0.0933	0.1213
R_L	0.275	0.176	0.141
R^2	0.99	0.995	0.984
Freundlich isotherm parameters			
K_F (l/g)	1.753	3.10	4.645
n	1.9	2.1	2.0
R^2	0.988	0.993	0.997
Dubinin–Radushkevich isotherm parameters			
q_s (mg/g)	10.18	12.57	16.29
K_{ad} (mol^2/KJ^2)	$1 \times 10 - 5$	$5 \times 10 - 6$	$2 \times 10 - 6$
E (KJ/mol)	0.223	0.316	0.5
R^2	0.947	0.940	0.875

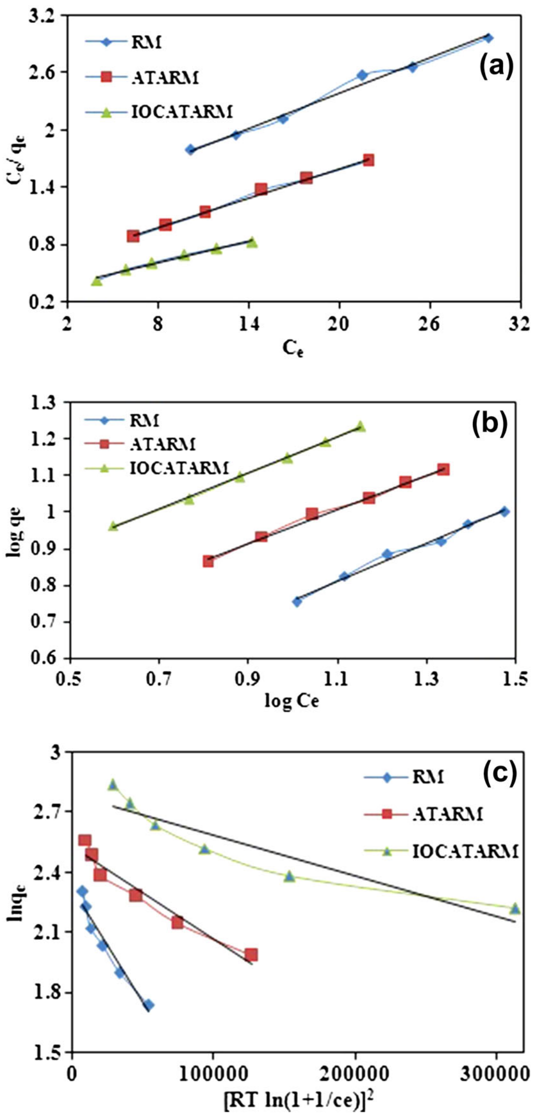

Fig. 5 **a** Langmuir isotherm plot for lead (II) on RM, ATARM and IOCATARM, **b** Freundlich isotherm plot for lead (II) on RM, ATARM and IOCATARM, **c** Dubinin–Radushkevich plot for lead (II) on RM, ATARM and IOCATARM

of the adsorbate in the solution (mg/l), q_e is the equilibrium metal ion concentration on the adsorbent (mg/g). A plot (Fig. 5a) of C_e versus C_e/q_e gives a straight line and the constants q_m and k_L are obtained from the slope and intercept, respectively. The essential parameter of Langmuir isotherm is separation factor R_L and it can be expressed as

$$R_L = 1/1 + k_L C_0$$

where k_L is the Langmuir constant (l/mg) and C_0 is the initial concentration of adsorbate (mg/l). From Table 2, it is confirmed that the Langmuir isotherm shows the maximum adsorption of adsorbate (q_m) per gram which is higher in IOCATARM (27.02 mg/g) compared with other adsorbent. This may be due to the surface area and the coated iron oxide enhances the adsorption of lead (II). Also, the R_L that lies between 0 and 1 indicates the favorable higher adsorption, while R_L value greater than 1 indicates an unfavorable adsorption process (Resmi et al. 2012; Akl et al. 2015). In the present study, the obtained R_L value is found to be 0.275 for RM, 0.176 for ATARM and 0.141 for IOCATARM. The results of R_L values show the favorable affinity of lead (II) on all three adsorbents. A comparative analysis on the removal of lead (II) ions using various adsorbents is shown in Table 3. From the table, it is confirmed that the adsorption capacity (q_m) for IOCATARM is higher and preparation cost of adsorbent is also low compared with other reported adsorbent (Shekinah et al. 2002; El-Ashtoukhy et al. 2008; Nale et al. 2012; Resmi et al. 2012; Tzu et al. 2013; Chaouch et al. 2014; Raikar et al. 2015).

