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Sorption of Lanthanum and Erbium from Aqueous Solution by Activated Carbon Prepared from Rice Husk

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ABSTRACT

A biomass agricultural waste material, rice husk (RH) was used for preparation of activated carbon by chemical activation using phosphoric acid. The effect of various factors, e.g. time, pH, initial concentration and temperature of carbon on the adsorption capacity of lanthanum and erbium were quantitatively determined. It was found that the monolayer capacity is 175.4 mg/g for La(III) and 250 mg/g for Er(III). The calculated activation energy of La(III) adsorption on the activated carbon derived from rice husk was equal to 5.84 kJ/ mol while 14.6 kJ/ mol for Er(III), which confirm that the reaction is mainly particle–diffusion controlled. The kinetics of sorption was described by a model of a pseudo-second-order. External diffusion and intra-particle diffusion were examined. The experimental data show that the external diffusion and intra-particle diffusion are significant in the determination of the sorption rate. Therefore, the developed sorbent is considered as a better replacement technology for removal of La (III) and Er(III) ions from aqueous solution due to its low cost and good efficiency, fast kinetics, as well as easy to handle and thus no or small amount of secondary sludge is obtained in this application.

Keywords: Lanthanum/ Erbium/ Rice husk/ activated carbon, recovery/ treatment.

INTRODUCTION

Lanthanum is found in rare-earth minerals such as cerite, monazite, allanite, and bastnasite. Monazite and bastnasite minerals are principal ores in which lanthanum occurs in percentages up to 25 percent and 38 percent respectively. Mischmetals are used in making lighter flints, contains about 25 percent lanthanum. Because lanthanum compounds bring about special optical qualities in glass, it also used for the manufacture of specialized lenses. In addition, compounds of lanthanum with fluorine or oxygen are used in making carbon-arc lamps for the motion picture industry. Lanthanum salts are included in the zeolite catalysts used in petroleum refining due to its stabilizing action on the zeolite at high temperatures. Erbium's everyday uses are varied. It is used in nuclear technology as a nuclear poison, as in neutron–absorbing control rods. It is commonly used as a photographic filter, and because of its resilience it is useful as a metallurgical additive. Other uses, used in nuclear technology as a nuclear poison, as neutron absorbing control rods. When added to vanadium as an alloy, erbium lowers hardness and improves workability. Erbium is commonly used in YAG lasers for cosmetic laser procedures and mild to medium depth skin resurfacing.

The environmental pollution is the most serious problem that should be taken into consideration due to increasing population and growth of technology. However, a number of investigations have been performed to prevent environmental pollution. The adsorption process has

been used in the water and waste water industry for removal of color, odor and organic pollution. In order to concentrate aqueous nuclear waste solutions containing metal ions into smaller volume, many processes are being used, such as precipitation, ion-exchange, solvent extraction and adsorption. Adsorption onto various solids is important from purification, environmental and radioactive waste disposal point of view[1-3]. The pre-concentration and separation procedures on adsorption phenomena are important in nuclear and radiation chemistry, industry, medicine and daily life[3]. Lanthanides elements are the important fission product isotopes produced from irradiated nuclear fuel. Its removal is of major important in treatment and disposal of radioactive wastes and its adsorption on solids is important for there pre-concentration and recovery because they have numerous applications in electrical and nuclear industry.

Interest in the adsorption of metal ions for recovery purposes has increased manifold in recent years, because of its simplicity, selectivity and efficiency[1]. The adsorption process is suitable to adsorb and separate low molecular weight compounds and free metals. Useful adsorbents include carbon-based adsorbents such as activated carbon, zeolite-based adsorbents, silica-based adsorbents, alumina-based adsorbents, and adsorptive resins such as styrene-vinyl benzene copolymers and acrylic polymers, of which; activated carbon is preferable.

