Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Factors Affecting on the Sorption/Desorption of Eu (III) using Activated Carbon

H. M. H. Gad[a]; N. S. Awwad[a]
[a] Egyptian Atomic Energy Authority, Hot Laboratories and Waste Management Centre, Cairo, Egypt

To cite this Article Gad, H. M. H. and Awwad, N. S.(2007) 'Factors Affecting on the Sorption/Desorption of Eu (III) using Activated Carbon', Separation Science and Technology, 42: 16, 3657 — 3680
To link to this Article: DOI: 10.1080/01496390701626495
URL: http://dx.doi.org/10.1080/01496390701626495

Separation Science and Technology, 42: 3657–3680, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701626495

Factors Affecting on the Sorption/Desorption of Eu (III) using Activated Carbon

H. M. H. Gad and N. S. Awwad
Hot Laboratories and Waste Management Centre, Egyptian Atomic Energy Authority, Cairo, Egypt

Abstract: The sorption and desorption of Eu (III) on H-APC activated carbon using a batch technique has been studied as a function of carbon type, shaking time, initial pH solution, temperature, particle size of carbon, and concentration of the adsorbent and the adsorbate. The influence of different anions and cations on adsorption has been examined. The experimental data have been analyzed by Langmuir, Freundlich, and Temkin sorption isotherm models and the adsorption data for Eu (III) onto activated carbon were better correlated to the Temkin isotherm and the maximum absorption capacities obtained was 46.5 mg g^{-1}. Anions of phosphate, carbonate, oxalate, and acetate were found to increase the adsorption of Eu (III), whereas nitrate, chloride and all studied cations, potassium, sodium, calcium, magnesium, and aluminum have a negative effect on the adsorption capacity. More than 99% europium adsorbed on H-APC eluted with 0.5 M HCl solution. The activated carbon prepared from apricot stone using 70% H_3PO_4 could be considered as an adsorbent that has a commercial potential for Eu (III) treatment.

Keywords: Activated carbon, apricot stone, Eu (III), sorption/desorption, diverse ions, desorbing agents

INTRODUCTION

Europium is attractive to the atomic industry, since the elements can be used in control rods and as nuclear poisons. These poisons are materials added to a

Received 10 February 2007, Accepted 28 May 2007

Address correspondence to H. M. H. Gad, Hot Laboratories and Waste Management Centre, Egyptian Atomic Energy Authority, P. O. 13759, Cairo, Egypt. Fax: +20-2-4620806; E-mail: hmhgad@yahoo.com

nuclear reactor to balance the excess reactivity at start-up, and are so chosen that the poisons burn out at the same rate as the excess activity decreases. The television industry uses considerable quantities of europium, such as europium-activated yttrium orthovanadates. These europium give a brilliant red color and are used in the manufacture of television screens. Europium is mostly dangerous in the working environment, due to the fact that its damps and gases can be inhaled with air, this can cause lung embolisms, especially during long-term exposure. It can be a threat to the liver when it accumulates in the human body. Also, europium is dumped in the environment in many different places, mainly by petrol-producing industries. It can also enter the environment when household equipment is thrown away leading to gradual accumulation in soils and water and this will eventually lead to increasing concentrations in humans, animals, and soil particles. With animals, europium causes damage to cell membranes, which has several negative influences on reproduction and on the functions of the nervous system.

For treatment of waste containing the high concentration of europium, in order to reach environmental standards, extraction, precipitation, and adsorption can be used. Adsorption on activated carbon has been increasingly applied (1). Furthermore, it is well known that the best activated carbons for removal of positively charged species are carbons with acidic functional groups that display ion-exchange properties (2). The development of acidic surface groups can be carried out by low temperature activation in the presence of air producing an L carbon (3). Activated carbons are now in use for the treatment of potable water (4) and wastewater, particularly for the removal of heavy metals (5), and hazardous materials. The adsorption properties of activated carbons are essentially attributed to their large surface area, large total pore volume, high degree of surface reactivity, and favorable pore size distribution (6). The texture (surface area and porosity) of activated carbons can be easily modified or even tailored to suit a specific application (7). The chemistry of the surface of activated carbon also plays a dominant role in determining its adsorption properties and consequently its use (8). It is also possible to modify the surface chemistry of activated carbons by controlling the amount and strength of the surface functional groups, particularly those of the carbon–oxygen type (9).

Cheap raw materials have been recommended for the preparation of activated carbons. Agricultural by-products, which exist in large amounts, represent a solid pollutant to the environment. Many years ago these by-products were used as a fuel in rural areas but now they do not find any application of commercial interest. The preparation of activated carbons from agricultural by-products has therefore been encouraged, since they are cheap precursors and their use in this manner would prevent their accumulation.

Among other countries, Egypt is rich in many agricultural by-products that can be used for the preparation of activated carbon, viz., cotton stalks and corn stalks, rice straw and rice husks, corncobs, date pits, some fruit stones, some nutshells and olive stones (10). Apricot stones have been used in the present study for the preparation of activated carbons.

In the present work, the adsorption of europium ions on activated carbon obtained from apricot stone treated with H_3PO_4 has been studied and the possible use of this carbon for removing europium ions from aqueous solution has been evaluated. These investigations lead to the optimum raw material composition and conditions of treatment for producing effective carbon adsorbents appropriate for the removal of europium ions from waste water.

EXPERIMENTAL

Preparation of Adsorbents

An apricot stone was crushed to 1 mm particle size, and four different types of adsorbents were prepared from it. Firstly, 30 g of crushed apricot stone was used without any treatment (AP). Secondly, 30 g of crushed sample was subjected to carbonization in a stainless-steel reactor that was placed in a tube furnace at heating rate of 50°C/10 min at atmospheric pressure up to of 500°C for 80 min (C-AP). Thirdly, crushed apricot stone was used for the preparation of activated carbons by one-step chemical activation using H_3PO_4 (H-APC) or KOH (K-APC). In each type 30 g of crushed apricot stone was soaked in pre-diluted phosphoric acid of 70% (v/v) concentration starting with an 85 wt.% H_3PO_4 (BDH), or 70% KOH. The crushed apricot stone was soaked in 50 mL H_3PO_4 (or KOH) solution, slightly agitated to ensure penetration of the acid (or base) 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/10 min) to 500°C for 80 min as a hold time. The product was thoroughly washed with hot distilled water, and finally dried at 110°C. All the physicochemical characterizations of adsorbents were summarized in Table 1.