The Freundlich isotherm suggests that the adsorption occurs at heterogeneous surface and it is used to determine the adsorption intensity of the adsorbent toward the adsorbate. It is expressed by the following formula

$$\log q_e = \log k_F + 1/n \log C_e$$

where k_F is Freundlich adsorption capacity and n is Freundlich isotherm constant. A plot of log C_e versus log q_e (Fig. 5b) gives a linear variation, where the coefficients k_F and n can be calculated from the intercept and slope, respectively. k_F value for IOCATARM is higher than other two adsorbents and the values are 1.753, 3.10 and 4.645 for RM, ATARM and IOCATARM, respectively. The higher k_F value confirms the greater adsorption capability of IOCATARM. The obtained n value that lies between 1 and

Table 3 Comparison of the adsorbent capacity of IOCATARM with other adsorbents for removal of lead (II) ions

Adsorbent	q_m (mg/g)	References
Activated carbon prepared from Eichhornia	16.61	Shekinah et al. (2002)
Alginate–bentonite	5.8	Tzu et al. (2013)
Natural and activated rice husk	1.4 and 3.0	Raikar et al. (2015)
Pomegranate peel	21.97	El-Ashtoukhy et al. (2008)
Activated carbon prepared from maize cob	3.15	Nale et al. (2012)
Acid-activated clay	10.1	Resmi et al. (2012)
Activated carbon prepared from Algerian dates	11.8	Chaouch et al. (2014)

10 indicates the favorable adsorption (Lashkenari et al. 2011; Nethaji and Sivasamy 2014). From Table 2, it is observed that the *n* values of normal RM, ATARM and IOCATARM are found to be 1.9, 2.1 and 2.0, respectively and hence confirm the favorable adsorption of lead (II).

The physical or chemical nature of the adsorption of metal ions in the adsorbent was analyzed using Dubinin–Radushkevich isotherm model. The linear form of the Dubinin–Radushkevich isotherm (Foo and Hameed 2010; Jadav et al. 2015) can be written as

$$\ln q_e = \ln(q_s) - (k_{ad}\varepsilon^2)$$

$$\varepsilon = RT\ln[1 + 1/c_e]$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), q_s is the theoretical isotherm saturation capacity (mg/g), k_{ad} is the Dubinin–Radushkevich isotherm constant (mol^2/kJ^2) and ε is the Polanyi potential, *R* is the gas constant (8.314 J/mol K), *T* (K) is the absolute temperature and c_e is the adsorbate equilibrium concentration (mg/l). The mean adsorption energy *E* (KJ/mol) is obtained by the equation.

$$E = 1/[2k_{ad}]^{1/2}$$

The isotherm constants q_s and K_{ad} are calculated from the slope and intercept of the plot of ln q_e versus ε_2 (Fig. 5c). Also, the figure gives the mean adsorption energy *E* (KJ/mol) which estimates the type of adsorption process. If $E < 8$ kJ/mol, the adsorption process is physical in nature, and if it is in the range 8–16 kJ/mol, the adsorption process is chemical in nature (Radjenovi and Medunic 2015). In the present work, the physical nature of the adsorption is confirmed from Table 2. The mean free energy *E* is found to be 0.223, 0.316 and 0.5 for RM, ATARM and IOCATARM, respectively. The obtained value of regression coefficient (R^2) for all three adsorbents represents the isotherm is better fit to the experimental data.

Adsorption kinetics

In the present investigation, the adsorption rate during the removal of lead (II) was examined by the two kinetic models such as pseudo-first-order and pseudo-second-order. The integral form of pseudo-first-order kinetics equation expressed as

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t$$

where q_t (mg/g) is the amount of adsorbed metal ions on the adsorbent at time *t* (min), q_e (mg/g) is the amount at equilibrium and k_1 (min^{-1}) is the rate constant of pseudo-first-order (Venkatesan and Rajagopalan 2016). The values of $k_1$and q_e are calculated from the slope and intercept of the plot log (q_e–q_t) versus t which is shown in Fig. 6a.

