Lead Removal from Aqueous Solution Using Silica Ceramic: Adsorption Kinetics and Equilibrium Studies

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Abstract

Kinetics adsorption of lead from aqueous solution using silica ceramic has been investigated in batch methods. The effect of solution pH, initial metal ion concentration, temperature and adsorbent mass on metal ion removal has been studied. The process of lead adsorption follows pseudo second-order rate expression and obeys the Langmuir's model with high correlation coefficient ($R^2 > 0.99$) and better than other equations. The maximum removal achieves 2.7 mg/g. The result indicates that under the optimum conditions, the maximum adsorption value for Pb(II) comply the silica ceramic is a potential adsorbent for Pb(II).

Keywords: Adsorption, Kinetic, Removal, Lead, Silica ceramic

1. Introduction

Industrial wastewaters are considered as the most important source of heavy metal pollutions among various heavy metals. Lead is a significant element metal that contaminated the water both natural and anthropogenic activities. Lead (Pb) found in natural deposits and process include mineral breakdown, sedimentation of from dust storms, volcanic eruptions, forest fires etc. Anthropogenic activities of lead contamination including and smelting operations, commonly used in household plumbing materials and water service lines, metal plating, battery recycling, combustion of leaded gasoline, atomic energy installation, leatherworking, photography, salvages yards, urban and industrial waste, continuous of fertilizer, pesticides and use of Pb bullets (Sing et al., 2006; Heil et al., 1999) automobile, and oil industries produce more heavy metal ions that other industries (Reed and Arunachalam, 1994). It directly or indirectly causes damage or dysfunction to liver, reproductive system, brain and central nervous system, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women etc.

A variety of methods have been proposed for the treatment of wastewaters containing lead metals such as chemical precipitation (Matlock et al., 2001), electrochemical reduction, ion exchange (Inglezakis et al., 2007), membrane separation, flotation, biosorption (Nourbakhsh et al., 2002; Gupta and Ali, 2004) and adsorption (Mohan and Chander, 2006; Gupta and Sharma, 2002). Adsorption is being popular to be an economically viable alternative technique for removing lead from wastewater and water supplies. In recent years, there is an increase interest in using non-chemical and low-cost adsorbent (Salim et. al., 2007) to remove heavy metals from wastewater. The objective of the present study is to determine the functionality and sorption kinetics of silica ceramic as a low-cost adsorbent material to remove Pb(II) from aqueous phase.

2. Material and Method

2.1 Adsorbent

Study used silica ceramic (powder particle size, <0.05mm) obtained from EKOAIRANDO Co. Ltd. Kochi, Japan having major chemical ingredients SiO_2, Na_2O, Al_2O_3, CaO and K_2O.

2.2 Adsorbate

The synthetic Stock solution of Pb (II) (1000 mg/L) was prepared using $Pb(NO_3)_2$ (Kanto Chemical Inc. Ltd., Japan) by dissolving in acidified ultra distilled water. The stock solution was diluted with distilled water to obtained desired concentration ranging from 5 to 70 mg/L. Solutions of the 0.1 M HCl and 0.1 M NaOH were used for pH adjustment.

2.3 Analytical method

The surface area of the silica ceramic was measured by N_2 adsorption using single point Brunauer, Element and Teller (BET) (Micrometric ASAP 2020, USA) procedure. The surface structure was examined by scanning electron microscopy (SEM-EDS, JEOL-JSM-6500F, Japan). Lead analysis was conducted by Atomic Absorption Spectrometer (AAnalyst200, Perkin-Elmer, Singapore) at a weave length of 283.31 nm. All samples were analyzed after filtering within 24 hours of collection.

2.4 Batch kinetics experiments

Batch experiments were conducted for optimum dose, equilibrium time, effect of concentrations, and effects of temperature. Silica ceramic was added as per dose requirements to round bottom glass bottles of 100 ml capacity with 50 ml of Pb solutions of desire concentration (10-50 mg/L) and (5.5 -6.5) pH range. The flasks were capped and placed on a mechanical shaker at a speed of 140 rpm at 30 °C, and samples were taken at predetermined intervals. All samples were filtered by a 0.45 μm membrane filter and analyzed for Pb. The amount of adsorbed Pb was calculated using Eq. (1) by the difference of initial and residuals amounts of Pb in solution divided by the mass of adsorbent. The removal efficiency, R_e, (determined as the Pb removal percentage relative to initial concentration) using Eq. (2) of the system, was calculated as:

$$q_e = \frac{(C_0 - C_e)}{M} \times V \tag{1}$$

$$R_e = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

Where, q_e (mg/g) is the amount of the Pb adsorbed per unit mass of silica ceramic. C_0 and C_e are the initial and equilibrium (or at any time) ion concentration (mg/L), respectively, V is the volume in liter of solution and M is the mass (g) of the silica ceramic.