Reagents

A stock solution (1000 mg l^{-1}) of europium was prepared by dissolving a known weight of europium oxide in nitric acid. The final volume of this solution was completed to 100 mL using deionized water. Required concentrations were prepared by appropriate dilution of stock solution at room temperature in deionized water. All other chemicals, unless specified otherwise,

Table 1. Physicochemical characterization of four adsorbents derived from apricot stone

Types of adsorbents	AP	C-AP	H-APC	K-APC
Apparent density (g cc^{-1})	0.48	0.44	0.50	0.76
Packed density (g cc^{-1})	0.72	0.61	0.65	0.95
pH	6.4	6.8	3.5	9.5
Water solubility (%)	*nd	nd	5.95	nd
Acid solubility (%)	nd	nd	9.4	nd
Base solubility (%)	nd	nd	0.194	nd
Water adsorbability (%)	nd	nd	237.8	nd
Adsorbability to Eu (III) (mg g^{-1})	10.9	17.78	29.34	28.35
Methylene blue (MB)	70.1	40.5	130.8	203.8
Iodine number	80.5	104.6	600	204.8
Yield (%)	100	27.11%	51.7%	125%
BET surface area (s.a.) (m^2)	nd	99.87	554.04	98
Micro pore surface area, S_n^α (m^2 g^{-1})	nd	107.3	554.04	101.57
Specific surface area, S^α (m^2 g^{-1})	nd	62.65	834	268.55
Langmuir s.a. (m^2 g^{-1})	nd	154	651	124
Average pore size Å	nd	12	21	16.35
Average pore width Å	nd	35.14	36.20	45.85
Total pore volume, V_p (cc g^{-1})	nd	6.0×10^{-2}	51×10^{-2}	8.2×10^{-2}
Meso-pore volume, V_{meso} (cc g^{-1})	nd	0.0121	0.31	0.042
Micro-pore volume, V_o^α (cc g^{-1})	nd	0.048	0.20	0.04

nd = Not done.

were of analytical-reagent grade, and doubly distilled water was used throughout.

Characterization of Activated Carbon

Elemental analysis (CHNS) of the carbon H-APC was performed in the micro analytical center at Cairo University. The infrared spectra of adsorbents were obtained from a Fourier Transform Infrared Spectrophotometer (FTIR) using the KBr disc technique (11). The surface area and the porous structure of adsorbents were measured by N_2 adsorption isotherm at 77 K using surface area and pore size analyzer, model NOVA 1000e.

Sorption Experiments

Different factors affecting on the sorption process, e.g., carbon type, contact time, initial pH solution, adsorbent weight and batch ratio (V/M), the particle size of the carbon, initial Eu (III) concentration, and temperature, have been investigated using a batch technique. In all cases, 10 mL aliquots of the Eu (III) solutions were contacted with 20 mg of the carbon in stoppered polyethylene bottles (The blank experiments demonstrated the negligible sorption of Eu (III) on the bottles walls). The conditions of the solution were adjusted and the bottles were shaken using a thermostatic shaker (Kottermann D-1362, Germany) to achieve equilibration concentration. Each mixture was filtered throughout 0.45 μm filter paper. The samples were analyzed using 10 mm quartz absorption cells at $\lambda_{\max} = 655$ nm using a Shimadzu model 160A double-beam UV spectrophotometer using arzenazo (III).

Desorption Experiments

These were conducted by removing the solution left after the sorption experiments and replacing it by a 20 mL of desorbing agents (zero concentration of Eu (III)). This is followed by shaking for predetermined time intervals up to 180 min. Then, the concentration of Eu (III) was determined as mentioned before.

Calculation

The amount of metal ion sorbed-uptake (mg g^{-1})-at time t, q_t, was calculated from the mass balance equation:

$$q_t = (C_0 - C_t)V/M \tag{1}$$

When t is equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, and the amount of metal ion sorbed at equilibrium, q_e, is calculated using Eq. (1). And K_d, the distribution coefficient, was calculated from the equation:

$$K_d = (C_0 - C_e)/C_e \cdot V/M \tag{2}$$

Where, C_0 and C_e are the initial and equilibrium Eu (III) concentration, V is the volume of the solution, and M is the weight of the adsorbent. All the adsorption experiments were run in duplicate. The difference in results for the duplicates was typically less than 5%.

RESULTS AND DISCUSSION

Characterizations of th Four Adsorbents

The characterizations of four adsorbents used were listed in Table 1. It can be seen that both the surface area and pore size varied widely. The maximum value is 554.04 $m^2\,g^{-1}$ for H-APC whereas the values are 98 $m^2\,g^{-1}$ and 99.87 $m^2\,g^{-1}$ for K-APC and C-APC respectively. Mesopore and micropore volume of sample H-APC are 51.0×10^{-2} and 20.0×10^{-2} cc g^{-1} but they are 8.2×10^{-2}, 6.0×10^{-2} and 4.0×10^{-2}, 4.8×10^{-2} $cm^3 g^{-1}$ for K-APC and C-APC respectively indicating the development of porous structure by H_3PO_4 activation. The higher surface area and porous structure of H-APC activated carbon may be facilitates the intraparticle diffusion of Eu (III) ions through the particles of activated carbon increasing the uptake of Eu (III) ion from solution.

The suspension of H-APC carbon is acidic in solution having a pH value of 3.5. This means that hydrogen ions (H^+) released from the surface of H-APC sample and this leads to:

(1) the feasibility of ion exchanger between the H^+ of the carbon surface and Eu (III) from solution.

(2) After release of H^+ the surface becomes negatively charged leading to the electrostatic attraction between it and the positively charged Eu (III) increasing the uptake of Eu (III) form solution. On the other hand, the higher uptake of K-APC sample for Eu (III) may be due to precipitation rather than adsorption.

Selection of Adsorbent Type

The four types of adsorbents were tested for the removal of Eu (III) from solution. The preliminary investigation showed that the uptake of the four adsorbents take the following order: 10.9, 17.78, 29.34, and 28.35 mg g^{-1} for AP, C-APC, H-APC, and K-APC respectively. This proves that the type of activation has a significant effect on the uptake of Eu (III). So, the carbon H-APC is only used in further experimental runs due to its highest capacity.

Analysis of H-APC Activated Carbon

The chemical composition of the raw apricot stone (12) and H-APC carbon is summarized in the Table 2. The analysis of the activated carbons precursors,

Table 2. Analysis of raw apricot stone and H-APC carbon

	Proximate analysis, wt.%			Elemental analysis, wt.%				
Parameter	Moisture	Ash	Volatile matter	C	H	S	N	O (Differ.)
Apricot stones (15)	6.4	0.2	80.6	55.6	6.8	0.1	0.2	37.3
H-APC	8.5	16.3	—	57.1	3.89	0.8	1.36	20.6

apricot stones, appear to be very suitable raw materials for the preparation of activated carbons because of their low sulfur, ash content, high carbon, and oxygen content.

Infrared Characterization of Activated Carbon

Infrared characterization of activated carbon is important for: (1) providing information on structure, such as the functional groups contained in the carbon, possibly mineral constituents, etc., (2) providing basic spectra of the activated carbon for comparison with spectra of the same carbon containing adsorbed material (13) as shown in (Fig. 1).

An infrared spectrophotometer was used to obtain the Fourier transform infrared spectra (FT-IR) of the H-APC sample in the range 4,000–400 cm^{-1}. The most characteristic features of these spectra are: The presence of significant vibration at the 3430.1 cm^{-1} assigned to H_2O or intra-molecular H-bonded (-OH) and/or NH groups. Bands for C-H vibrations in aliphatic groups were also observed at 2852.5 and 2923.3 cm^{-1} and free carboxylic acids (1697.1 cm^{-1}), cyclic lactones (single peak at 1756.2 cm^{-1}) were observed. The presence of the bands characteristic to carboxylate functionalities were observed at 1564.0 and 1536.3 cm^{-1}. Whereas, the bands at 1218.0 and 981.4 cm^{-1} may be attributed to C-O stretching in carboxylate, ether, and alcohol. The first band at 1218.0 cm^{-1} could be assigned, moreover, to an O-H bending in -COOH and it appears that, generally thermal treatment at 500°C enhances the amplitude of these bands.