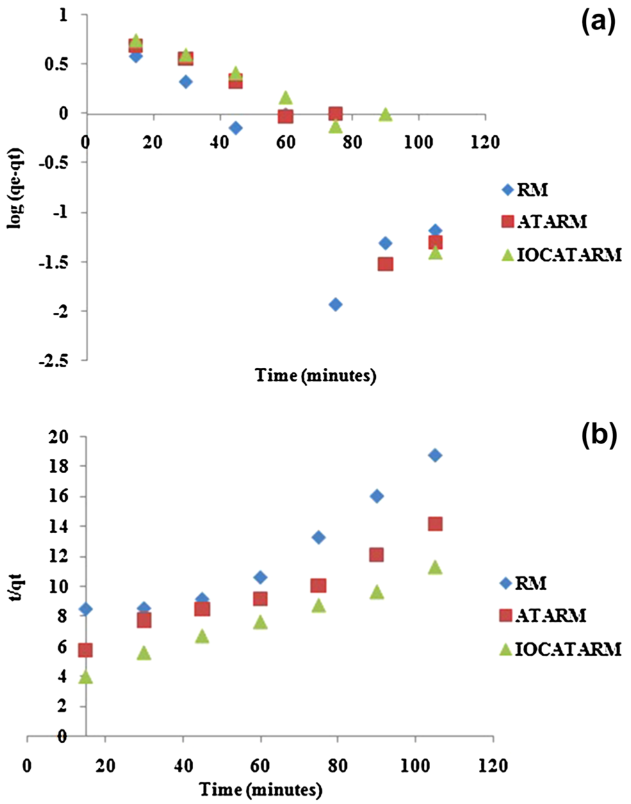

Fig. 6 **a** Pseudo-first-order model for adsorption of lead (II) on RM, ATARM and IOCATARM and **b** pseudo-second-order model for adsorption of lead (II) on RM, ATARM and IOCATARM

The pseudo-second-order kinetic model represents as

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

where q_t (mg/g) is the amount of adsorbed metal ions on the adsorbent at time *t* (min), q_e (mg/g) is the amount at equilibrium and k_2 (g/mg/min) is the rate constant of pseudo-second-order (Montazer-Rahmati et al. 2011; Ackacha 2013). The value of q_e and k_2 can be determined from the slope and intercept of the plot t/q_t versus *t* (Fig. 6b).

The kinetic reaction has taken place at an initial metal concentration of 50 mg/l at various contact time. Adsorption kinetic parameters of lead (II) removal are given in Table 4. The table confirms that the pseudo-second order model is a well-fitting model compared to the pseudo-first order model because the correlation coefficient (R^2) is higher for the pseudo-second order model.

Table 4 Adsorption kinetic parameters for lead (II) removal

Adsorbents	q_e (mg/g)	Pseudo-first order model K_1 (min^{-1})	Correlation coefficient value R^2	Pseudo-second order model k_2 (g/mg/min)	Correlation coefficient value R^2
Red mud	8.403	0.0552	0.710	0.00284	0.909
Acid-treated activated red mud	11.76	0.0552	0.835	0.001595	0.960
Iron oxide-coated acid-treated activated red mud	13.15	0.04375	0.777	0.00187	0.992

Conclusion

The present work reports the removal of lead (II) with low cost using RM, ATARM and IOCATARM. The results from the batch experiment have revealed that the IOCATARM is good and efficient adsorbent for the removal of lead (II) from the aqueous solution compared with previous reported adsorbents. Also, the experiment confirms that the maximum adsorption is attained for the pH 6, adsorbent dosage of 0.5 g and 90 min of contact time. Isotherm models such as Langmuir, Freundlich and Dubinin–Radushkevich model are analyzed and comparative results are reported. The results show that the regression coefficient of Langmuir, Freundlich and Dubinin–Radushkevich isotherm model is 0.984, 0.997 and 0.875, respectively, which indicates the good agreement with all isotherm models used. The adsorption capacity (q_m) obtained by Langmuir model was found to be 27.02 mg/g and the separation factor R_L value for the adsorption of lead (II) on IOCATARM was 0.141, which confirm the favorable uptake of the lead (II). The values of Freundlich constant n that lie between 1 and 10 indicate the favorable adsorption. The obtained n value from Freundlich isotherm is 2.0 which represents the good adsorption of lead (II) by the adsorbent. Dubinin–Radushkevich model confirms the physical nature of the adsorption for the lead (II) removal. Kinetic models have determined the rate of adsorption of lead (II) follows pseudo-second-order models. All the experimental results confirm the IOCATARM is a potential candidate for the removal of lead (II).

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