2.5 Batch isotherms studies

After determining the optimum pH, temp and equilibrium time, isotherm studies were conducted by varying the mass of silica ceramic. Representative masses (0.3, 0.4, 0.5…..0.9 and 1.0 g) of silica ceramic were add into 25 ml of solution containing 10 mg/L of Pb ion for 3h, which is equilibrium time for the silica ceramic ion. The initial pH of the metal solutions was adjusted to an optimum value of 3.5 with 0.1 M NaOH or HCl.

3. Results and Discussion

3.1 Adsorbent characterization

The details physio-chemical properties are given in Table 1. The major components of chemical compositions of the silica ceramic are silicon, aluminum, sodium, calcium and potassium compounds. Both elemental and mineralogical characterization of silica ceramic verified its compositions. Scanning electron microscopy was performed on silica ceramic at different magnification to determine surface structure. The working tension was 15 KV. Scanning electron micrographs for intra structure of silica ceramic is shown in Figure 1 (A) and (B). The mineralogical analysis is shown in Figure 2. The figures indicate that silica ceramic has an extensive surface area, and it can be used as a potential adsorbent.

3.2 Effect of pH

pH of solution is one of the most important parameters for adsorption of heavy metals from contaminated aqueous solution. Adsorption of Pb was studied at various pH and results are given away in Figure 3. The initial pH of solution varied from 2.45 to 11.5. In this experiments adsorbate concentration was 25 mg/L, ceramic mass was 0.3 g to 1.0 g and contact time was 18 h.   From this figure it is clear that lead adsorption efficiency is high at bellow pH 4.5.   This result showed similar trend to lead removal by zeolite and sepiolite (Turan et al., 2005); and by natural phosphate (Mouflih et. al., 2006).

3.3 kinetics study

3.3.1 Effect of concentration

To evaluate the sorption characteristics of silica ceramic for lead ions, the change of sorption capacity with time for different initial solution concentrations has been investigated. A series of experiments were undertaken by varying the initial Pb concentration in the range 10 – 50 mg/L on removal kinetics of Pb from the solution. Figure 4 showed that adsorption of Pb(II) by silica ceramic increases as the initial Pb (III) concentration increased. The contact time required to reach the equilibrium of Pb(II) solution within 180 min. However, the experimental data were measured at 600 min to confirm the complete equilibrium was reached.

3.3.2 Adsorption Kinetics

The adsorption kinetic data of lead are analyzed using three kinetics models were applied mainly, pseudo-first order, pseudo-second order and, intra-particle diffusion model rate equations.

Lagergren suggests the pseudo-first order kinetics rate equation (Lagergren, 1898), which is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

Where k_1 is the pseudo-first order rate constant, q_e represents adsorption capacity. The integrating rate law by applying the initial condition of t = 0 to t and q_t = 0 to q_t, Eq.(3) becomes:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{4}$$

Where, q_e and q_t both (mg/g) are the amount of Pb(II) adsorbed per unit of mass of silica ceramic at equilibrium and time t. respectively, and K_1 the rate constant (1/min). The value for the K_1 was calculated from the slope of the linear plot of log $(q_e - q_t)$ versus t [Figure 5. (a)]. The K_1 values and correlation coefficients R^2 are given in Table 2.

The pseudo-second order reaction rate equation used by Ho et al (Ho et al., 1996) to study the kinetics of adsorption of heavy metals on peat. This model was also applied to assess the kinetics of adsorption of Pb(II) on silica ceramic. The equation is as follows:

$$\frac{dq_t}{dt} = k_2(q_e^2 - q_t)^2 \tag{5}$$

where k_2 is the rate constant of pseudo second-order adsorption. The integrating rate law Eq.(5), after applying the initial conditions (McKay and Ho, 1999), and rearranging it gives as linearized form of pseudo second-order rate kinetics expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

In addition, initial rate of adsorption is h is:

$$h = k_2 q_e^2 \tag{7}$$

Where, q_e and q_t both (mg/g) are the amount of Pb(II) adsorbed per unit of mass of silica ceramic at equilibrium and time t. respectively, and K_2 is the rate constant of pseudo second order adsorption (g/mg min). The kinetics plots between t/q_t versus t were plotted for the different initial concentrations [Figure 5. (b)]. Slope and intercept values were solved to give the value of pseudo-second order rate constant (Table 2).