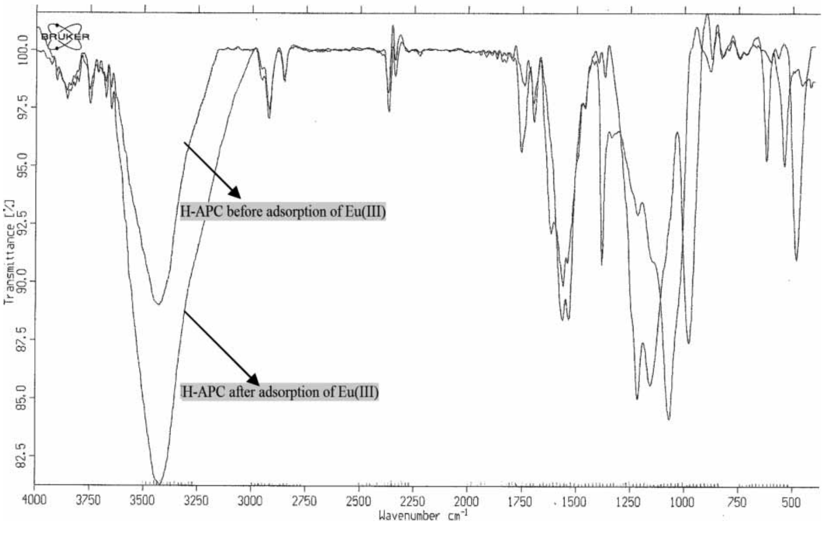

Figure 1. FTIR of H-APC activated carbon before and after adsorption of Eu (III).

A several bands below 900 cm^{-1} may be attributed to the phosphorus and some metal present in the ash content of the sample. And the presence of the hydroxyl group, aliphatic, ether, aromatic and phenolic groups, as well as conjugated C═C bonds, were indicated in the sample.

Factors Affecting on the Adsorption of Eu (III) onto H-APC

The parameters affecting on sorption of Eu (III) onto H-APC such as contact time, pH, particle size, concentration of adsorbent and adsorbate, interfering ions, and temperature have been investigated.

Effect of Contact Time

The adsorption experiments were carried out for contact times ranging from 5 to 180 min with fixed amounts of adsorbent (0.02 g) at 293 K. The results were plotted in (Fig. 2) from which it is clear that the sorption capacity increased rapidly where over 98% of the Eu (III) is adsorbed during the first 30 min and then becomes constant. So, the equilibrium time considered for further work has been taken as 120 min.

It is important to determine the rate at which Eu (III) ions are removed from aqueous solution in order to apply adsorption by porous solids to wastewater treatment. Adsorption of Eu (III) ions can be assumed to occur mainly in three stages during the process by porous adsorbents (17):

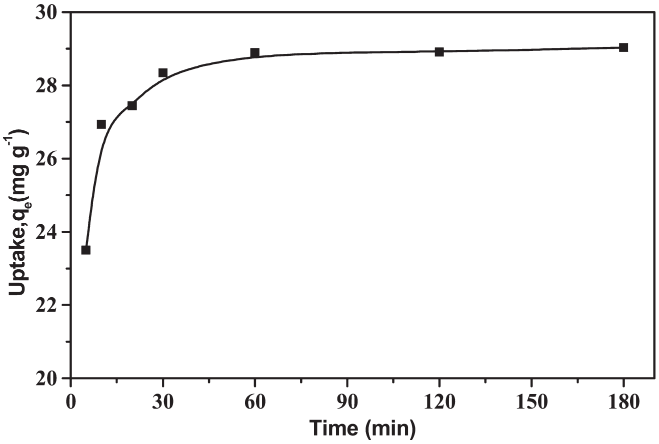

Figure 2. Effect of contact time on Eu (III) sorption onto H-APC activated carbon. Conditions: (Initial concentration (C_0): 50 mg l^{-1}, pH: 5, Temperature (T): 20°C, Weight (W): 0.02 g, Volume (V): 20 ml, Agitation speed: 300 rpm).

i. mass transfer of Eu (III) ions from aqueous solution to the adsorbent surfaces,
ii. migration of Eu (III) ions or intraparticle diffusion of Eu (III) ions within the pores of adsorbents, and
iii. interaction of Eu (III) with the available sites on the interior surfaces, binding the pore and capillary spaces of the adsorbent.

One or more of the previous stages may control the rate at which metal cations are adsorbed and the quantity of metal cations adsorbed onto the adsorbents.

Adsorption Kinetic Study

In order to investigate the adsorption processes of Eu (III) onto H-APC carbon, three kinetic models were used.

Pseudo-first-order Model

The adsorption kinetic data were described by the Lagergren pseudo-first-order model. The Lagergren equation is commonly expresses as follows:

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

where, q_t and q_e are adsorption capacity at time t and equilibrium, respectively (mg g^{-1}), k_1 is the rate constant of pseudo-first-order adsorption (l min^{-1}). The integration of Eq. (3) with the initial condition, $q_t = 0$ at $t = 0$ leads to (14):

$$\mathrm{Log}(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{4}$$

Plot the values of $\log(q_e - q_t)$ versus t give a linear relationship from which k_1 and q_e can be determined from the slope and intercept, respectively (Fig. 3). If the intercept is not equal q_e then the reaction is not likely to be a first order reaction even if this plot has a high correlation coefficient with the experimental data (15). The relationship between the initial solute concentration and the rate of adsorption will not be linear when pore diffusion limits the adsorption process. (Fig. 3) shows that the first 20 min of data fits well with the Lagergren model and thereafter the adsorption data deviates from the theory. Thus, the model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Furthermore, the calculated q_e values are too low compared with experimental q_e values and the correlation coefficient R is relatively low for adsorption data (Table 3), which indicates that the adsorption of Eu (III) onto H-APC is not a first-order reaction.

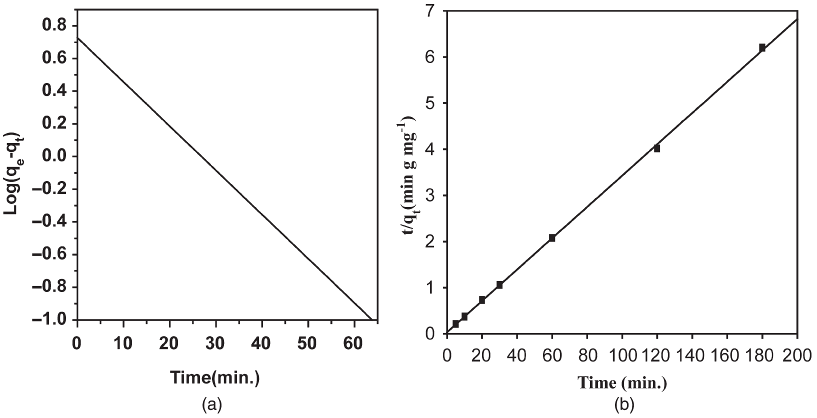

Figure 3. (a) Pseudo-first-order and (b) Pseudo-second-order kinetic plot for Eu (III) adsorption onto H-APC activated carbon. Conditions: (C_0: 50 mg l^{-1}, pH: 5, T: 20°C, W: 0.02 g, V: 20 ml, Agitation speed: 300 rpm).

