Adsorption of Rare Earth Elements (REEs) onto Activated Carbon Modified with Potassium Permanganate ($KMnO_4$)

Naoki Kano[1,*], Meiling Pang[2], Yanling Deng[2] and Hiroshi Imaizumi[1]

[1]*Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Niigata 950-2181, Japan*

[2]*Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan*

Abstract: The adsorption capacity of activated carbon modified with potassium permanganate ($KMnO_4$) for rare earth elements (REEs) from aqueous solution was investigated. The modified activated carbon was characterized by SEM (scanning electron microscopy), FT-IR (Fourier transform infrared spectrometer), and N_2 adsorption-desorption tests. Adsorption experiments from aqueous solutions containing known amounts of some REEs (i.e. La, Lu, Yb, Eu, Y, Sc) onto the carbon were explored in a batch system. The amount of REEs adsorbed at different pH values, initial concentrations, and contact times were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) in order to determine the optimum conditions for REEs adsorption. The adsorption of REEs on the activated carbon was well fitted by the Langmuir isothermal adsorption equation. The rates of adsorption were found to conform to pseudo-second order kinetic. These results present the modified activated carbon as an efficient adsorbent for REEs, hence creating new avenues for the treatment of industrial waste waters including pollutants. It is very significant information from the viewpoint of environmental protection.

Keyword: Adsorption, modified activated carbon, rare earth elements (REEs), adsorption isotherms, kinetics.

1. INTRODUCTION

Environmental pollution became a popular issue in the world with the rapid development of modern industry and agriculture [1, 2]. In particular, water pollution due to heavy metal has become one of the largest problems in recent years [3, 4]. On the other hand, the demand of rare earth elements (REEs) in modern technology has increased remarkably over the past years [5, 6]. However, the shortage of trace metals including REEs (and the necessity of stable supply for these metals) has been concerned in recent years. Therefore, the development of the removal (or recovery) method for the trace metals is important from the viewpoint of resources recovery as well as environmental protection.

In recent decades, geochemical processes controlling metal migration and deposition in the earth's surface environment has been intensively and increasingly attracting much interest of scientists [7-9]. Rare earth is used in many industrial activities including mining and refining, which can cause environmental consequences if not properly managed. Therefore, it is significant to remove (or recover) metallic elements within the scope of permissible concentration before discharging into subsurface environments. Considering the technical, economical and health-related points, the adsorption process seems to be a more appropriate technology for the removal (and/or recovery) of REEs from pollutants [10, 11].

There are many conventional methods for the removal of heavy metals from wastewater. These methods include chemical precipitation, ion-exchange, evaporation, reverse osmosis, membrane filtration, and adsorption [12]. Among them, adsorption is proven to be economical and effective method for the removal of a number of contaminates from water [13, 14].

Activated carbon (AC) has shown great potential for the removal of various inorganic, organic pollutants and radionuclides due to properties such as large surface area, microporous structure and high adsorption capacity. Powdered activated charcoal, which is one of the representative paradigms among nanostructured carbon materials, continues to attract tremendous attention in the past two decades due to their unique physical and chemical properties [15, 16]. In particular, chemical functionalization of AC can modify their physical and chemical properties, leading to the improvement of their performance for specific applications [17-19].

The modification of AC is known to play a key role in enhancing the adsorption efficiency because of the change in the surface morphology and the function by particular functional groups [17, 20, 21]. The employed adsorbent can be regenerated by suitable desorption process [22, 23].

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*Correspondence Address to this author at the Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Niigata 950-2181, Japan; Tel: +81-25-262-7218; Fax: +81-25-262-7218;
E-mail: kano@eng.niigata-u.ac.jp

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It is known that potassium permanganate ($KMnO_4$) can be a powerful oxidizing agent, and used for the improvement of the capabilities in ACs [24-26]. The physicochemical properties of AC may be improved after oxidation, which made ACs possess not only a more hydrophilic functional groups (e.g. -COOH) but also more negatively charged surface [27, 28].

Then, $KMnO_4$ was selected as oxidizing agent for the modification of AC in this work.

The modification of AC, which provides ACs comparable performance for its water purification capabilities, is gaining prominence in a range of applications. It is an established fact that the AC surface can display acidic, basic and/or neutral characteristics depending on the presence of surface functional groups [29].

Considering the above-mentioned, the uptake experiments for the adsorption of REEs from aqueous solution by AC modified with $KMnO_4$ was carried out in this work. Two kinds of the concentrations of $KMnO_4$ (0.01 mol/L and 0.03 mol/L) were used to investigate the efficiency of activated carbon as adsorbent for REEs for more practical use in future. Furthermore, to evaluate the characteristics of AC modified with $KMnO_4$ in this work, the surface morphology, the specific surface area and the functional group of the material were determined by SEM (Scanning Electron Microscope), BET (Brunaeur, Emmet and Teller) method, and FT-IR respectively.