Activated carbons are the most popular adsorbents used for the removal of toxic substances from water. This could be related to their extended surface area, high adsorption capacity, micro porous structure and special surface reactivity[4]. However, the adsorptive capacity of activated carbons depends mainly on the precursor nature, the operating conditions of adsorption (such as temperature and pH) and the nature of the adsorbate. About 50% of industrially available activated carbons are derived from precursors of botanical origin [5]. These precursors are usually low-cost agricultural residues with no notable applications except as fuels for energy generation. Numerous agro-waste biomaterials have been used for the production of activated carbons, including rice husk, apricot stones, nutshells and date pites [6-9]. Rice husk used in this study is one of them, due to high surface area, high adsorption capacity, micro porous structure and special surface reactivity [6]. This work presents results on the adsorption of lanthanum and erbium by chemically (phosphoric acid) activated rice husk. Effect of various factors, e.g. time, pH, initial concentration and temperature on the adsorption capacity of lanthanum and erbium on rice husk carbon were quantitatively determined. Adsorption isotherms and adsorption kinetics of sorption for La(III) and Er(III) were evaluated and discussed.

MATERIALS AND METHODS

Preparation of lanthanide solution

The stock solution of lanthanide nitrate (1000 mg.l^{-1}) was prepared by dissolving a certain amount of metal oxide in nitric acid. The resultant nitrate solution was carefully evaporated to dryness, washed by distilled water, and then dissolved in 0.1 M sodium nitrate solution (at $\text{pH} = 3.5 \pm 0.1$). Initial pH of lanthanide solution was adjusted by the addition of HNO_3 or NaOH. The concentration of lanthanide metal ion was determined spectrophotometrically by Arsenazo (III) method. The samples were analyzed at wave length 650 using a Shimadzu model 160A double-beam UV spectrophotometer.

Preparation of rice husk used as activated carbon

Rice husk was chosen as a precursor for the production of activated carbons by one-step chemical activation using H₃PO₄. In each experiment a known weight of rice husk was soaked in pre-diluted phosphoric acid of various concentrations. Starting with an 85 wt.% H₃PO₄ (BDH), the concentration of 70 wt.% was obtained by dilution. The parent rice husks mass (as such) was soaked in enough H₃PO₄ solution to cover it completely, slightly agitated to ensure penetration of the acid throughout, then the mixture heated to 80 °C for 1 h and left overnight at room temperature to help appropriate wetting and impregnation of the precursor. The impregnated mass was dried in an air oven at 80°C overnight, then, admitted into the reactor (ignition tube), which was then placed in a tubular electric furnace open from both ends. The temperature was raised at the rate of (50 °C/5 min) to the required end temperature. The carbonization process was carried out at temperature of 700 °C for 2.5 h. The product was thoroughly washed with hot distilled water, and finally dried at 110 °C. The particle size of activated carbons was kept constant at <0.125 mm.

Characterization of activated carbon

Particle size was determined using sieves of different particle size. Packed and apparent densities were determined by a tamping procedure using a 25 ml graduated glass cylinder. The texture characteristics were determined by the standard N₂ adsorption isotherms, followed by their analysis to evaluate the porous parameters. Nitrogen adsorption isotherms were conducted at liquid nitrogen temperature using a NOVA 1000 instrument (Chromatic). From the BET plots the "monolayer equivalent surface area" (S_{BET}), the total pore volumes estimated from the volume of nitrogen adsorbed at p/p° = 0.95 (V_f) and an average pore radius from $r = 2V_p/S_{BET}$ were found to equal 451.82 m²/g , 0.3437 cc/g and 15.2 Å respectively.

Batch kinetic studies

To investigate the factors affecting on the pre-concentration and recovery of lanthanides from nitrate solution (effect of contact time, pH, concentration of adsorbate and temperature), adsorption experiments were carried out by agitating 0.03 g of adsorbent with 10 ml of metal ion solution having concentration 50 mg l⁻¹ in a series of bottles of 50 ml capacity at a temperature of 25 ± 1 °C at 200 rpm using a thermostatic shaker (Kottermann D-1362, Germany). The samples were withdrawn from the shaker at predetermined time intervals (5–180 min), and adsorbents were separated from the solution by centrifugation at 5000 rpm for 5 min and the residual lanthanide was determined. The amount of adsorption at time t, q_t (mg/g), was calculated by:

$$q_t = (C_0 - C_t) V/M \dots\dots\dots (1)$$

And the amount of adsorption at equilibrium, q_e (mg.g⁻¹), was calculated by:

$$q_e = (C_0 - C_e) V/M \dots\dots\dots (2)$$

Also, the static distribution ratio K_d was calculated as follows:

$$K_d = (C_0 - C_e/C_e) V/M \dots\dots\dots (3).$$

where C₀ and C_t (mg.L⁻¹) are the liquid-phase concentrations of lanthanide metal ions at initial time, t = 0.0 and at any time t, respectively. C_e (mg.L⁻¹) is the concentrations at equilibrium, V is the volume of the solution (L) and M is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

Effect precursors type on the removal of lanthanides

The type of precursor of chemically (H_3PO_4) prepared activated carbon has a significant effect on there capacity of removal of lanthanides as shown in table (1). The results obtained indicated that there is a high variation in the efficiency of some type of prepared activated carbon (peanut shell , corn cobs and rice husk) toward lanthanides. From the data obtained, it is found that rice husk treated by 7M H_3PO_4 is the best one for removal the both of light rare earth (La) and heavy rare earth (Er). Subsequently, this type of activated carbon can be used in the separation of lanthanides. Consequently, rice husk with La(III) and Er(III) were chosen as an adsorption system for further investigation.

Table 1

Factors Affecting on the Removal of La and Er from solution by rice husk

activated carbon.

Effect of pH of the solution

The removal of metal ions from aqueous solution by adsorption is dependent on the pH of the solution which affects the surface charge of adsorbents , the degree of ionization and species of adsorbate. The maximum sorption uptake (q_e) increased from 9.11 mg.g^{-1} at pH 1.0 to 10.14 mg.g^{-1} at pH 4.0 for La and from 8.14 to 12.89 for Er (Fig. 1). Beyond pH 5.0 and due to the formation of suspended gelatinous lanthanides hydroxides adsorption of La and Er ions was reduced[10]. Similar results were reported by Brown et al. [11] for adsorption of lanthanum and cerium on root of plant. Metal distribution data from aqueous solutions are plotted as $\log K_d$ versus pH in Fig.2. The distribution functions are straight lines (with correlation coefficient, $r = 0.918$) with a slope of 0.037, indicating that no protons are released in the adsorption reaction of La(III) or Er(III) ions by the rice husk activated carbon [11]. This means that the mechanism of adsorption may be electrostatic attraction or complex formation.

Fig.1&2

Effect of contact time and initial concentration

Adsorption experiments were carried out for different contact times with a fixed adsorbent dose of 0.03g/10 ml at pH 3.5. The experimental results demonstrate the effect of initial La(III) and Er(III) concentrations ($50\text{--}300 \text{ mg.l}^{-1}$) with time is shown in Fig. 3 . The results show that the equilibrium of La(III) and Er(III) reached within the first thirty minutes of adsorption for two metal ions. In the beginning, the ions adsorbed occupied selectively the active sites on the adsorbent. As the contact time increased the active sites on the adsorbent were filled and the rate of adsorption became slower gradually and reached a plateau. For practical consideration 1h time was presumed to represent the equilibrium time for the adsorption of metal ions.

When the initial La(III) and Er(III) concentration increases from 50 to 300 mg.l^{-1} , the adsorption density increases from 9.6 mg.g^{-1} to 57 mg.g^{-1} for La(III) and from 12.2 to 72.3 mg.g^{-1} for Er(III). The result showed that the removal of La(III) and Er(III) is concentration dependent. At higher

initial concentrations the available adsorption sites of adsorption became fewer and hence the percentage removal of metal ions depends upon the initial concentration. For fixed adsorbent dose the total available adsorption sites are limited thereby adsorbing almost the same amount of the adsorbate, this results in a decrease in percentage removal of the adsorbate corresponding to an increase in initial sorbate concentration, Fig.4. It can also be concluded that higher removal at low concentration is important in terms of industrial application.