Pseudo-second-order Model

The adsorption kinetic may be described by the pseudo-second-order model (16), which is generally given as the following:

$$dq_t/d_t = k_S(q_e - q_t)^2 \tag{5}$$

Where k_S (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant of adsorption. Integrating Eq. (5) and noting that $q_t = 0$ at $t = 0$, the following equation is obtained:

$$t/q_t = 1/k_S q_e^2 (1/q_e)t \tag{6}$$

The initial sorption rate, h (mg g^{-1} min^{-1}), at $t \rightarrow 0$ is defined as:

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

Table 3. Kinetic parameters for the removal of Eu (III) by H-APC activated carbon

Parameter	q_e, exp. (mg g^{-1})	q_e, calc. (mg g^{-1})	R (linear)	SD	k_1 (l min^{-1})	k_S (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})
Pseudo-first-order	29.03	5.33	0.982	0.13	0.0623	—	—
Pseudo-second-order	29.03	29.46	0.999	0.05	—	0.0340	0.0338

SD = Standard deviation.

The plot of t/q_t versus t give a straight line as showed in (Fig. 3), confirming the applicability of the pseudo-second-order equation. Values of k_S and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plot of t/q_t versus t, respectively. The values of R and q_e also indicated that this equation produced better results (Table 3), and the calculated q_e value is mainly equal to the experimental data. This indicates that the Eu (III)-H-APC adsorption system obeys the pseudo-second-order kinetic model for the entire sorption period.

Intra-particle Diffusion Model

Adsorption is a multi-step process involving the transport of the adsorbate (Eu (III)) from the aqueous phase to the surface of the solid (H-APC) particles, then followed by diffusion of the solute into the pore interiors. If the experiment is a batch system with rapid stirring, there is a possibility that the transport of the sorbent from the solution into pores (bulk) of the adsorbent is the rate controlling step (17). This possibility was tested in terms of a graphical relationship between the amounts of Eu (III) adsorbed and the square root of time (18). Since the Eu (III) is probably transported from its aqueous solution to the H-APC by intraparticle diffusion, so the intraparticle diffusion is another kinetic model which should be used to study the rate-limiting step for Eu (III) onto H-APC. The intra-particular diffusion is commonly expressed by the following equation:

$$q_t = k_{\mathrm{id}} t^{1/2} + I \tag{8}$$

where k_{id} is the intra-particle diffusion rate constant (mg g^{-1} min$^{-1/2}$) and I is the intercept (mg g^{-1}). The values of q_t were found to give two lines part with values of $t^{1/2}$ (Fig. 4) and the rate constant k_{id} directly evaluated from the slope of the second regression line. The value of intercept I, which is related to the thickness of the boundary layer was ($I = 24.44$ mg g^{-1}) calculated. The shape of (Fig. 4) shows two intersecting lines depending on the exact mechanism; the first one of these lines represents the surface adsorption at the beginning of the reaction and the second one is the intraparticle diffusion at the end of the reaction. As still there is no sufficient indication about which of the two steps is the rate-limiting step. Ho (19) has shown that if the intraparticle diffusion is the sole rate-limiting step, it is essential for the q_t versus $t^{1/2}$ plots to pass through the origin, which is not the case in (Fig. 4), it may be concluded that the surface adsorption and the intraparticle diffusion were concurrently operating during the Eu (III) H-APC interactions.

Effect of Initial pH of Solution on Eu (III) Uptake

The pH of the system is very effective on the adsorption capacity of the adsorbate molecule presumably due to its influence on the surface properties of the adsorbent and the ionization/dissociation of the adsorbate (33).

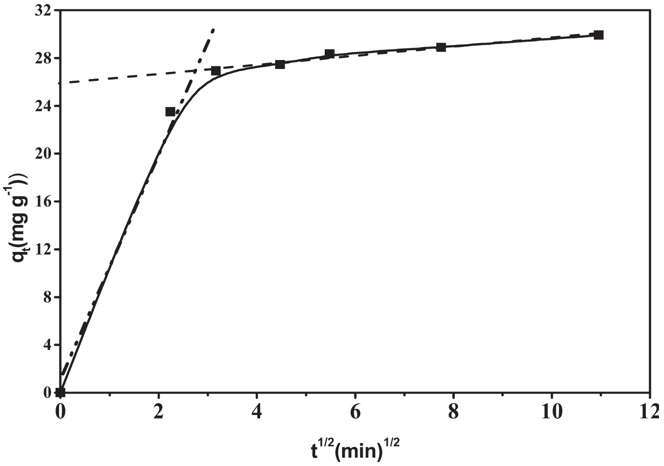

Figure 4. Weber and Morris intraparticle diffusion plot for Eu (III) onto H-APC. Conditions: (C_0: 50 mg l^{-1}, pH: 5, T: 20°C, W: 0.02 g, V: 20 ml, Agitation speed: 300 rpm).

However, two possible mechanisms of adsorption of Eu (III) onto H-APC adsorbent may be considered:

a. electrostatic interaction between the adsorbent and Eu (III) and
b. the chemical reaction between the Eu (III) and the adsorbent. (Fig. 5) shows the effect of pH on the removal of Eu (III) from solution.

At the acidic pH, (high concentration of H^+ ions), the uptake of Eu (III) is relatively low due to the competition between H^+ ions and Eu (III) ions at the surface of H-APC decreasing the adsorption of Eu (III). As the pH of the solution increased (increasing OH^- concentration), the uptake of Eu (III) from the solution increased presumably due to:

a. the increase of the sorption with the pH may be explained by the increasing sorption of Eu (III) on surface complexing sites due to their increasing deprotonization and/or due to the decreasing competition of H_3O^+ and H^+ ions.
b. When pH increases beyond 5, precipitation starts due to the formation of complexes in the aqueous solution. Thus, the optimum adsorption proceeds at pH 5 as shown in (Fig. 5).

Effect of Particle Size

In order to examine the effect of particle size on Eu (III) adsorption, the particle diameters were studied in the range of (<250, <500, <1000 and

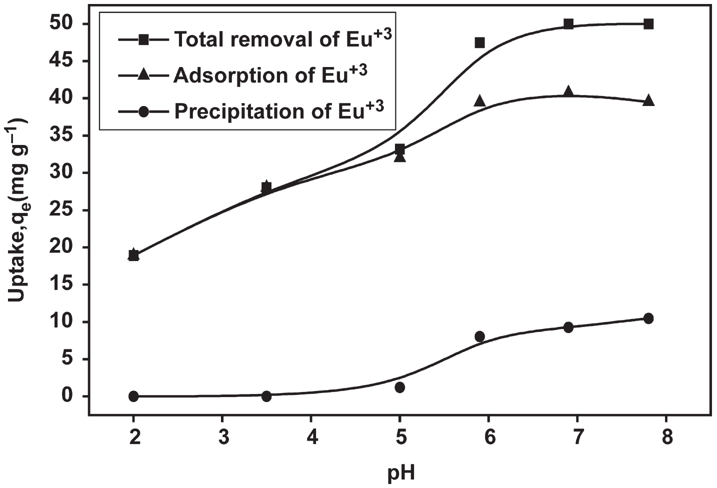

Figure 5. Effect of initial pH of solution on the adsorption of Eu (III) onto H-APC. Conditions: (C_0: 50 mg l^{-1}, pH: 2–8, T: 20°C, W: 0.02 g, V: 20 ml, Agitation speed: 300 rpm, time = 2 h).

1000 μm) at a fixed H-APC dose and an initial Eu (III) concentration of 50 mg l^{-1} as shown in (Fig. 6). The adsorption capacity for Eu (III) increased with a decrease in the particle size.

