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A. M. Raichur[a]; V. Panvekar[a]
[a] Department of Metallurgy, Indian Institute of Science, Bangalore, India

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REMOVAL OF As(V) BY ADSORPTION ONTO MIXED RARE EARTH OXIDES

A. M. Raichur* **and V. Panvekar**

Department of Metallurgy, Indian Institute of Science,
Bangalore 560012, India

ABSTRACT

Arsenic pollution of water is a major problem faced worldwide. Arsenic is a suspected carcinogen in human beings and is harmful to other living beings. In the present study, a novel adsorbent was used to remove arsenate [As(V)] from synthetic solutions. The adsorbent, which is a mixture of rare earth oxides, was found to adsorb As(V) rapidly and effectively. The effect of various parameters such as contact time, initial concentration, pH, and adsorbent dose on adsorption efficiency was investigated. More than 90% of the adsorption occurred within the first 10 min and the kinetic rate constant was found to be about $3.5\,\mathrm{mg\,min^{-1}}$. Adsorption efficiency was found to be dependent on the initial As(V) concentration, and the adsorption behavior followed the Langmuir adsorption model. The optimum pH was found to be 6.5. The presence of other ions such as nitrate, phosphate, sulphate, and silicate decreased the adsorption of As(V) by about 20–30%. The adsorbed As(V) could be desorbed easily by washing the adsorbent with pH 12 solution. This study demonstrates the applicability of naturally occurring rare earth oxides as selective adsorbents for As(V) from solutions.

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*Corresponding author. Fax: +91-80-3600472; E-mail: amr@metalrg.iisc.ernet.in

Key Words: Arsenic; Adsorption; Rare earth oxide; Anion; Desorption

INTRODUCTION

Arsenic pollution of water occurs due to various reasons such as natural leaching of rocks containing arsenic, mining, processing of mineral deposits (1), and discharge of industrial pollutants (2). Although arsenic is needed as a micronutrient for the human body, it is carcinogenic when consumed in larger quantities over a period. Therefore, arsenic needs to be removed before water can be used for drinking. In India, in several parts of the country, especially in the eastern region, arsenic contamination is a major problem that has led to severe health problems. The maximum contaminant level is 0.05 ppm for arsenic in drinking water (3). Most of the contaminated ground water has arsenic concentrations much higher than the permissible limit and has to be treated.

Major treatment methods to remove arsenic from water include complexation with ferric iron and coprecipitation with hydrous metal oxides (4,5), lime softening (6), adsorption using ion exchange resins and activated alumina (7), and flotation (8–10). Precipitation and coagulation of arsenic with ferric sulphate and lime produces a lot of sludge that needs to be filtered. Adsorption with activated alumina has been used widely in the industry. Hydrous metal oxides of rare earth elements have been shown to have a high adsorption capacity for anions (11).

In recent years, several other adsorbents have been used to remove arsenic from solution. Some of them include carbon (12), lanthanum oxide (13), manganese green sand (14), iron-coated spent catalyst (15), and lanthanum impregnated silica gel (16). Of these adsorbents, lanthanum-based compounds and pure lanthanum oxide have shown tremendous potential for adsorption of arsenic. However, pure lanthanum oxide is expensive and could be the major disadvantage for it to be used commercially.

In the present study, naturally occurring rare earth oxides from Southern India have been studied as possible adsorbents for arsenate [As(V)]. The rare earth oxides occur as mixtures of various oxides and have been hence referred to as mixed rare earth oxides in this paper. The main objective was to study the feasibility of using these mixed rare earth oxides for adsorbing As(V) from synthetic solutions. In this study, the kinetics of adsorption along with the effect of pH, concentration, and dose on adsorption of As(V) was carried out. The adsorption isotherm was studied to determine the adsorption capacity. The effect of other anions on As(V) adsorption was also evaluated.

MATERIALS AND METHODS

The mixed rare earth oxide adsorbent was obtained from Indian Rare Earths Limited, Ernakulam, India. The as-received material was in the form of fine powder and the chemical composition is given in Table 1. The material was used in the as-received condition.

The adsorbent was characterized for its particle size distribution using a Malvern ZetaSizer (Malvern Instruments, Malvern, UK). The surface area was determined using a Quantasorb surface area measurement apparatus (Quantachrome Corp., Syosset, NY).