Figure 5 (b) and Table 2 shows that highly significant regression line ($R^2 > 997$) and the data were well fitted only to the pseudo second-order rate equation. The straight line was obtained indicating that the process follow a pseudo second order kinetics for various concentration of Pb(II). While the initial Pb(II) concentration increases from 10 mg/L to 50 mg/L, the adsorption capacity, q_{exp}, increase from 0.9594 to 2.7048 mg/g. This indicates that the initial Pb(II) concentration plays a key role in determining the adsorption capacity of Pb(II) on silica ceramic. It is also observed in Table 2 that when initial Pb(II) concentration increase from 10 mg/L to 50 mg/L, the rate constant, k_2 decrease from 277.397×10^{-3} to 19.223×10^{-3} g/mg min and values of initial sorption rate h are also decrease from 258.853×10^{-3} to 151.849×10^{-3} mg/g min.

Lagergren pseudo first order and pseudo second-order rate equations cannot identify the diffusion mechanisms during the sorption process and uptake varies almost proportionately with the half-power of time, $t^{1/2}$, rather than t. A nearly linear variation in the quantity sorbed with $t^{1/2}$ is predicted for a large initial fraction of reactions controlled by rates of

intra-particle diffusion. Therefore, the experimental kinetic data were tested against intra-particle diffusion model. The initial rate of intra-particle diffusion can be determined by the most-widely applied intra-particle diffusion equation for sorption system is given by Weber and Morris (Weber and Morris, 1963):

$$q_t = k_i t^{1/2} + C \tag{8}$$

Where, q is the amount of Pb (II) adsorbed (mg/g) at time t, k_i the intra-particle diffusion constant (mg/g min$^{1/2}$), and C is the intercept.

The values of k_i indicate an enhancement in the rate of adsorption. It is observed in Table 2 that when initial Pb(II) concentration increase from 10 mg/L to 50 mg/L, the intra-particle diffusion constant, C and k_i increase from 0.5316 to 0.9613 and from 27.1×10^{-3} to 101.6 ×10^{-3} g/mg min respectively.

3.3.3 Effect of temperature

Effect of temperature on removal of Pb (II) were performed at three different temperatures, i.e., 20, 30, and 40°C. The results are shown in Figure 6, which indicates that the Pb (II) uptake increases from 2.42 to 2.86 when temperature of the solution increases from 20 to 30°C. After that, sorption uptake increase slowly from 2.86 to 2.90 mg/g when temperature of the solution increases 30 to 40°C. The adsorption of lead on silica ceramic is highest at 40°C. That means the sorption of Pb (II) is in favor of temperature indicates that the mobility of the lead molecule increases with an increase in the temperature. Therefore, it is revealed that the process is endothermic.

3.3.4 Effect of adsorbent doses

The effect of adsorbent dose was studied at a fixed initial concentration of 20 mg/L by silica ceramic mass varied from 5 to 40 g/L. The general trend indicates that 5 to 25 g/L of sorbent dose uptake large amount of Pb(II), rapidly and 30 to 40 g/L dose uptake little amount but slowly (Figure 7).   At 10 g/L, removal efficiencies of 97.9% were observed and thereafter efficiency was 100% occurred slowly. The reason of removal efficiency increased due to the increase of adsorbent dose that means increase of the total available surface area of the adsorbent particles.

3.4 Adsorption Isotherm

The equilibrium adsorption isotherm is of importance in the design of adsorption systems (Wang et al., 2005). Several isotherm equations are available and the Langmuir isotherm is selected in this study. The Langmuir adsorption isotherms assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application to many sorption process of monolayer adsorption. The Langmuir adsorption isotherm can be written as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{9}$$

The Langmuir parameters were obtained by fitting the experimental data to the linearized equation derived from Eq. (9):

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \tag{10}$$

$$\frac{1}{q_e} = \frac{1}{b q_m} \frac{1}{C_e} + \frac{1}{q_m} \tag{11}$$

Where, q_e is the adsorbent amount (mg/g) of the Pb (II), C_e is the equilibrium concentration of the Pb(II) in solution (mg/L), q_m is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption (L/mg).