This is because the adsorption being a surface phenomenon, the smaller particle size offered a comparatively large surface area and, hence, higher adsorption occurred at equilibrium (20, 32). According to Weber (21), the

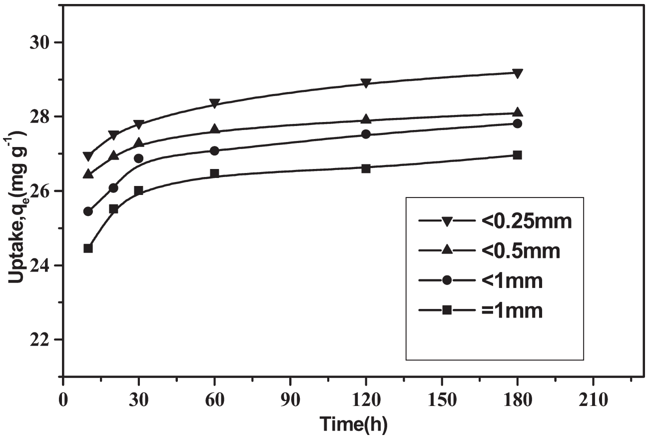

Figure 6. Effect of particle size on the adsorption of Eu (III) onto H-APC activated carbon. Conditions: (C_0: 50 mg l^{-1}, pH: 5, T: 20°C, W: 0.02 g, V: 20 ml, Agitation speed: 300 rpm, time = 2 h).

breaking of the larger particles tends to open tiny cracks and channels on the particle surface, providing added surface area which can be employed in the adsorption process. Besides adsorption at the outer surface of the H-APC there is also the possibility of intraparticle diffusion from the outer surface into the pores of the material. The diffusional resistance to mass transfer is greater for large particles. Because of various factors, such as diffusional path length or mass transfer resistance, contact time, and blockage sections of the particle may not be utilized for adsorption and consequently the adsorption capacity of large particles may be low.

Effect of Adsorbent Weight and Batch Ratio (V/M)

The effect of the adsorbent dose versus the amount adsorbed, q_e (mg g^{-1}) was illustrated in (Fig. 7). It is apparent that by increasing the adsorbent dose the adsorption efficiency (total amount of Eu (III) adsorbed from solution), increases (22) but the adsorption density (amount adsorbed per unit mass (q_e)) decreases. It is readily understood that the number of available adsorption sites increases by increasing the adsorption dose and it, therefore, results in the increase of removal efficiency. The decrease in the adsorption density with an increase in the adsorbent dose is mainly due to unsaturation of adsorption sites through the adsorption reaction. Another reason may be due to the particle interaction, such as aggregation, resulting from high sorbent concentration. Such aggregation would lead to a decrease in the total surface area of the sorbent and an increase in the diffusional path length (27). Particle interaction may also desorb some of the sorbate that is only loosely and reversibly bound to the carbon surface. Also it was found that the best V/M ratio is 3000 mL g^{-1}.

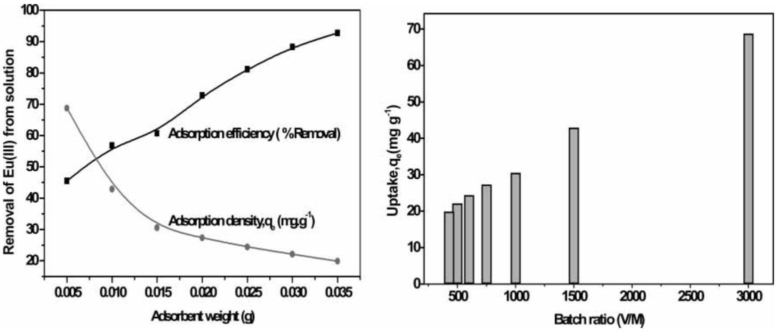

Figure 7. Effect of adsorbent weight and batch ratio (V/M) on the adsorption of Eu (III) onto H-APC activated carbon. Conditions: (C_0: 50 mg l^{-1}, pH: 5, T: 20°C, W: 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035 g, V: 20 ml, Agitation speed: 300 rpm, time = 2 h).

Effect of Temperature

Figure 8 shows the results of a series of kinetic experiments at (20, 40, and 60°C) for the adsorption of Eu (III) onto H-APC activated carbon, and it was clear that the uptake increases as the temperature increases, indicating better adsorption at higher temperatures (i.e., endothermic process). The increase in the amount of Eu (III) adsorbed at equilibrium with an increase in temperature may either be due to acceleration of some originally slow adsorption steps or to the creation of some new active sites on the adsorbent surface at higher temperature.

Thermodynamics Studies

The thermodynamic parameters obtained for the sorption process were calculated using the equations:

$$\ln K_d = \Delta S^0/R - \Delta H^0/RT \tag{9}$$

where K_d is the distribution coefficient (mL g^{-1}), ΔS^0 is standard entropy (J mol^{-1} K^{-1}), ΔH^0 is standard enthalpy (kJ mol^{-1}), T is the absolute temperature (K), and R is the gas constant (8.314 J mol^{-1} K^{-1}). The experiments were carried out at 293, 313, and 333 K for Eu (III) concentration 50 mg l^{-1}. The values of ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of linear regression of $\ln K_d$ versus $1/T$ (Fig. 9). The standard Gibbs free energy ΔG^0 values (kJ mol^{-1}) were calculated from the equation (24):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10}$$

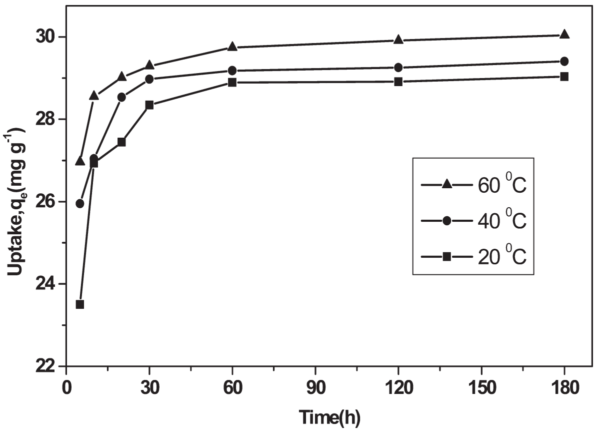

Figure 8. Effect of temperature on the adsorption of Eu (III) onto H-APC activated carbon. Conditions: (C_0: 50 mg l^{-1}, pH: 5, T: 20, 40, 60°C, W: 0.020 g, V: 20 ml, Agitation speed: 300 rpm, time = 2 h, Particle size = whole particle size studied above).

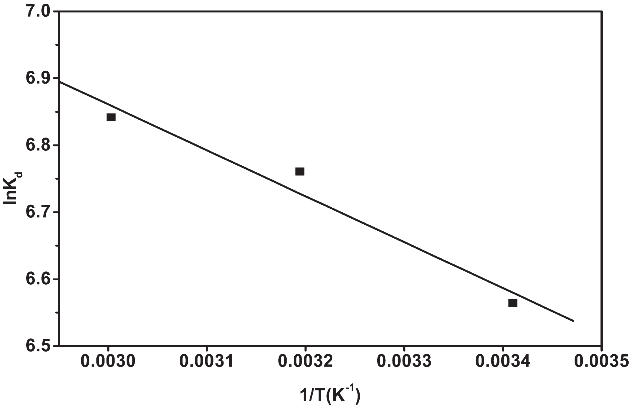

Figure 9. Graphical determination of ΔH^0 and ΔS^0. Conditions: (C_0: 50 mg l^{-1}, pH: 5, T: 20, 40, 60°C, W: 0.020 g, V: 20 ml, Agitation speed: 300 rpm, time = 2 h, Particle size = whole particle size studied above).