Standard solutions of arsenic were prepared by dissolving appropriate amount of sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$; Loba Chemie, Mumbai, India) in double distilled water. A stock solution of 1000 mg L^{-1} As(V) was first prepared and all solutions for adsorption and analyses were prepared by appropriate dilution of the freshly prepared stock solution. Natural pH of the distilled water was about 6.7–6.8 and all experiments were conducted at 29 ± 1°C, which is the room temperature. The pH adjustments were done using dilute HCl or NaOH. The chemicals used in this study were of analytical grade quality and double-distilled water was used throughout the study.

Batch adsorption tests were conducted to study the effect of various parameters on the adsorption efficiency of As(V) onto rare earth oxides. To 100 mL of the solution, required amount of adsorbent was added and mixed in an orbital shaker at 150 rpm for different intervals of time. After the required time intervals, the suspension was filtered through a Whatman No. 42 filter paper (Laboratory Supplied Company, Bangalore, India) and the filtrate was acidified. The filtrate was analyzed for residual arsenic concentration using an ICP Spectrometer (Jobin-Yvon, Longjumean Cedex France). The instrument was calibrated each time the analysis was done.

Each adsorption test was conducted twice to obtain reproducible results with an error of less than 5%. In case of deviations larger than that, more tests

Table 1. Chemical Composition of the Mixed Rare Earth Oxide

Composition	Percent
La_2O_3	44.0
CeO_2	2.0
Pr_6O_{11}	10.5
Nd_2O_3	36.5
Sm_2O_3	5.0
Y_2O_3 and other rare earth oxides	Balance

were conducted as required. The analytical results could be reproduced with an accuracy of greater than 95%.

RESULTS AND DISCUSSION

Characterization of Adsorbent

The adsorbent was characterized in terms of surface area and particle size. It was found that the adsorbent had a mean particle size (d_{50}) of 4.34 μm while the surface area was found to be about 6.75 $m^2 g^{-1}$.

Effect of Contact Time and Initial Concentration

The variation of As(V) adsorption onto mixed rare earth oxide as a function of time is shown in Fig. 1. It was observed that with a fixed amount of adsorbent,

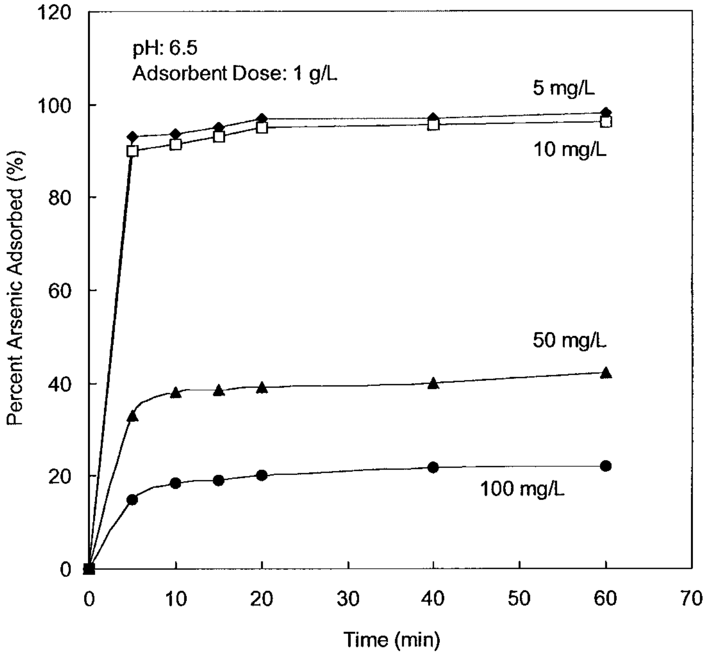

Figure 1. Adsorption kinetics of As(V) onto mixed rare earth oxide at different initial concentrations.

the amount of As(V) adsorbed increased with time. The loading capacity (i.e., the amount of As(V) adsorbed per gram of adsorbent) increased with time and concentration, and then attained a constant value after about 10 min. The kinetic rate constant was calculated to be about 3.5 mg min^{-1} per gram of the adsorbent. The time to reach equilibrium appeared to be independent of the initial arsenic concentration although a slight change was observed in the case of 100 mg L^{-1}. The adsorption of fluoride decreased from nearly 98 to about 20% by increasing the As(V) concentration from 5 to 100 mg L^{-1}, which can be attributed to saturation of the surface sites.