2. EXPERIMENTAL SECTIONS

2.1. Materials

Activated carbon used in the study was purchased from the Sigma-Aldrich, Inc., USA. This product is untreated and granular with a particle size of less than 75 microns (100-400 mesh). The carbon is prepared from wood which has been chemically activated. Chemical reagents including $KMnO_4$ were purchased from Kanto Chemical Co., Inc. (Japan). For all experiments, each stock solution was suitably diluted with deionized water for use. All reagents used were of analytical grade, and water (> 18.2 MΩ) which was treated by an ultrapure water system (Advantec aquarius: RFU 424TA) was employed throughout the work.

2.2. Apparatus

The concentration of REEs was determined by ICP-AES (inductively coupled plasma-atomic emission spectrometry, SEIKO SPS1500). The modified activated carbon was characterized using FT-IR (Fourier transform infrared spectroscopy, FTIR-4200, Jasco, Japan) in pressed KBr pellets, SEM (scanning electron microscopy, JCM-6000, JEOL) and N_2 adsorption/desorption tests (Micromeritics TriStar 3020). The measurement of pH in solution was carried out using a pH meter (HORIBA, F-21, Japan).

2.3. Modification of Activated Carbon Modified with Potassium Permanganate

The AC was washed with deionized water (at 80 °C) to remove fine powder and contaminants, then dried at 110 °C for 2 h before use. 5 g of the activated carbon were placed in a 200 mL conical flask containing 50 mL $KMnO_4$ solution (0.01 or 0.03 mol/L). Adjusting the temperature to 25 °C and stirring for 12 h, the resulting solution was filtrated through 0.45 μm membrane filter. Then, the carbon was washed with deionized water until the pH (of the filtrate) is constant. The activated carbon was dried at 70 °C for 6 h. The pristine and modified (i.e. modified with 0.01 mol/L and 0.03 mol/L $KMnO_4$ solution) activated carbons were described as AC_0, AC_{K1} and AC_{K3}, respectively as below.

2.4. Adsorption Experiments

For investigating the effects of pH, contact time, sorbent dose and initial concentration on the adsorption of REEs, the following adsorption experiments were performed using AC_0, AC_{K1} and AC_{K3}. Activated carbons were thoroughly mixed into the solution (50 mL) containing known amount of REEs in a 200 mL conical flask, and the suspensions were shaken in a water bath at room temperature (25±2 °C). Adsorption experiments were conducted in the pH range of 2-8, adsorbent dosage of 50mg, contact time from 30 min to 12h, and initial concentration of 100 $\mu g \cdot L^{-1}$. The pH of each solution was adjusted by using 0.1 $mol \cdot L^{-1}$ NaOH and 0.1 $mol \cdot L^{-1}$ HNO_3.

Adsorption isotherms of REEs onto carbons were measured at varying initial REEs concentrations under optimized conditions.

Following each adsorption experiment, the suspension containing carbon and the above standard solution was filtered through a 0.45 *μ*m membrane filter (Advantec Mixed Cellulose Ester, 47 mm) to remove REEs that have been adsorbed into the carbon, and the concentration of REEs in the filtrate was determined with an ICP-AES.

The metal uptake by the carbons was calculated using the following equation:

$$q = \frac{(C_i - C_e)}{m} \cdot V \tag{1}$$

where q is the adsorption capacities of REEs using unmodified and modified activated carbon at equilibrium (mg · g^{-1}), C_i and C_e are the initial and equilibrium concentrations of metal ions in a batch system respectively (mg · L^{-1}), V is the volume of the solution (L), and m is the weight of adsorbent (g).

2.5. Adsorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of concentration at constant temperature. The quantity adsorbed is usually normalized by the mass of the adsorbent to allow the comparison of different materials [30-32]. Two common adsorption model, Langmuir and Freundlich isotherm model was applied to evaluate the adsorption data obtained in this study.

Langmuir model assumes monolayer sorption onto a surface and is given by

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \tag{2}$$

where C_e is the concentration of REEs in a batch system at equilibrium (mg·L^{-1}), q_e is the amount of adsorption of REEs at equilibrium (mg·g^{-1}), $q_{\max}$ is the maximum adsorption capacity on the surface of activated carbon (mg·g^{-1}), K_L is the equilibrium adsorption constant (L·mg^{-1}). A plot of C_e/q_e versus C_e gives a straight line with slope of $1/q_{\max}$, and intercept is $1/(K_L q_{\max})$, K_L can be related to the adsorption free energy ΔG_{ads} (J·mol^{-1}), by the following equation:

$$n\Delta G_{\mathrm{ads}} = -RT \ln K_L \tag{3}$$

where R is the gas constant (8.314 J·K^{-1}mol^{-1}), T is the absolute temperature at equilibrium (K), and K_L is the equilibrium constant at temperature T.

The equilibrium constant, b can be calculated from:

$$K_L = q_e / C_e \tag{4}$$

where C_e and q_e were same as mentioned above in Eq. (2).

The equilibrium adsorption constant [33, 34] (K_L) can be used to determine the suitability of the adsorbent to adsorbate by using dimensionless parameter, Hall separation factor [35] (R_L), which is defined as:

$$R_L = \left(\frac{1}{1 + K_L C_0}\right) \tag{5}$$

where C_0 (mg·L^{-1}) is the initial concentration.