The values of ΔH^0, ΔS^0, and ΔG^0 are reported in Table 4. In fact, the positive value of enthalpy change ΔH^0 for the processes further confirms the endothermic nature of the process, the positive entropy of adsorption ΔS^0 reflects the affinity of the adsorbent material toward Eu (III), and the negative free energy values ΔG^0 indicate the feasibility of the process and its spontaneous nature without an induction period.

Effect of Initial Concentration of Eu (III)

Figure 10 shows that the uptake of Eu (III) increases with increasing the initial concentration of the solute up to 200 mg l^{-1}. Above this concentration and at the equilibrium, which was attained after 120 min of contact between the solute and H-APC activated carbon, there was no further rise probably due to the limited active sites available to adsorption of Eu (III) on the carbon surface.

Adsorption Equilibrium Study

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the

Table 4. Thermodynamic parameters for the adsorption of Eu (III) onto H-APC

		ΔG^0 (kJ mol^{-1})		
ΔH^0 (kJ mol^{-1})	ΔS^0(J mol^{-1} k^{-1})	293 K	313 K	333 K
8.648	4.306	−7.13	−7.20	−7.30

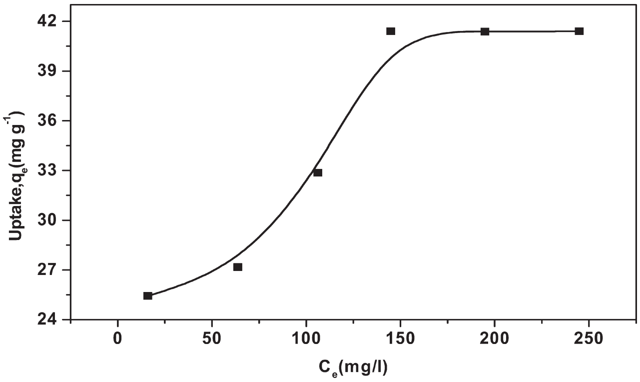

Figure 10. Effect of initial concentration on the adsorption of Eu (III) onto H-APC. Conditions: (C_0: 50, 100, 150, 200, 250, 300, 350 mg l^{-1}, pH: 5, T: 20°C, W: 0.020 g, V: 20 ml, Agitation speed: 300 rpm, time = 2 h).

equilibrium curves. Various isotherm equations have been used to describe the equilibrium characteristics of adsorption.

Freundlich and Langmuir Isotherms

The Freundlich (25) isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, whereas in the Langmuir (26) theory the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. The Freundlich model Eq. (11) and the Langmuir model Eq. (12) are given below:

Freundlich isotherm:

$$\log q_e = \log \mathrm{K_F} + 1/n \log C_e \tag{11}$$

Langmuir isotherm:

$$C_e/q_e = 1/K_L q_m + C_e/q_m \tag{12}$$

Where $\mathrm{K_F}$ is the Freundlich constant (L mg^{-1}), $1/n$ the heterogeneity factor, K_L the Langmuir adsorption constant (L mg^{-1}) related to the energy of adsorption and q_m signifies adsorption capacity (mg g^{-1}). These models were tested with the equilibrium adsorption data of Eu (III) onto H-APC adsorbent. To quantify the adsorption capacity of carbon H-APC for removal of Eu (III), two-parameter isotherm models Eqs. (11) and (12) were applied in linearized form (27) as shown in (Fig. 11). As seen, the Langmuir isotherm fits better to the experimental data than the Freundlich isotherm does for Eu (III) adsorption onto H-APC activated carbon. The values of the parameters for the Langmuir and Freundlich isotherms are given in Table 5.

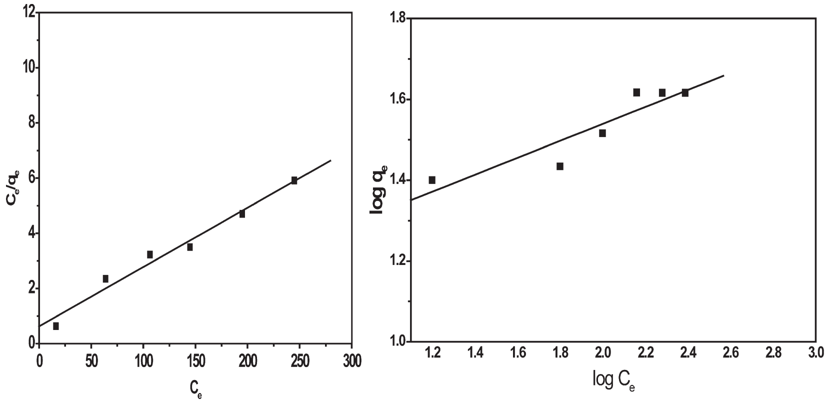

Figure 11. Langmuir and Freundlish linearized form of adsorption of Eu (III) onto H-APC. Conditions: (C_0: 50, 100, 150, 200, 250, 300, 350 mg l^{-1}, pH: 5, T: 20°C, W: 0.020 g, V: 20 ml, Agitation speed: 300 rpm, time = 2 h).

Dimensionless Separation Factor

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L which describes the type of isotherm and is defined by:

$$R_L = 1/(1 + K_L C_0) \tag{13}$$

where; $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible.

The values of R_L for $C_0 = 150$ mg l^{-1} are given in Table 5. The values of R_L obtained were found to be less than one for Eu (III) adsorption onto H-APC carbon confirming that the adsorption process is favorable. From the Freundlich isotherm, the value of $1/n$ was also found to be less than one, showing that the adsorption process is favorable (28).

The Temkin Isotherm

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform

Table 5. Langmuirian and Freundlich coefficients of Eu (III) on H-APC carbon

Langmuir parameters				Freundlish parameters			
K_L (l mg^{-1})	q_m (mg g^{-1})	R^2	R	$1/n$	n (l mg^{-1})	K_F (l mg^{-1})	R^2
0.034	46.5	0.9877	0.164	0.21	4.76	13.16	0.9178

distribution of the binding energies, up to some maximum binding energy (29). The Temkin isotherm equation is given as:

$$q_e = RT/b \ln(K_T C_e) \tag{14}$$

Eq. (14) can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{15}$$

where $B_1 = RT/b$ and K_T are the constants. K_T is the equilibrium binding constant (L mol^{-1}) corresponding to the maximum binding energy, and constant B_1 is related to the heat of adsorption. A plot of q_e versus lnC_e (Fig. 12) enables the determination of the isotherm constants K_T and B_1. The values of K_T and B_1 as obtained are: 3.614 and 23.59 (L mg^{-1}) respectively; with the value of the correlation coefficient ($R^2 = 0.999$). It may be concluded that the Temkin isotherm represents the equilibrium data with the best fitting.