Based on Eq. (10) and Eq. (11) the isotherms were fitted to the adsorption data obtained. The Langmuir adsorption exponents for Eq. (10) and Eq. (11), the q_m and b are determined from the linear plots of C_e/q_e versus C_e (Figure not shown) and $1/q_e$ versus $1/C_e$ (Figure not shown) and calculated correlation coefficients for these isotherms, are shown in Table 3. The values of the Langmuir constant were calculated from the slopes and intercepts of the plots. The magnitude of Langmuir constant b is small (1.8561 L/mg) and the adsorption capacity q_m was determined as 2.7586 mg/g. In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter R_L was determined by using the following equation (Magdy and Daifullah, 1988):

$$R_L = \frac{1}{(1 + b C_0)} \tag{12}$$

Where, C_0 is the initial concentration and b is the Langmuir isotherm constant. The parameter R_L indicates the shape of isotherm. The process is irreversible if $R_L = 0$, favorable if $R_L < 1$, linear if $R_L = 1$ and unfavorable if $R_L > 1$. The Figure 9 shows that the R_L values at different initial Pb (II) concentration   indicating a highly favorable adsorption. As shown in Table 3 and Figure 8, the Langmuir equation represents adsorption process is very well and the correlation coefficient, R^2 value is indicating a very good mathematical fit.

4. Conclusions

The results of present investigations revealed that silica ceramic is potential adsorbent to removal the Pb(II) from aqueous phase. The pseudo-second order kinetic models fits very well with the adsorption behavior of Pb. The sorption suggested that the adsorption is high at low pH range. The amount of lead uptake at equilibrium increased with increasing solution concentrations, temperatures and decreasing pH, sorbent mass. The findings of the study show that silica ceramic has excellent potential for use in the removal of Pb from waste water, however further work is increase the adsorption capacity of silica ceramic. Currently study is being progress involving the activation of silica ceramic by acid and heat treatment.

Acknowledgements

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Table 1. Physical and chemical properties of absorbent used in the experiments

Chemical properties	wt. %	Physical properties	Value
SiO_2,	80.81	Surface area (BET), (m^2/g)	340.38
CaO	6.93	Median Pore diameter (A)	44.46
Al_2O_3	3.80	Pore Volume (cm^3/g)	0.3274
Na_2O	2.57	pH (1% Solution)	8.5
K_2O	1.84	Particle size, mm	< 0.05

Table 2. Lagergren constants, Pseudo second-order rate constants and Intra-particle diffusion constants for lead adsorption on silica ceramic at different initial concentration

Pb (mg/L)	q_{exp}	Lagergren constants		Pseudo second-order rate constants				Intra-particle diffusion	
		$K_1 \times 10^{-3}$	R^2	q_e	$K_2 \times 10^{-3}$	$h \times 10^{-3}$	R^2	C	$K_i \times 10^{-3}$
10	0.9594	34.775	0.7244	0.966	277.397	258.853	1	0.5316	27.1
20	1.8718	33.624	0.9455	1.912	44.380	162.248	0.9999	0.8416	60.4
30	2.5088	22.569	0.9176	2.6596	11.064	78.260	0.999	0.6858	97.5
40	2.6264	31.781	0.9421	2.7563	14.957	113.636	0.9981	0.8395	100.9
50	2.7048	32.703	0.8939	2.8106	19.223	151.849	0.9977	0.9613	101.6