The linearized Freundlich model isotherm is represented by the following equation:

$$\log_{10} q_e = \log_{10} K_F + (1/n) \log_{10} C_e \tag{6}$$

The plots of q_e *vs.* C_e in log scale can be plotted to determine values of $1/n$ and K_F from power equation depicting the constants of Freundlich model.

2.6. Kinetic Studies

Kinetic models have been proposed to determine the mechanism of the adsorption process which provides useful data to improve the efficiency of the adsorption and feasibility of process scale-up [36, 37]. In the present investigation, the mechanism of the adsorption process was studied by fitting pseudo first-order and second-order reactions to the experimental data.

The pseudo first-order model is given by the following equation:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{7}$$

where q_e and q_t are the adsorption capacities of REEs using carbon at equilibrium and time t, respectively (mol·g^{-1}), and k_1 is the rate constant of the pseudo-first-order adsorption (h^{-1}).

The linear form of the pseudo second-order rate equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{8}$$

where q_e and q_t are the adsorption capacities of REEs using carbon at equilibrium and time t, respectively (mol·g^{-1}), and k is the rate constant of the pseudo-second-order adsorption (g·mol^{-1}·h^{-1}).

3. RESULTS AND DISCUSSION

3.1. Characteristics of Modified Activated Carbon

The FT-IR spectra of the pristine and modified activated carbons (i.e. AC_0, AC_{K1} and AC_{K3}) are shown in Figure **1**. The carbons displayed the characteristic bands of the graphite structure of carbon at 1615 cm^{-1}. Hydroxyl groups (-OH) stretching band, which is one of the typical peaks of activated carbon, was found at 3300 to 3500 cm^{-1}. The peak at 3433 cm^{-1} may be related to the -OH stretch from deprotonated pristine and modified AC. The wide peak at 1550 to 1750 cm^{-1} shows the asymmetric stretch of the carboxylate group (-COOH). These peaks are generally in good agreement with those in other previous works [21, 38, 39].

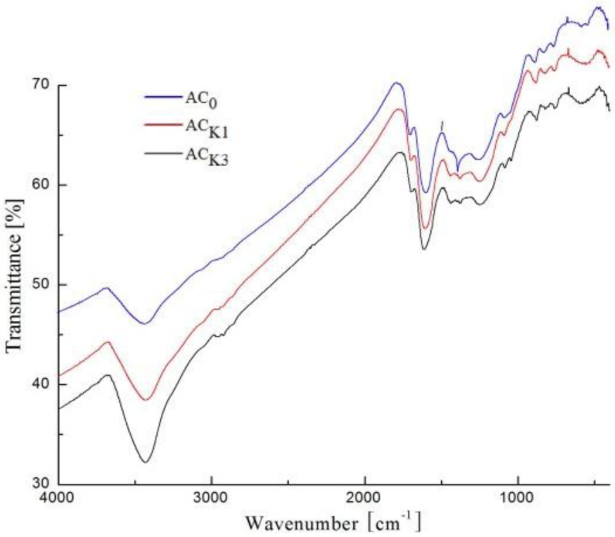


Figure 1: FT-IR spectra of AC_0, AC_{K1}, and AC_{K3}.

The surface properties of the ACs were investigated by N_2 adsorption (TriStar II 3020 Micromeritics), and the analytical results for the adsorption/desorption isotherms are shown in Table **1**.

The pore volume was calculated from the amount of N_2 adsorbed at the relative pressure of 0.99. The pore size was calculated from the adsorption average pore width (4V/A by BET) in this work. From Table **1**, it is found that the pore volume and pore size decreased significantly after modification with $KMnO_4$. The isotherm showed a type H1 isotherm with a clear hysteretic loop, which is characteristic of disordered micro-porous materials.

The SEM micrographs of the ACs are shown in Figure **2**. The modified AC (Figure **2B** and **2C**) seemed to exhibit a more compact stacking morphology than the pristine AC (Figure **2A**), due to cohesive forces, which may be generated from the introduction of oxygen containing functional groups. These results are consistent with those of N_2 adsorption-desorption experiment. The decrease of the pore volume and pore size may be related to the increase of acidic groups on the surface of activated carbon treated with $KMnO_4$.

3.2. Effect of pH

Aqueous solution pH can affect the surface charge of the adsorbent, the degree of ionization and speciation of metal ions and surface metal binding sites [40, 41]. The effect of initial pH on the adsorption of REEs on ACs was investigated over a pH range 2-6 under the initial concentrations of 100 $\mu g \cdot L^{-1}$, and the results are shown in Figure **3**. During the experiment, the pH range was kept below 7.0 in order to avoid any bulk precipitation of REE hydroxides. The adsorption capacity of each REEs on ACs reached maximum at pH3, and more than 80% was observed at pH3 in case of AC_{K3} than AC_0.

This pH dependency can be described by considering a decrease in the positive surface charges at aqueous solution pH [42, 43]. Then, pH 3 was selected as the optimal pH for further work.