Effect of Anions and Cations

Using the optimized parameters determined, the adsorption of Eu (III) onto H-APC carbon was studied in the presence of various anions and cations ($C_0 = 50$ mg l^{-1} for anions and cations). The results are listed in Table 6 and indicated that the capacity of the activated carbon for adsorption of Eu (III) can be markedly affected by certain anions and cations. Effect of anions on the adsorption of Eu (III) by H-APC take the following order according to higher capacity:

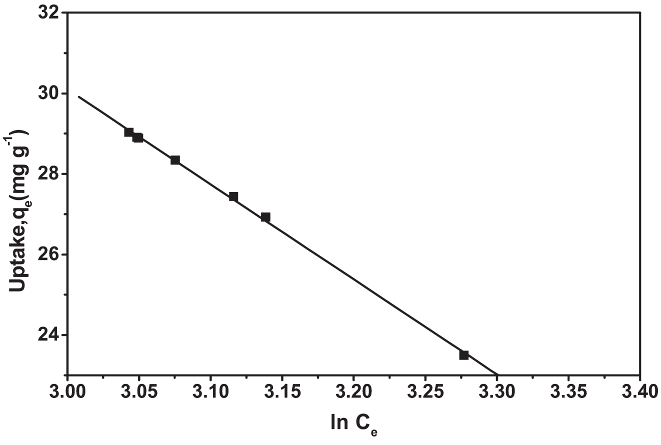

Figure 12. Temkin isotherm equation for Eu (III) adsorption onto H-APC activated carbon. Conditions: (C_0: 50, 100, 150, 200, 250, 300, 350 mg l^{-1}, pH: 5, T: 20°C, W: 0.020 g, V: 20 ml, Agitation speed: 300 rpm, time = 2 h).

Table 6. Effect of diverse ion on the adsorption of Eu (III) onto H-APC activated carbon

	Anions		Cations	
No.	Type	q_e (mg g^{-1})	Type	q_e (mg g^{-1})
1	Sodium acetate	29.65	Potassium nitrate	23.86
2	Sodium chloride	22.94	Sodium nitrate	22.64
3	Sodium carbonate	35.32	Calcium nitrate	22.18
4	Sodium oxalate	33.34	Magnesium nitrate	21.9
5	Sodium nitrate	24.02	Aluminum nitrate	12.62
6	Sodium phosphate	42.38	Eu (III) only	24.04

$$\text{Phosphate} > \text{carbonate} > \text{oxalate} > \text{acetate}$$
$$> \text{Eu (III) only} > \text{nitrate} > \text{chloride}$$

Some anions, such as chloride, form complexes with metal ions and therefore, affect the adsorption process (30). Whereas, phosphate anion forms an insoluble complex increasing the adsorbability of Eu (III) form solution as shown in Table 6.

Ca^{2+}, Mg^{2+}, K^+, and Na^+ are the common cations present in water that may compete with metal ions for adsorption and can affect the removal of metal ions (31). As seen from Table 6 all cations decreases the uptake of Eu (III) especially Al^{3+} which decreases the uptake to half of its value in the absence of Al^{3+}. This may be due to relative competition between the cations and Eu (III) onto the active centers of the H-APC carbon. The uptake of Eu (III) from solution using H-APC take the following order: Eu (III) only $> K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Al^{3+}$.

Desorption Studies

Desorption of Eu (III) from the spent adsorbent was studied. The carbon loaded with the maximum amount of Eu (III) were placed into desorption medium containing 0.5 M of different reagents and the amount of metal ions desorbed in 4 h was measured. Table 7 shows the results of desorption of Eu (III) using a different reagent. Obtained results demonstrated that 99.06% of the adsorbed Eu (III) was quantitatively desorbed from the loaded matrix of H-APC carbon to the suspending medium using 0.5 M HCl (and more than 95% by using 0.05 M HNO_3). The second and third adsorption cycles reveal that the H-APC carbon can be reused with very small loss in efficiency. Approximately 95% of the initial adsorption capacity is obtained in the third cycle.

Table 7. Desorption of adsorbed Eu (III) from using different desorbing reagents

			Effect of conc. of HCl		Effect of conc. of HNO_3	
No.	Reagents (0.5 M)	Desorption (%)	Concentration (M)	Desorption (%)	Concentration (M)	Desorption (%)
1	Hydrochloric	99.06	0.05	38.38	0.05	95.97
2	Nitric	92.73	0.1	61.58	0.1	95.82
3	Sulphoric	33.86	0.2	81.83	0.2	92.99
4	Oxalic	—	0.3	96.64	0.3	92.77
5	Tartaric	52.73	0.4	97.02	0.4	92.77
6	Phthalic	45.46	0.5	99.06	0.5	92.73

Treatment of Laboratory Wastewaters

The utilization of the H-APC activated carbon for wastewater treatment has been tested by treating the laboratory wastewaters. The composition of experimental wastewaters is a mixture of Eu (III), buffer solution and arsenazo (III) used in the determination of Eu (III) using UV-specrophotometer. Laboratory wastewater was collected from experimental work of Eu (III) and treated by H-APC prepared carbon to examine the efficiency of this carbon for treatment of wastewater. Table 8 shows the effect of the mass of activated carbon on the % removal of the constituents of laboratory wastewater. The % removal was found to increase with increase in mass of carbon as discussed above. The 99.1% removal was achieved only in 40 min of contact between carbon and laboratory wastewater. From these experimental results, it may be demonstrated that the 2.5 gm of H-APC can be successfully utilized as adsorbents for treating 1 L of laboratory wastewaters rich in Eu (III), buffer, and arsenazo (III).

Simple Economic Evaluation

Apricot stone is available in abundance as a waste from the agricultural by-products industries at no cost. However, the handling charges for the

Table 8. Treatment of laboratory wastewater using H-APC activated carbon

No.	Mass of H-APC	V/M (mL g^{-1})	% Removal
1	0.005	2000	97.55
2	0.010	1000	98.47
3	0.015	666.7	98.63
4	0.020	500	99.07
5	0.025	400	99.10

collection, transportation, and preparation of activated carbon will be involved. But the total cost of H-APC will be extremely low in comparison to those for commercial activated carbon (CAC). The cost of CAC makes the recovery of the Eu (III) and the regeneration of the adsorbent a must. However, the exhausted H-APC along with the adsorbed Eu (III) can be either regenerated or dried and used as a fuel in the boilers/incinerators, or can be used for the production of fire briquettes. The ash may be used to make fire-bricks, thus, disposing of Eu (III) through chemical fixation. This approach of H-APC disposal entails energy recovery from the H-APC and the safe disposal of the adsorbed Eu (III).

CONCLUSION

In this study, agriculture by-products such apricot stone was used for the preparation of low-cost adsorbents. One of these adsorbents (H-APC) has been investigated for the adsorption/desorption of Eu (III) from the aqueous solution. According to the results obtained, we can conclude that:

a. A small amount ($1\ g\ l^{-1}$) of H-APC could remove over 97% of Eu (III) within 30 min contact time between adsorbent and adsorbate.
b. The adsorption capacity of Eu (III) onto H-APC was increased by increasing of pH, temperature, concentration of Eu (III), decreasing particle size and dose of adsorbate, and the presence of (phosphate, carbonate, oxalate, acetate) anions.
c. On the other hand, the chloride and all cations (specially Al^{3+}) investigated were found to decrease the adsorption of Eu (III) onto H-APC activated carbon.
d. The experimental data showed perfect fitting with the Temkin isotherm, which confirm that the adsorption is characterized by a uniform distribution of binding energies, whereas the data obtained were in good agreement with the Langmuir isotherm with maximum adsorption capacity of $46.5\ mg\ g^{-1}$.
e. The results indicated that the adsorption kinetics follow the pseudo-second-order rate with intraparticle diffusion as one of the rate determining steps.
f. From the thermodynamic parameters, the positive ΔH^0 confirms the endothermic nature of the process, the positive ΔS^0 reflects the affinity of the adsorbent toward Eu (III), and the negative ΔG^0 indicate the feasibility of the process and its spontaneous nature without an induction period.
g. Hydrochloric acid was selected for regeneration of H-APC activated carbon, and it was found that the Eu (III) could be desorbed by 99.06% with 0.5 M HCl. Approximately 95% of the initial adsorption capacity is obtained in the third cycle.

h. 2.5 gm of H-APC can be successfully utilized as adsorbents for treating 1 L laboratory wastewaters rich in Eu (III), buffer, and arsenazo (III) only in 40 min.
i. From the economic point of view, the total cost of H-APC will be extremely low in comparison to those for commercial activated carbon (CAC).
j. This work confirms that the H-APC activated carbon prepared from apricot stone using 70% H_3PO_4 can be considered as an adsorbent that has a commercial potential for Eu (III) treatment (removal and/or preconcentration).