Fig.3&4

Adsorption kinetics

The effect of concentration on reaction rates is well known and important in understanding reaction mechanism. In order to quantify the changes in adsorption with time and also to evaluate kinetic parameters for different concentrations, two kinetic models were used, namely: a first-order kinetic equation developed by Lagergren (1898) and a pseudo-second-order kinetic equation described by the following equations [12]:

$$\text{Log } (q_e - q_t) = \text{log } q_e - k_1 t / 2.303 \quad (\text{First order equation}) \dots\dots\dots(4)$$

$$1/q_t = 1/q_e + 1/k_2 q_e^2 t \quad (\text{Pseudo-second-order equation}) \dots\dots\dots(5)$$

Where k_1 is the first-order rate constant of adsorption and k_2 is the pseudo-second-order rate constant of adsorption and q_e and q_t are the amounts of metal ion sorbed at equilibrium and at time t respectively. Kinetic parameters of these models are calculated from the slope and intercept of the linear plots of $\text{log } (q_e - q_t)$ versus t and $1/q_t$ versus $1/t$ (Fig.5&6).

Stander deviation, correlation coefficients (r) and error for La(III) is 0.0037, 0.995 and 0.002 respectively when described by the pseudo-second-order kinetic model while the values obtained with first order is 0.0489, 0.993 and 0.03 respectively and by the same degree for Er(III).

Based on stander deviation, correlation coefficients (r) and error values it is found that the adsorption of La(III) and Er(III) onto RH activated carbon can be best described by the pseudo-second-order kinetic model. The external mass-transfer constant (k_s) was calculated from the initial slope of the curve for C_t/C_0 versus time [13].

Fig.5&6

To characterize the intra-particle diffusion of the system, the relationship between specific sorption (q_t) and the square root of time ($t^{1/2}$) was evaluated based on the following expression[13]:

$$q_t = k_d t^{1/2} + C \quad \dots\dots\dots(6)$$

Where q_t is the quantity of metal ions adsorbed at time t (mg g^{-1}), k_d the initial rate of intra-particle diffusion ($\text{mg L}^{-1} \text{min}^{-1/2}$), and C is the y-intercept (Fig.7).

When the metal ion solution is mixed with the adsorbent, transport of the metal ions from the solution through the interface between the solution and the adsorbent occurs into pores in the particles. There are four main stages in the process of adsorption by porous adsorbents [13]. Fig. 7 illustrates the diffusion of the La(III) and Er(III) ions within RH activated carbon as a function of time and shows that intraparticle diffusion occurred in three stages for La(III) and Er(III) ions. The intraparticle diffusion constants for all three stages (k_{d1} and k_{d2}) are given in Table 2

Fig.7 & Table 2

Table 2 shows that the La(III) and Er(III) metal ions diffused quickly among the particles at the beginning of the adsorption process, then intraparticle diffusion (slowed down and stabilized). The deviation of these lines from the origin (i.e., a y-intercept other than 0) indicates that intraparticle transport is not the only rate-limiting step. It can be assumed that external mass transfer controls the rate of adsorption because of the very slow transfer speeds.

Adsorption isotherms:

The adsorption isotherm studies are of fundamental importance in determining the adsorption capacity of La(III) and Er(III) onto RH activated carbon and it diagnose the nature of adsorption.

The Langmuir and Freundlich isotherm models [11] were used to interpret equilibrium isotherm data. The Langmuir isotherm is based upon an assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is governed by the following relation:

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \dots\dots\dots (7).$$

Where q_e and C_e are the equilibrium concentration of Gd(III) on adsorbent and in solution respectively. Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively, Fig.8.

Fig.8

The Freundlich isotherm model assumes heterogeneous surface energies in which energy term in Langmuir equation varies as a function of surface coverage. The Freundlich isotherm equation is used in the general form.

$$\text{Log } q_e = \text{log } K_F + 1/n \text{ log } C_e \dots\dots\dots(8).$$

Where K_F and $1/n$ are Freundlich isotherm constants related to adsorption capacity and intensity of adsorption respectively.