Table 3. Langmuir isotherm constant for adsorption of Pb(II) by silica ceramic

Langmuir isotherm parameters	C_e/q_e	$1/q_e$
q_m (mg/g)	2.7586	2.7586
b (L/mg)	1.8561	1.8561
R^2	0.9999	1
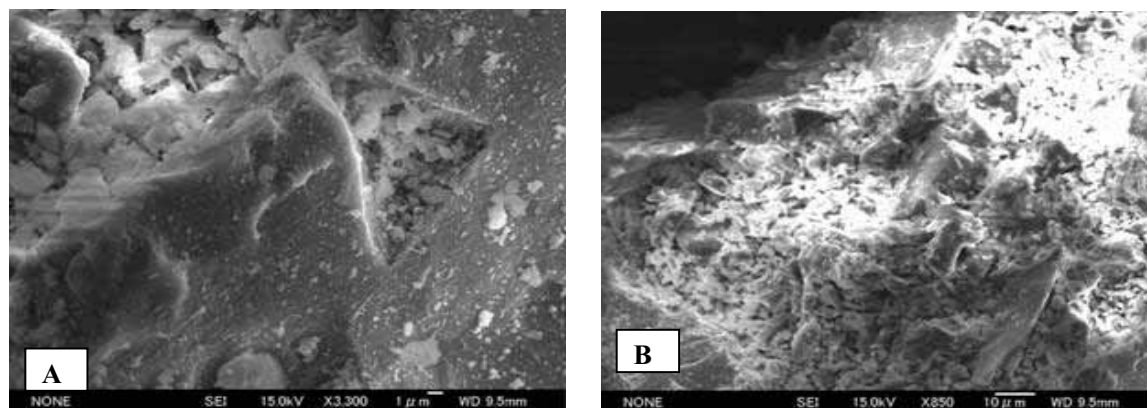
Figure 1. SEM of silica ceramic: (A) × 3300, 1μm; (B) × 850, 10μm
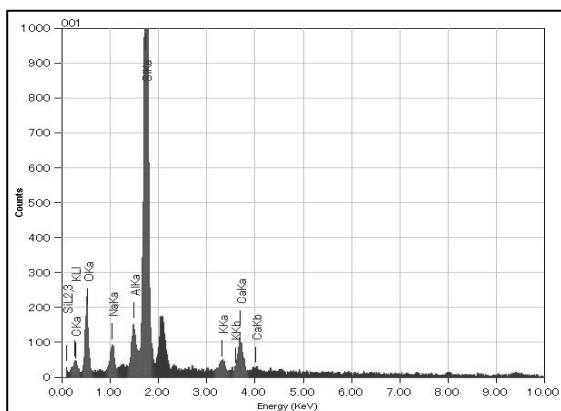
Figure 2. Elements spectrum of a selected silica ceramic obtained by SEM-EDS analysis
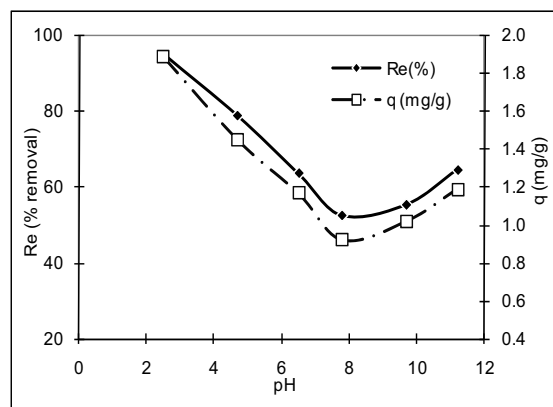
Figure 3. Effect of pH on adsorption of Pb(II) by silica ceramic at temperature 25°C
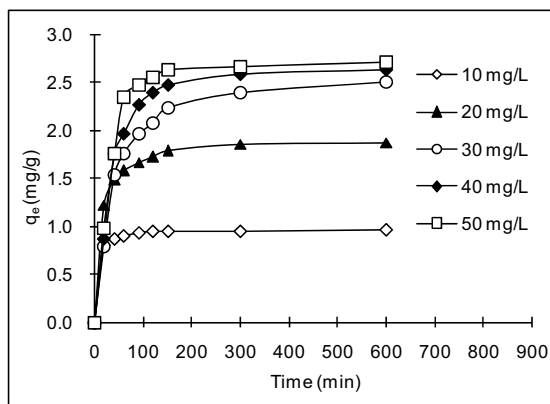
Figure 4. Effect of initial concentration on Pb(II) adsorption by silica ceramic at pH 5.5