Kinetics of Adsorption

The rate constants of As(V) adsorption onto mixed rare earth oxides has been interpreted in terms of the adherence of As(V) to the active sites of the adsorbent as well as its intraparticle diffusion within the pores of the adsorbent.

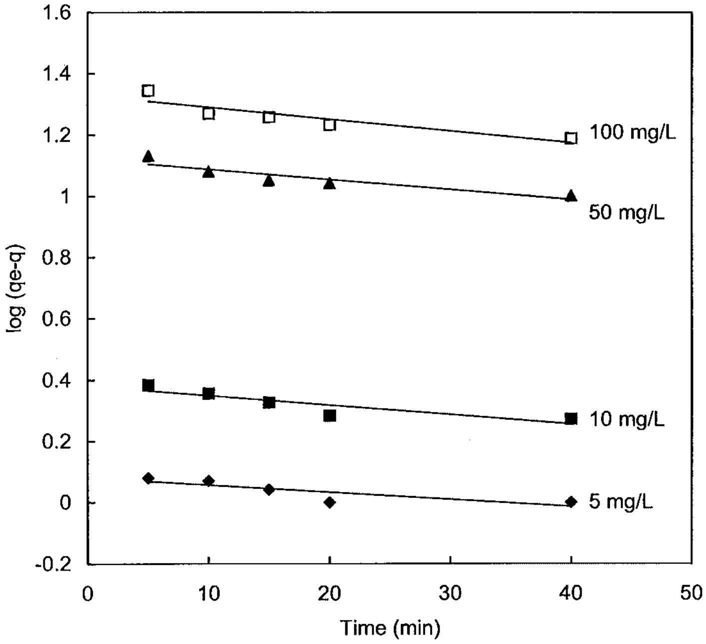

Figure 2. Lagergren plot for arsenic adsorption at different initial concentrations.

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The specific rate constant, K_r, was determined using the Lagergren equation (17)

$$\log(q_e - q) = \log q_e - \frac{K_r t}{2.303} \tag{1}$$

where $q_e$and q (mg g^{-1}) refer to the amount of As(V) adsorbed at equilibrium and at any time t, respectively. The plot of $\log(q_e - q)$ vs. time presented in Fig. 2 shows the straight-line curve indicating the applicability of the Lagergren equation and first-order kinetics. The values of the adsorption constant K_r were calculated from the slope of the plot and found to be 5.30, 7.14, 7.6, and $8.75 \times 10^{-3}\,\mathrm{min}^{-1}$ for the initial arsenic concentrations of 5, 10, 50, and $100\,\mathrm{mg\,L}^{-1}$, respectively. It is interesting to see that with change in arsenic concentration, the value of K_r also changes. The above equation is used assuming that only adsorption is taking place. However, it is possible that both adsorption and desorption of arsenic from the surface could be taking place simultaneously and this is not accounted for in the equation. Hence, the rate constant probably changes with initial arsenic concentration. If both the processes are taken into account, then the rate constant will not change with initial concentration.

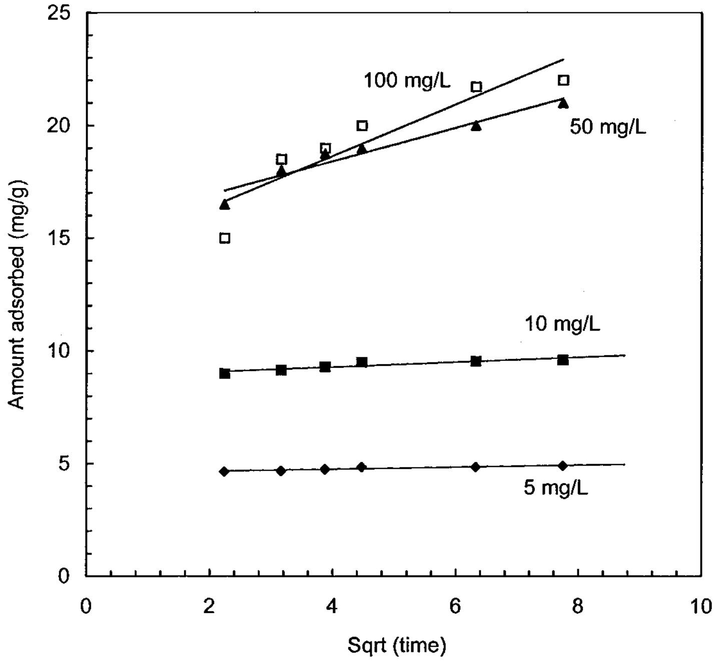

Figure 3. Intraparticle diffusion at different initial concentrations of arsenic.