REFERENCES

1. Savova, D., Petrov, N., Yardimb, M.P., Ekincib, E., Budinova, T., Razvigorova, M., and Minkova, V. (2003) The influence of the texture and surface properties of carbon adsorbents obtained from biomass products on the adsorption of manganese ions from aqueous solution. *Carbon*, 41: 1897.
2. Boehm, H.P. (1994) Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon*, 32 (5): 759.
3. Mattson, J.S. and Mark, H.B. (1971) In *Active Carbon: Surface Chemistry and Adsorption from Solutions*; Marcel Decker: New York.
4. Abdel-Halim, S.H., Shehata, A.M.A., and El-Shahat, M.E. (2003) Removal of lead ions from industrial waste water by different types of natural materials. *Water Res.*, 37: 1678.
5. Youssef, A.M., El-Nabarawy, Th., and Samra, S.E. (2004) Sorption properties of chemically-activated carbons 1. Sorption of cadmium(II) ions. *Colloids and Surfaces A: Physicochem. Eng. Aspects.*, 235: 153.
6. Cagnon, B., Py, X., Gusllot, A., and Stoeckli, F. (2003) Effect of cyclic oxidation by NaOCl on the microporous properties of activated carbons. *Microporous Mesoporous Mater.*, 57: 273.
7. El-Nabarawy, Th., Mostafa, M.R., and Youssef, A.M. (1997) Activated carbons tailored to remove different pollutants from gas streams and from solution. *Adsorption Science and Technology*, 15 (1): 59.
8. Salame, I.I. and Bandosz, T.J. (2002) Interactions of water, methanol and diethyl ether molecules with the surface of oxidized activated carbon. *Molecular Physics*, 100 (13): 2041.
9. Chorna, J., Burakiewicz-Mortka, W., Jaroniec, M., Li, Z., and Klinik, J. (1999) Phenotype of a recombinant store-operated channel: highly selective permeation of Ca^{2+}. *J. Colloid Interface Sci.*, 214: 438.
10. Youssef, A.M., Radwan, Abdel-Gawad, N.R.E.I., and Singer, G.A.A. (2005) Textural properties of activated carbons from apricot stones. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 252: 143.
11. Nakbanpote, W., Thiravetyan, P., and Kalambaheti, C. (2002) Comparison of gold adsorption by Chlorella vulgaris, rice husk and activated carbon. *Minerals Engineering*, 15: 549.
12. Savova, D., Apakb, E., Ekincib, E., Yardimb, F., Petrova, N., Budinovaa, T., Razvigorovaa, M., and Minkovaa, V. (2001) Biomass conversion to carbon adsorbents and gas. *Biomass and Bioenergy*, 21: 133.

13. Friedel, R.A. and Hofer' L.J.E. (1970) Spectral characterization of activated carbon. *Journal of Physical Chemistry*, 74: 16.
14. Ho, Y.S. and McKay, G. (1999) The sorption of lead(II) ions on peat. *Water Res.*, 33: 578.
15. Crini, G., Peindy, H.N., Gimbert, F., and Robert, C. (2007) Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrinbased adsorbent: Kinetic and equilibrium studies. *Sep. Purif. Technol.*, 53: 97.
16. Ho, Y.S., McKay, G., Wase, D.A.J., and Foster, C.F. (2000) Study of the sorption of divalent metal ions on to peat. *Adsorp. Sci. Technol.*, 18: 639.
17. McKay, G. (1983) The adsorption of dyestuff from aqueous solution using activated carbon: analytical solution for batch adsorption based on external mass transfer and pore diffusion. *Chem Eng J.*, 27: 187.
18. Weber, W.J. and Morris, J.C. (1963) Kinetics of adsorption on carbon from solution. *Journal Sanity Engineering Div. Am. Soc. Civil Eng.*, 89: 31.
19. Ho, Y.S. (2003) Removal of copper ions from aqueous solution by tree fern. *Water Res.*, 37: 2323.
20. Osman, M.A. and Samuel, D.F. (1983) *Chemistry of Water Treatment*; Butter worth's: MA.
21. Weber, W.J. Jr. (1967) *Principles and Applications of Water Chemistry*; Faust, S.A. and Hunter, J.V. (eds.), Wiley: New York.
22. Shukla, Alka, Zhang, Yu-Hui, Dubey, Margrave, P., Shyam, J.L., and Shukla, S. (2002) The role of sawdust in the removal of unwanted materials from water. *Journal of Hazardous Materials*, B95: 137.
23. Perlinger, J.A. and Eisenreich, S.J. (1991) In *Organic Substances and Sediments in Water*; Baker, R.A. (ed.), Lewis: Michigan.
24. Mellah, A., Chegrouche, S., and Barkat, M. (2006) The removal of uranium (VI) from aqueous solutions onto activated carbon: kinetic and thermodynamic investigations. *Journal of Colloid and Interface Science*, 296: 434.
25. Freundlich, H.M.F. (1906) Über die adsorption in lösungen. *Zeitschrift für Physikalische Chemie* (Leipzig), 57A: 385.
26. Langmuir, I. (1916) The constitution and fundamental properties of solids and liquids. *J, Am, Chem, Soc.*, 38: 2221.
27. Weber, W.J. (1972) *Pysicochemical Processes for Water Quality Control*; John Wiley: New York, (Chapter 5).
28. Faust, S.D. and Aly, O.M. (1987) *Adsorption Processes for Water Treatment*; Butterworth's.
29. Sai Sathish, R., Raju, N.S.R., Raju, G.S., Nageswara Rao, G., Anil Kumar, K., and Janardhana, C. (2007) Equilibrium and kinetic studies for fluoride adsorption from water on zirconium impregnated coconut shell carbon. *Separation Science and Technology*, 42: 769.
30. Shukla, Alka, Zhang Yu-Hui, P., Dubey, J., Margrave, L., and Shyam Shukla, S. (2002) The role of sawdust in the removal of unwanted materials from water. *Journal of Hazardous Materials*, B95: 137.
31. Anirudhan, T.S. and Sreedhar, M.K. (1998) Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. *Indian J. Chem. Technol.*, 5: 41.
32. Mahmut Özacar, I. and Ayhan, S_engil (2005) Adsorption of metal complex dyes from aqueous solutions by pine sawdust. *Bioresource Technology*, 96: 791.
33. Mellah, A., Chegrouche, S., and Barkat, M. (2006) The removal of uranium(VI) from aqueous solutions onto activated carbon: kinetic and thermodynamic investigations. *Journal of Colloid and Interface Science*, 296: 434.