3.3. Effect of Contact Time

In order to optimize the contact time required for achievement to equilibrium, adsorption experiments of REEs (initial concentration 100$\mu g \cdot L^{-1}$) from aqueous solutions were performed for 30 min to 12 h by using 50 mg of ACs at pH 3. The representative result is shown in Figure **4** for the case of Sc. It indicates that a relatively fast adsorption of REEs occurred onto AC_{K1} and AC_{K3} than onto AC_0.

Hence, the optimized contact time was taken 8 h for the rest of the experimental work.

Table 1: Textural Characteristics of Activated Carbon

Adsorbent	BET surface area [$m^2 \cdot g^{-1}$]	Pore volume [$cm^3 \cdot g^{-1}$]	Pore size [nm]
AC_0	381	0.402	4.23
AC_{K1}	373	0.390	4.18
AC_{K3}	346	0.348	4.03

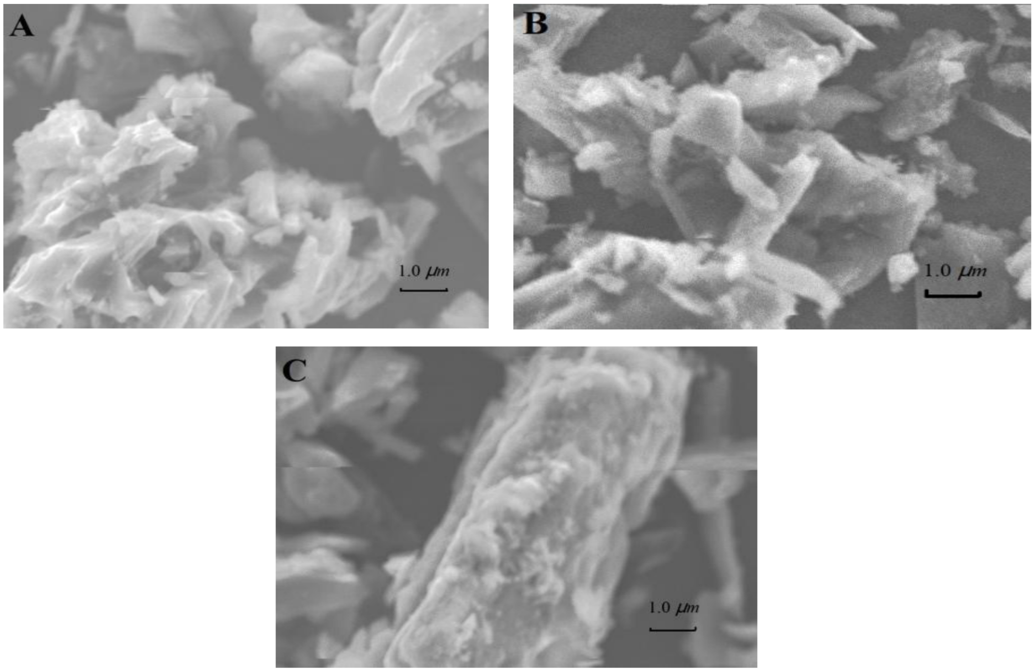
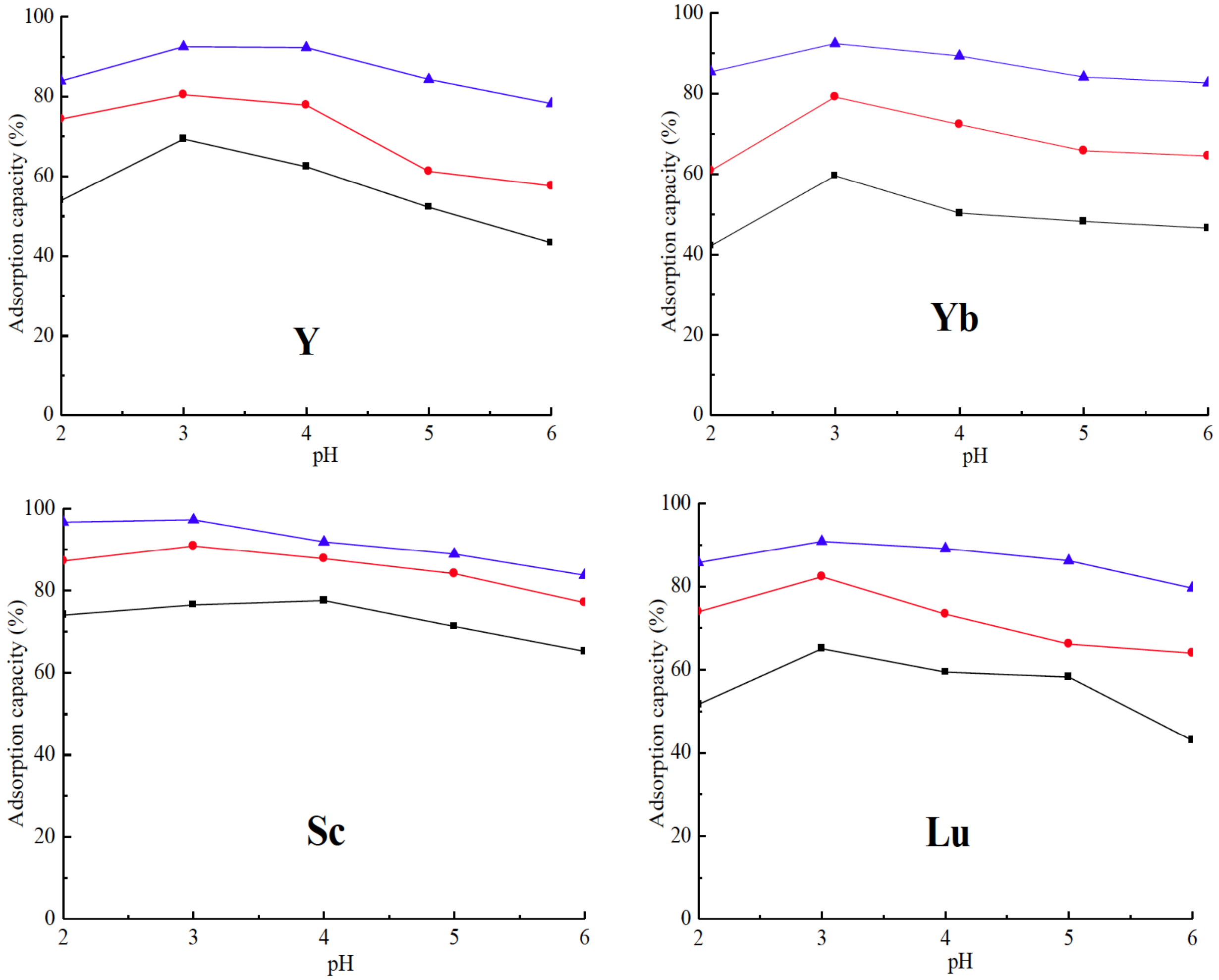