Apart from the adsorption taking place on the outer surface of the adsorbent, the arsenic ions can also diffuse into the interior of the porous adsorbent. This was studied by plotting the square root of the time for different initial concentrations of As(V) and is shown in Fig. 3. A linear relationship was observed indicating the control of adsorption by intraparticle diffusion (18). The intraparticle diffusion rate constants were calculated from the slopes of the curves and were found to be 0.046, 0.108, 0.739, and 1.142 $\mathrm{mg\,g^{-1}\,min^{-0.5}}$ for initial As(V) concentrations of 5, 10, 50, and 100 $\mathrm{mg\,L^{-1}}$, respectively.

Loading Characteristics

The effect of varying concentrations of mixed rare earth oxide on adsorption of As(V) at pH 6.5 and As(V) concentration of 50 $\mathrm{mg\,L^{-1}}$ is shown in Fig. 4. The adsorbent concentration was varied from 0.2 to 2.9 $\mathrm{g\,L^{-1}}$ of the solution, and the contact time was fixed at 60 min. The amount of arsenic adsorption increased with the increase in the adsorbent dose until it reached an

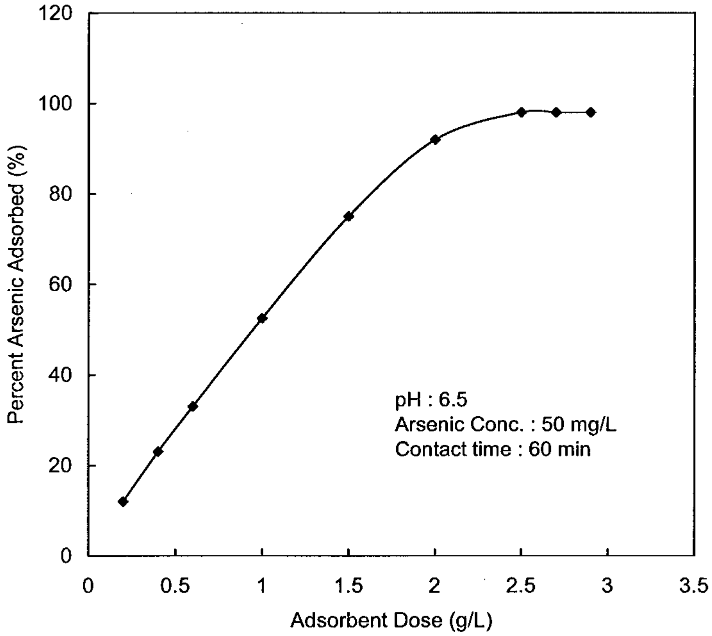

Figure 4. Effect of adsorbent dose on the amount of arsenic adsorbed.

equilibrium value at about 2.5 g L^{-1}. This corresponds to an adsorption capacity of nearly 20 mg of As(V) per gram of adsorbent.

Adsorption Isotherms

The adsorption isotherm for As(V) onto the rare earth oxide at a constant temperature of 29°C (room temperature) and pH 6.5 was calculated. The As(V) concentration used was 50 mg L^{-1} and contact time of 60 min was maintained. The data correlated well in the linear form of the Langmuir adsorption isotherm model given by the equation below:

$$\frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{C_e}{a} \tag{2}$$

where C_e is the equilibrium concentration (mg L^{-1}), x/m the amount adsorbed at equilibrium (mg g^{-1}), and a and b are the Langmuir constants. The linear plot shown in Fig. 5 indicates the applicability of the equation. It demonstrates that a