The isotherm constants of all the previous equations are very useful parameters for predicting adsorption capacities and also for incorporating into mass transfer relationships to predict the design of batch reactors. The values of all the isotherm constants were calculated from the slope and intercept of the plots using regression analysis and are shown in (Fig.8&Table 3a,b).

(Table 3a , b)

The higher values for Er over the La using the two model , may be due to ionic radius of *lanthanum* is around 1.18 Å while that of *erbium* ions is around 0.88 Å.

Effect of temperature:

Temperature has a direct influence on the amount of the adsorbed substance. In the present investigation, the adsorption experiments were performed in the temperature range of 30 to 60 °C. It was found that, according to the adsorption isotherm, the amount of La and Er adsorbed on RH activated carbon increase with the solution temperature.



Since diffusion is an endothermic process, it would be expected that an increased solution temperature would result in increased adsorption capacity. The results of the present investigation on temperature effect also support the conclusion that La(III) and Er(III) sorption is controlled by pore diffusion.

The first order kinetic plots of the data are presented in Fig (9). The values of the apparent rate constants were calculated from the slopes of the straight lines obtained. The plot of the calculated values of rate constants vs. $1/T$ was found to obey the Arrhenius equation

$K_a = A e^{-E/RT}$ (where T is the absolute temperature and R is the gas constant) Fig.(7).

The calculated activation energy (E) of La(III) and Er(III) adsorption on the RH activated carbon show that, E equals to 5.84 kJ/mol for La(III) and 14.6 kJ/mol for Er(III), which confirm that the reaction is mainly particle-diffusion controlled. As recommended previously [14,15], the energy of activation below 50 kJ/mol generally indicated a film and particle diffusion-controlled process, and higher values represent chemical reaction process.

The enthalpy of activation (ΔH) was calculated from equation:

$$\Delta H = E - RT \dots\dots\dots(9).$$

and was found to be equal 3.37 kJmol⁻¹ for La and 12.12 for Er while the entropy of activation (ΔS) was calculated from:

$$K = RT/Nh e^{\Delta S/RT} e^{-\Delta H/RT} \dots\dots\dots(10).$$

where K is specific reaction rate at 25^oC, N is the Avogadro's number and h is Plank's constant and was found 0.06 kJmol⁻¹ for La and 0.05 for Er(III). The standard Gibbs free energy ΔG^0 values (kJ mol⁻¹) were calculated from the equation [16]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \dots\dots\dots(11).$$

The negative value for the Gibbs free energy for La(III) and Er(III) is -14.27 and -2.78 kJ mol⁻¹ respectively shows that the adsorption process is spontaneous

From the data obtained shows that the adsorption process mainly controlled by the enthalpy of activation (ΔH), due to the quite difference between La and Er, 3.37 kJmol⁻¹ for La and 12.12 for Er while narrow difference in values of entropy was obtained.

Fig.9

CONCLUSION

The results obtained showed that RH activated carbon prepared from rice husk (a waste and an inexpensive precursor), can be readily used for the removal of La(III) and Er(III) from aqueous solutions. The removal of La and Er by RH activated carbon is favored at a pH 3.5. Removal of > 95 % has been achieved under optimum conditions. The percentage removal was found to depend on the time, temperature and initial concentration of adsorbate all clearly affected the removal efficiency. We also found that the Langmuir and Freundlich isotherms could both be used to model isothermal sorption of La(III) and Er(III) on RH activated carbon. The kinetics of sorption can be described by a

model of a pseudo-second-order reaction .Two models of transfer were examined: external diffusion and intra-particle diffusion. The experimental data show that intra-particle diffusion is significant in the determination of the sorption rate. The adsorption process was also thermodynamically spontaneous under natural conditions with a negative value of ΔG^0 . High adsorption capacity of RH activated carbon (175 and 250 mg/g) for La(III) and Er(III) respectively was obtained.

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