Figure 2: SEM micrographs of the surface of activated carbon: (**A**) unmodified; (**B**) modified with 0.01 mol/L $KMnO_4$; (**C**) modified with 0.03 mol/L $KMnO_4$.



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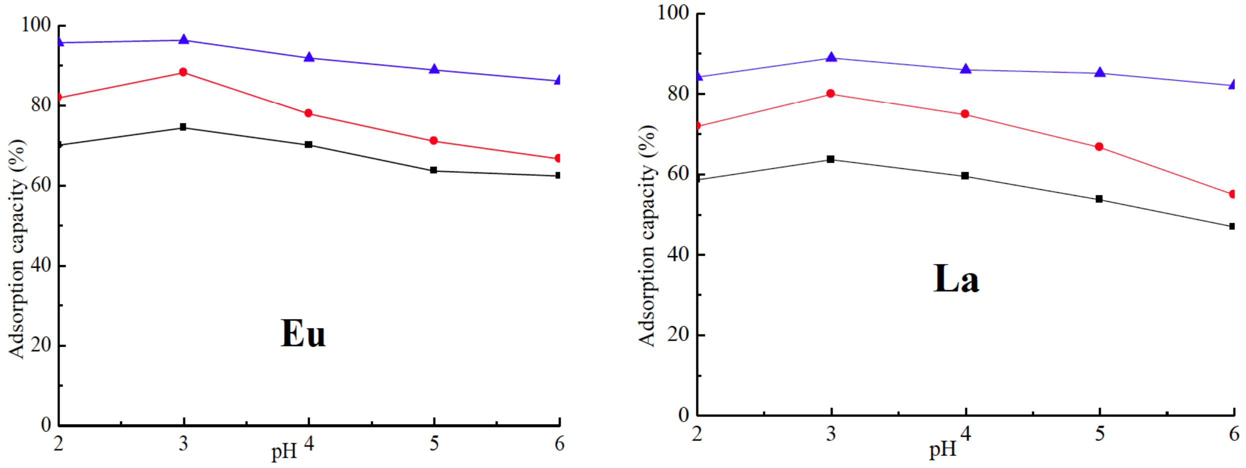


Figure 3: Effect of pH on the removal of REEs using ACs (■: AC$_0$; ●:AC$_{K1}$; ▲: AC$_{K3}$).

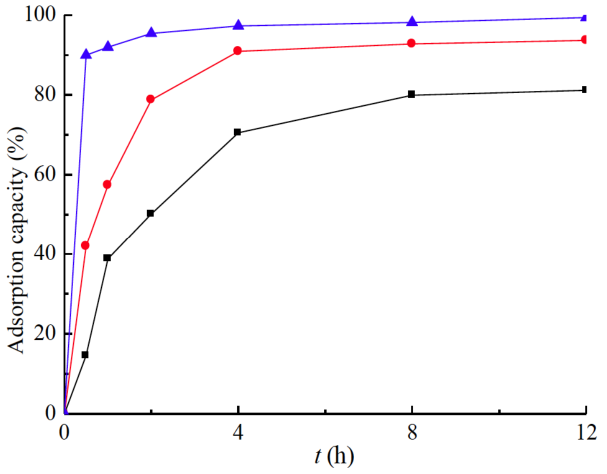


Figure 4: Effect of contact time on the removal of Sc using ACs (■: AC$_0$; ●:AC$_{K1}$; ▲: AC$_{K3}$).