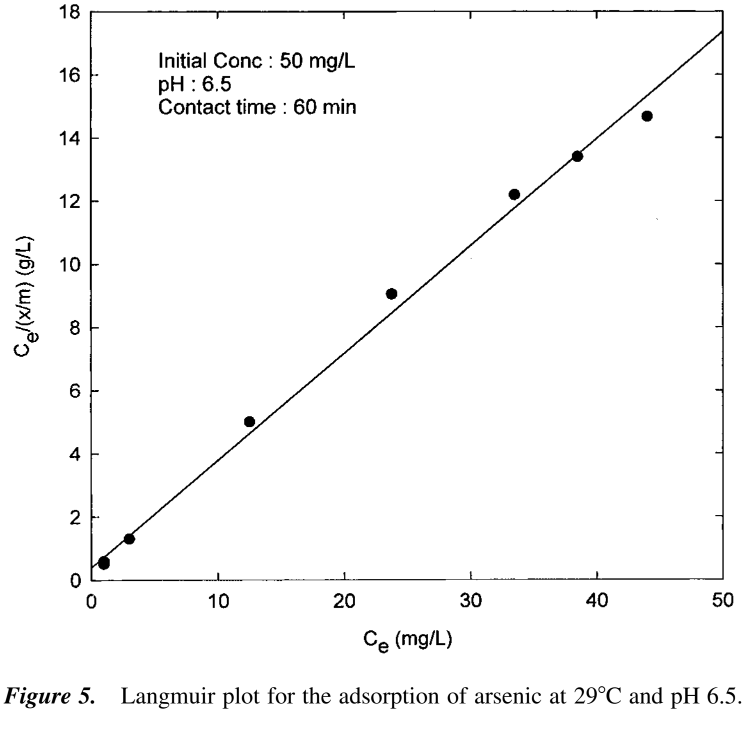

Figure 5. Langmuir plot for the adsorption of arsenic at 29°C and pH 6.5.

monolayer of arsenic is formed on the surface of the rare earth oxide adsorbent. The values of Langmuir constants *a* and *b* were found to be 2.945 mg g^{-1} and 0.8673 L mg^{-1}, respectively.

Effect of PH

The extent of adsorption of anions is governed strongly by the pH of the solution. The pH of the aqueous solution is an important variable, which controls the adsorption at the adsorbent and water interface. Hence, the adsorption of As(V) on mixed rare earth oxides was studied at different pH values ranging from 2 to 12 and the results are presented in Fig. 6. A maximum in the adsorption efficiency was observed in the pH range 6–6.5. Above pH 6.5, the adsorption of As(V) decreases gradually with increase in pH, which could be due to the presence of hydroxide ions on the surface of the adsorbent. Adsorption was found to decrease in the acidic pH range also.

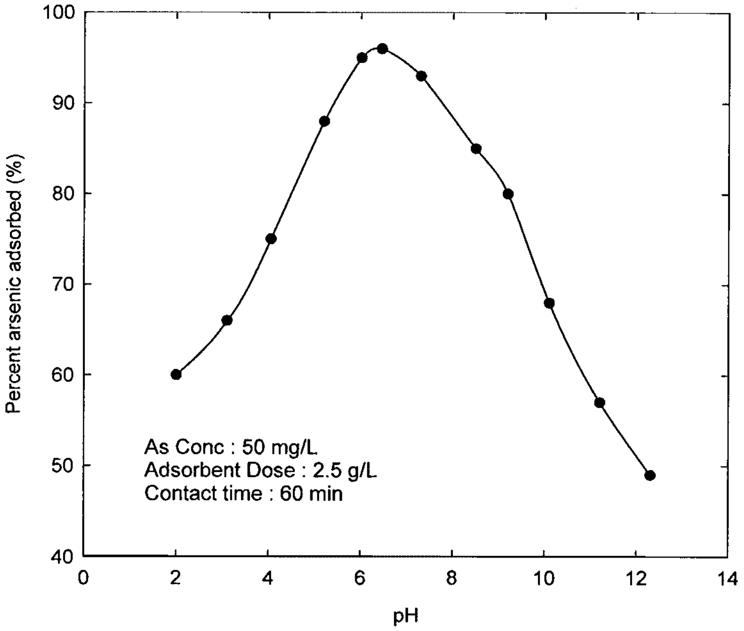

Figure 6. Effect of pH on arsenic adsorption.