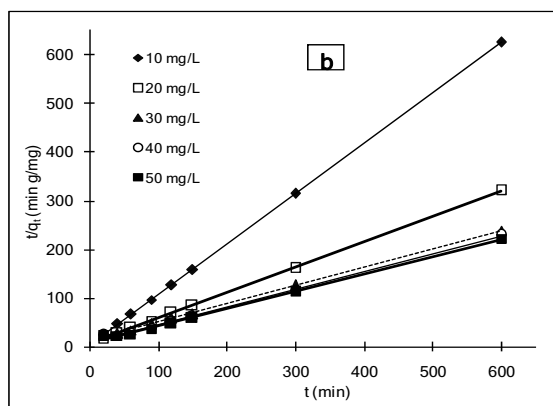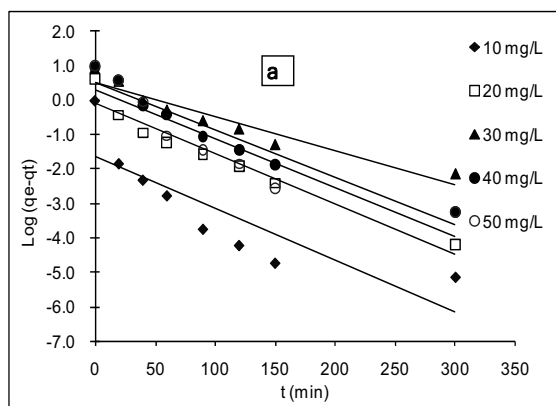
Figure 5. Kinetics analysis of pb(II) adsorption by linear plots of (a) pseudo first-order, (b) pseudo second-order rate equations
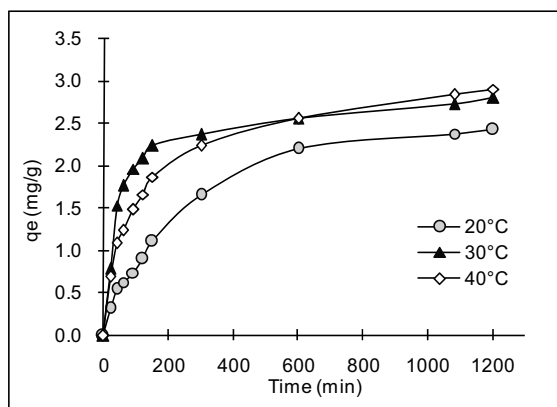
Figure 6. Effect of temperature on Pb(II) adsorption
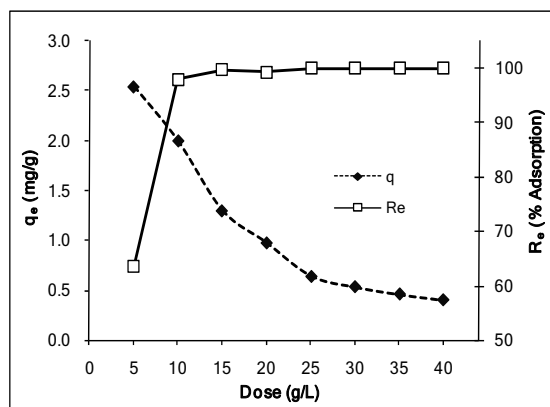
Figure 7. Effect of adsorbent dose on Pb(II) adsorption.
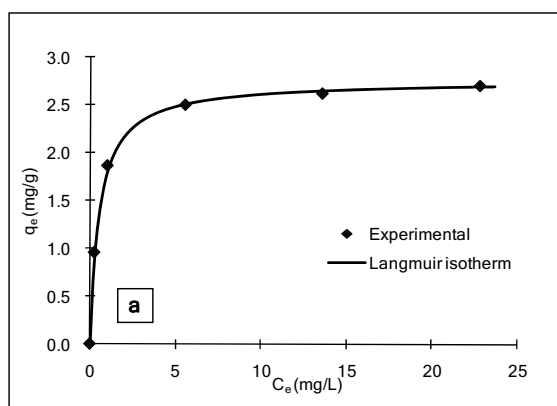
Figure 8. Langmuir adsorption isotherm of Pb(II) on silica ceramic
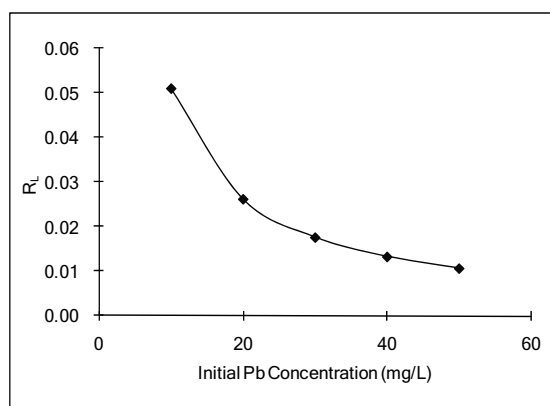
Figure 9. Separation factor for Pb(II) adsorption using silica ceramic