3.4. Adsorption Isotherms

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes. The adsorption data obtained for REEs using ACs were analyzed by Langmuir and Freundlich equations. The correlation coefficient (R^2) of these isotherms for REEs on ACs is shown in Table **2** along with other relevant parameters.

From Table **2**, it is found that the adsorption capacity of REEs by AC$_{K1}$ and AC$_{K3}$ were larger than that by AC$_0$. It indicates that the surface modification by the impregnation of $KMnO_4$ was effective. Adsorption of REEs onto these materials may be occurred by ion exchange between functional groups such as carboxylic or phenolic hydroxyl and metallic ions.

Then, the improvement of the adsorption capacity may be attributable to the creation of the functional groups (e.g., -COOH) by carbon oxidation as well as the formation of the adsorption site by production of MnO_2 with the impregnation of $KMnO_4$.

From Table **2**, it is also found that R^2 value for REEs is comparatively large, and favorable adsorption of REEs by ACs was presented. Particularly, R^2 values in Langmuir isotherm are large for all REEs. This result suggests that the adsorption of REEs on ACs mainly occurred by monolayer reaction. From the nature of the material, multiple binding sites are available, and both physical and chemical adsorptions may occurred in these ACs.

Based on the data, the linear plots of C_e/q_e-C_e were presented for Langmuir, and are shown in Figure **5**. It is indicated that favorable adsorption for REEs by the activated carbon is presented.

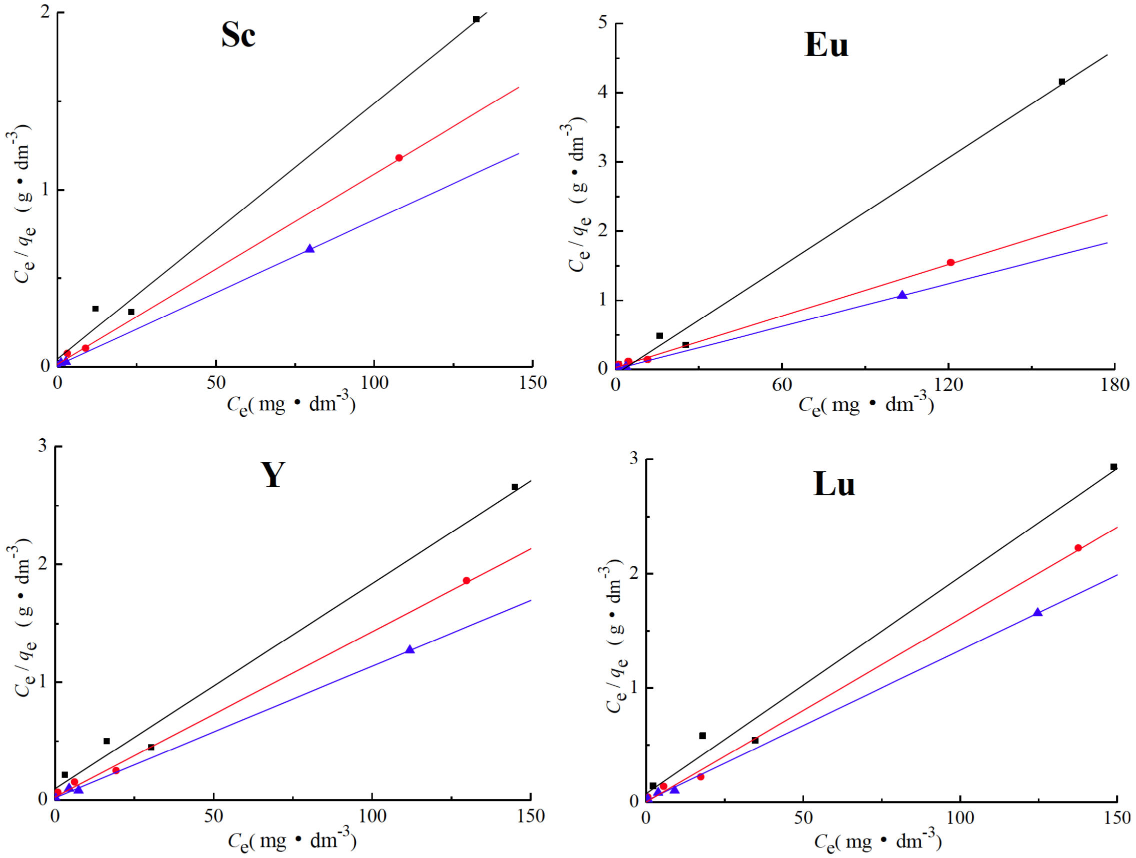
3.5. Kinetic Studies

Kinetic models were tested in this study for the sorption of REEs onto ACs under optimized experimental conditions. The results for rate constant (k) and the amount of adsorbed REEs (q_e) are shown in Table **3** along with the regression coefficients (R^2). From this table, it is found that the pseudo second-order kinetic model provided more comparable than the pseudo first-order model.