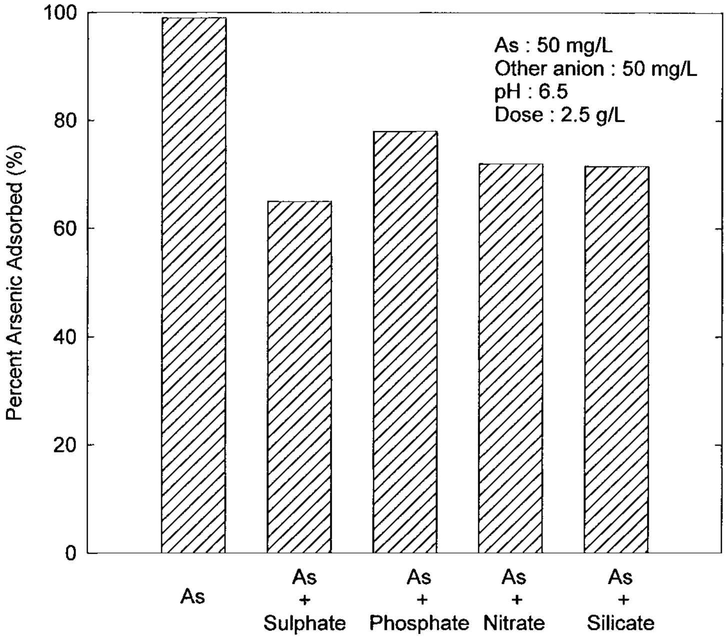

Figure 7. Effect of anion concentration on adsorption of arsenic by mixed rare earth oxide.

Effect of Other Ions

Generally, industrial wastewater contains various ions together. These ions can also adsorb onto the rare earth oxide, which will thereby affect the efficiency of arsenic adsorption. To determine the effect of such ions, $50\,mg\,L^{-1}$ each of nitrate, sulphate, phosphate, and silicate were mixed with $50\,mg\,L^{-1}$ of As(V) and adsorption tests were carried out at pH 6.5 for 60 min. The results are shown in Fig. 7. It is clear that the presence of other ions definitely decreases the amount of As(V) adsorbed onto the mixed rare earth oxide. The extent of decrease in the arsenic adsorption is dependent on the type of ion present. In the presence of phosphate, adsorption of As(V) decreased from 98 to 79% while in the case of nitrate and silicate it decreased to 70%. Sulphate seemed to affect the adsorption of arsenic onto rare earth oxide most (adsorption of As(V) decreased to 64%) indicating that it competes strongly with arsenic. Even in the presence of other ions, there is still some selectivity with respect to As(V) adsorption onto the mixed rare earth oxides.

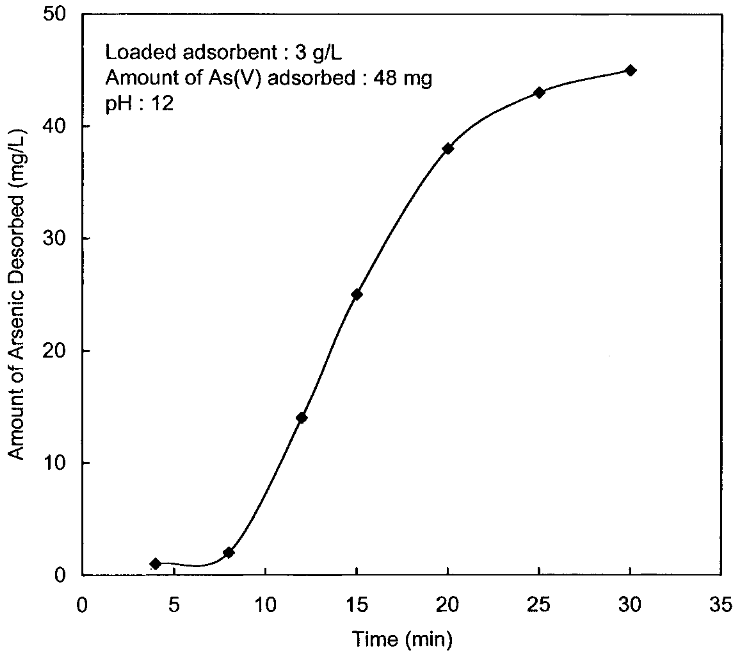

Figure 8. Kinetics of desorption of arsenic from the surface of mixed rare earth oxide.