It implies that the adsorption kinetics based on the experimental values is in good agreement with the pseudo second-order kinetic model. It is considered that the rate determining step might be chemical, and that the adsorption process involves the valency forces through sharing electrons between the metal ions and adsorbent.

Table 2: Coefficient of Langmuir and Freundlich Isotherms for REEs

		Langmuir isotherm			Freundlich isotherm		
		q_{max} [μg·g^{-1}]	K_L [L·μg^{-1}]	R^2	K_F [(μg·g^{-1})·(L·μg^{-1})$^{1/n}$]	1/n	R^2
La	AC_0	48.0	0.291	0.992	11.9	0.334	0.779
	AC_{K1}	57.9	0.341	0.998	23.8	0.245	0.773
	AC_{K3}	71.0	1.11	0.999	28.2	0.252	0.763
Yb	AC_0	53.1	0.250	0.996	15.3	0.282	0.912
	AC_{K1}	70.8	0.418	0.999	21.0	0.304	0.844
	AC_{K3}	84.6	0.612	0.999	31.4	0.261	0.845
Lu	AC_0	52.7	0.257	0.993	15.1	0.289	0.859
	AC_{K1}	62.4	1.48	0.999	26.4	0.238	0.828
	AC_{K3}	75.9	1.78	1.00	31.0	0.247	0.820
Eu	AC_0	38.4	0.378	0.996	18.2	0.282	0.957
	AC_{K1}	80.6	0.433	1.00	25.2	0.300	0.821
	AC_{K3}	97.2	1.76	1.00	42.8	0.235	0.837
Y	AC_0	57.4	0.182	0.993	13.2	0.342	0.839
	AC_{K1}	71.2	0.559	0.999	23.0	0.286	0.873
	AC_{K3}	89.5	0.601	0.999	33.5	0.256	0.882
Sc	AC_0	69.3	0.330	0.996	26.7	0.367	0.974
	AC_{K1}	93.0	0.797	1.00	43.0	0.301	0.985
	AC_{K3}	121.5	1.22	1.00	58.1	0.288	0.982



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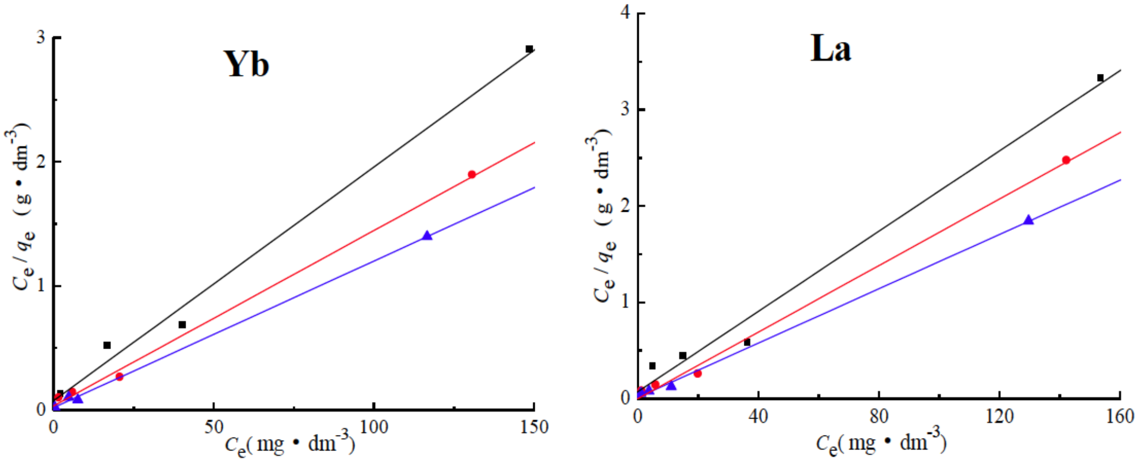

Figure 5: Langmiur isotherm of REEs adsorption onto ACs (■: AC_0; ●:AC_{K1}; ▲: AC_{K3}).

Table 3: Kinetic Coefficient for REEs Adsorption on Adsorbents

		pseudo-first-order			pseudo-second-order		
		q_e (μg·g^{-1})	k_1 (h^{-1})	R^2	q_e (μg·g^{-1})	k_2 (10^{-2}·g·μg^{-1}·h^{-1})	R^2
La	AC_0	46.6	0.394	0.981	83.5	0.776	0.995
	AC_{K1}	49.7	0.401	0.980	92.9	1.39	0.999
	AC_{K3}	69.7	0.440	0.959	99.9	1.56	0.999
Yb	AC_0	43.9	0.377	0.955	82.7	0.126	0.995
	AC_{K1}	60.0	0.390	0.979	97.6	1.08	0.999
	AC_{K3}	85.0	0.428	0.959	102	1.80	1.00
Lu	AC_0	38.4	0.337	0.954	58.8	0.236	0.964
	AC_{K1}	50.8	0.339	0.959	95.1	1.26	0.999
	AC_{K3}	66.0	0.381	0.907	99.1	1.99	0.99
Eu	AC_0	39.1	0.432	0.992	79.4	0.378	0.994
	AC_{K1}	50.6	0.457	0.951	101	1.22	0.998
	AC_{K3}	82.1	0.529	0.968	104	2.41	1.00
Y	AC_0	45.9	0.288	0.986	93.5	0.471	0.993
	AC_{K1}	48.0	0.440	0.954	97.8	1.41	1.00
	AC_{K3}	79.3	0.462	0.959	103	1.63	0.999
Sc	AC_0	8.48	0.261	0.957	91.3	0.942	0.993
	AC_{K1}	51.3	0.477	0.968	98.9	1.54	0.996
	AC_{K3}	66.7	0.553	0.951	100	1.90	1.00

Generally, the adsorption takes place in two steps. The first linear region represents the stage of film diffusion, which is the diffusion of REEs from the bulk solution to the external surface of the ACs. The second region can be attributed to intraparticle diffusion stage due to the rough surface and voids within the ACs. The film diffusion stage is larger than the intraparticle diffusion stage, which is represented by larger slope (k_p). The lower slope for the intraparticle diffusion indicates more gradual process, which is consistent with the parameters of Weber's intraparticle diffusion model [44]. Most of the plots do not pass through the origin, indicating the intraparticle diffusion is not the rate limiting step [45]. The intercept reflects the boundary layer effect, that is, the larger the intercept, the greater the contribution of the surface adsorption in the rate controlling steps [46].

3.6. Regeneration Studies

From industrial and technological point of view, it is desirable to recover and reuse the adsorbed material. Then, preliminary regeneration experiments were conducted using AC_{K3} after adsorption of La(III) at pH 3. In each desorption experiment, 50 mg of the spent adsorbent after adsorption was treated with 50ml of each desorption agent, and then filtered. La(III) content in the filtrate was determined by ICP-AES. Adsorption and desorption studies have been continued during five cycles by using HCl (5% and 10%), HNO_3 (5% and 10%) and NaOH (5% and 10%) at 90°C for 4h as eluent. The adsorption capacity after desorption using the above leaching agents are shown in Figure **6**.

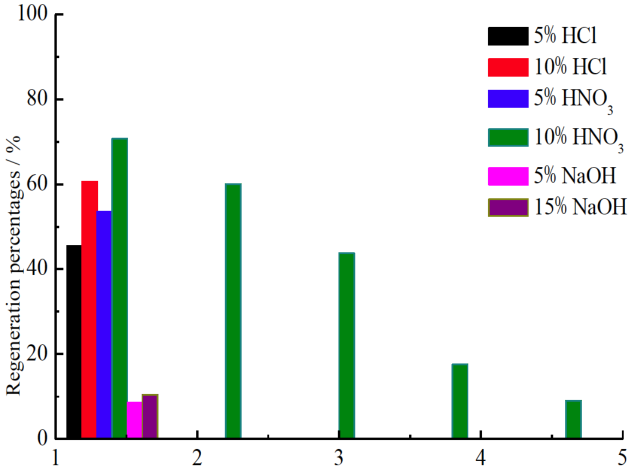

Figure 6: The adsorption capacity after desorption using various leaching agents for La (III).

From this figure, it is found that the desorption rate of La (III) from the adsorbent are dependent upon the nature of the extracting solution, and 10% HNO_3 is more suitable for the desorption agent. ACs still present the high adsorption capacity towards La within 3 cycles.

4. CONCLUSIONS

The present study investigated the efficiency of activated carbon modified with $KMnO_4$ as adsorbent for REEs by batch techniques. The following conclusions can be drawn considering the results of this work.

(1) Adsorption capacity of REEs by AC_{K1} or AC_{K3} were larger than that by AC_0. It indicates that the surface modification with $KMnO_4$ was effective. Adsorption of REEs onto these materials can generally be attributed to ion exchange between functional groups such as carboxylic or phenolic hydroxyl and metallic ions.

(2) The adsorption isotherm of REEs by ACs was more suitably described by Langmuir model, and the correlation coefficients were more than 0.99 for all REEs. It suggests that monolayer chemical adsorption of REEs on ACs is more dominant.

(3) The rates of adsorption were conformed to pseudo-second order kinetic model while investigating the adsorption kinetics, and the correlation coefficients were both more than 0.99 for all REEs. This analysis revealed that the rate determining step might be the adsorption processes involved the valency forces through sharing electron between the metallic ions and adsorbents.

(4) Desorption of La (III) from the adsorbent has been found to depend upon the nature of the extracting solution. ACs still present the high adsorption capacity towards La for the adsorption/desorption behavior within 3 cycles by 10% HNO_3.

From this work, it was quantitatively clarified to some extent that ACs could be an efficient adsorbent for REEs. They created new avenues for the treatment of industrial waste waters including pollutants. It is very significant information from the viewpoint of environmental protection.

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