Desorption Studies

The ultimate objective of the present work is to develop an adsorbent that can be reused thereby making it cost effective. For reusability, the adsorbed arsenic should be desorbed easily. First, As(V) ($50\,\mathrm{mg\,L^{-1}}$) was adsorbed onto the adsorbent ($3\,\mathrm{g\,L^{-1}}$) at pH 6.5. Then the solution was filtered and the adsorbent was transferred to 100 mL of water and the pH was adjusted. Desorption studies were conducted in shake flasks by conditioning the suspension at that pH for the required time. Figure 8 shows the results of the kinetics of desorption at pH 12. Initially, desorption is slow but after about 10 min, the desorption rate increases and most of the arsenic is removed in about 30 min. The effect of pH on desorption was also studied and is shown in Fig. 9. In the acidic pH range, hardly any arsenic is desorbed. Whatever arsenic is released into the solution can be attributed to leakage. However, as the pH increases above pH 7, the adsorbed arsenic starts to leach back into the solution. At around pH 12, about 45 mg of the adsorbed arsenic could be desorbed in about 30 min, which corresponds to a regeneration efficiency of 93%. Of course, the adsorption efficiency in the next cycle will be decreased. These studies suggest that the rare earth oxides can be

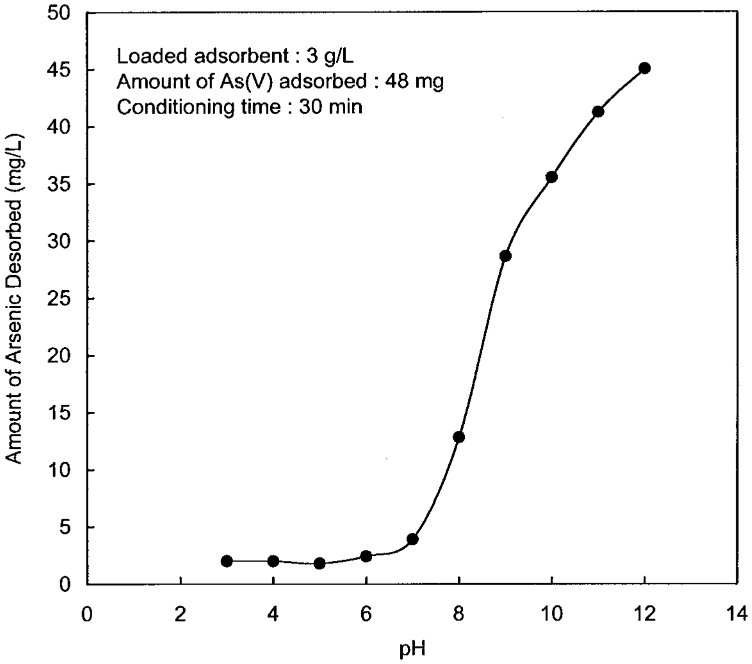

Figure 9. Desorption of arsenic from the surface of mixed rare earth oxide as a function of pH.

used in a continuous column to adsorb arsenic. Once the column is saturated, the adsorbent can be regenerated and reused. The exact life cycle of the adsorbent will have to be determined by continuous column adsorption studies. Arsenic that is stripped from the adsorbent can then be precipitated easily since it is concentrated. Thus, the volume of the water that has to be treated can be reduced greatly by using this adsorption–desorption technique. This will probably lead to an economical process for the treatment of arsenic.

CONCLUSIONS

In the present study, a new adsorbent was studied for the removal of As(V) from the solution. The method is simple and has shown great potential for the selective removal of As(V). The main conclusions that can be drawn from the above study are given below.

1. The kinetics of adsorption of arsenic onto rare earth oxide was found to be very rapid. Most of the adsorption took place in the first 10 min. The kinetic rate constant was found to be about 3.5 mg min^{-1} per gram of the adsorbent. Adsorption was found to be dependent on both initial concentration and the time of contact.
2. The adsorption followed the linear form of Langmuir adsorption isotherm model. The adsorbent was found to load as high as 20 mg of As(V) per gram of adsorbent.
3. The optimum pH was found to be about 6.5 for As(V), adsorption, which makes it very suitable for use in drinking water treatment.
4. Other ions such as phosphate, nitrate, sulphate, and silicate did affect the adsorption of As(V). Phosphate had the least effect while sulphate had the maximum effect on arsenic adsorption.
5. Desorption studies showed that the As(V) can be desorbed easily at pH 12, thus indicating that the adsorbent can be reused, thereby making it attractive economically.

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