

Surface modified granular activated carbon for enhancement of nickel adsorption from aqueous solution

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(Received 19 March 2009 • accepted 6 May 2009)

Abstract—Coal-based granular activated carbon was modified with acetates of sodium, potassium and lithium at concentrations of 10 and 15% and used as adsorbents to explore the adsorption mechanism of nickel ion in aqueous solution. Acetate treatment reduced surface area and pore volume of the activated carbons, but the adsorption amount of Ni(II) on the modified activated carbons (MAC) was greater than that on the virgin activated carbon. The adsorption depended on pH of the solution with an optimum at 4.5 and the adsorbed nickel could be fully desorbed by using 0.05 M HCl solution. The maximum adsorption capacity of nickel ion on Li (15 wt%) modified activated carbon was 151.3 mg/g and the adsorption isotherm follows Langmuir, Sips, and Redlich-Peterson isotherm models better than the Freundlich isotherm model. The kinetic data was better fitted by a non-linear form of the pseudo-first order than the pseudo-second order, but the difference between two kinetic models was small.

Key words: Activated Carbon, Surface Treatment, Nickel, Adsorption, Desorption

INTRODUCTION

Rectifying environmental pollutants from industrial wastes and wastewaters is an important environmental problem of global concern. Environmental pollutants contain organic and inorganic hazardous materials and heavy metals. The heavy metals such as lead, cadmium, nickel, copper and zinc, are among the most common pollutants found in industrial effluents. The metals are of special concern due to their toxicity and persistency properties in nature.

Nickel is a toxic metal that is extensively used in electroplating, silver refineries and storage battery industries. Exposure to nickel has been known to cause severe health disorders to humans [1-3]. Hence, it is necessary to remove nickel from industrial wastewater before being discharged. Several methods such as chemical precipitation, electrochemical reduction, reverse osmosis, membrane filtration, electro dialysis, adsorption and biosorption [4] are widely used to remove the heavy metals. Due to the cost and suitability, carbon adsorption is the smartest process among these methods. The removal of toxic metals using adsorption by activated carbon has been extensively studied [5-18].

Activated carbon is able to adsorb heavy metals because of its large surface area, micro-pore character and acidic functional groups. Adsorption capacity and selectivity for specific environmental pollutants can be tailored by modifying their pore structure and surface chemical properties [19,20]. Oxidative and non-oxidative methods have been used to modify the interfacial region of the activated carbon. Non-oxidative surface modification using impregnation, anchoring and grafting has offered a substantial interest in recent

years. For example, tannic acid modified activated carbon (MAC) has an effective removal capacity for metal ions [12]. Activated carbon modified with sodium diethyl dithiocarbamate [13], cetylpyridinium chloride [14], Fe^{3+} [15], citric acid [17] and sodium acetate [18] has been used for the removal of heavy metals from aqueous solution.

The objective of this study was to remove nickel(II) ions from aqueous solution and compare the adsorption performance of three acetates, namely sodium, potassium and lithium-modified activated carbons, with the unmodified granular activated carbon. The nickel adsorption equilibrium and kinetics were determined at various pH and concentration conditions. Langmuir, Freundlich, Sips and Redlich-Peterson equations were employed to quantify the adsorption equilibrium.

EXPERIMENTAL PROCEDURE

1. Materials

Granular activated carbon (GAC) was purchased from Calgon, Japan and analytical grades of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{C}_2\text{H}_3\text{O}_2\text{Na}$, $\text{C}_2\text{H}_3\text{O}_2\text{K}$ and $\text{C}_2\text{H}_3\text{O}_2\text{Li}$ (Sigma Aldrich Ltd., Korea) were used without further purification. Acid and bases were of the highest purity obtained from Sigma Aldrich. Doubly distilled deionized water was used throughout the experiment.

2. Preparation of Surface Modified Activated Carbon

Granular activated carbon was washed twice with deionized water to remove any impurity, then dried in an oven at 110 °C for 24 h. Granular activated carbon (10 g) was treated with 200 ml aqueous solution of 10% and 15% of acetates of sodium, potassium and lithium for 72 h. The impregnation was carried out at 70 °C till the complete evaporation of water and then dried in oven at 120 °C for 24 h

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to produce modified activated carbon such as NaAC10, NaAC15, KAC10, KAC15, LiAC10 and LiAC15, respectively. The dried material was washed with deionized water till the washing liquid became free from metal ion and dried.

3. Analytical Methods

According to the BET method, the physical properties such as surface area, micropore area and average pore diameter were measured with a Micromeritics ASAP 2020. Scanning electron microscopy (SEM, S-4200 Hitech, Japan) was used to observe the surface structure of acetate treated carbon before and after adsorption of Ni(II) ions. Ni contents for activated carbon before and after adsorption of Ni(II) ion was observed by Energy dispersive X-ray (EDX-KeveX Superdry). FT-IR spectra for the samples were recorded on an FT-IR spectrophotometer (FTS-3000MX, Digilab) using KBr pellet.

Batch adsorption studies were conducted to determine the equilibrium time needed to reach saturation. Three samples at the same condition were prepared. Then each equilibrium amount of adsorption was averaged from the samples which were within $\pm 3\%$. Adsorption kinetics were carried out using 10 ml of metal ion solution containing the desired concentration at initial pH 4.5 and 500 mg of adsorbent in a vial (agitation speed 185 rpm). In the experiment, the desired pH of the solution was measured at every 30 min interval and maintained at 4.5 ± 0.1 by the drop-wise addition of acid or bases when required.

At predetermined time intervals, samples were withdrawn and separated by centrifugation at 15,000 rpm for 15 min, and Ni(II) ion content in the supernatant was determined by UV spectrophotometer (1601 PC, Shimadzu). The amount of metal ion adsorbed was calculated from the difference between the quantity of metal ions added to the modified activated carbon and the metal ion content of the supernatant with the following equation:

$$q = \frac{V(C_0 - C_f)}{M} \quad (1)$$

where q is the amount adsorbed (mg/g); C_0 and C_f are the initial and equilibrium nickel concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M the mass of carbon (g). The pH of the aqueous solution was adjusted by using 0.1 M HCl and 0.1 M NaOH solutions.

RESULTS AND DISCUSSION

1. Characterization of Adsorbents

As shown in Table 1, the surface area and pore volume of GAC were reduced after treatment with acetates. On the other hand, the average pore diameter was slightly increased. This may be due to

several factors such as pore entrance blockage by oxygenated surface functional groups and large molecules of residual humic-type compounds, electrostatic repulsion of surface probe molecules and erosion of carbon by acetates [18]. It is noted that the reduction of surface area of LiAC15 was smaller than the others, while the micropore volumes of all three modified GAC are almost same. Furthermore, LiAC15 has the largest average pore diameter in the modified activated carbons. In this study, the adsorption capacity of the surface modified activated carbons was compared to that of the virgin GAC.

Fig. 1 shows the SEM micrographs of GAC, NaAC15, LiAC15 and nickel adsorbed LiAC15. There are small cavities, cracks and attached fine particles over the activated carbon surface, forming a system of complicated pore networks. Comparison of these micrographs shows that sodium and lithium acetate modification leads to an increase of fine particles on the carbon surface. However, the surface of the activated carbon adsorbed by Ni(II) (Fig. 1(d)) does not show any large difference from that of nickel unloaded carbons.

Fig. 2 shows FT-IR spectra of LiAC15 and nickel adsorbed LiAC15. From the spectra (A) of Fig. 2, the peak at $3,433 \text{ cm}^{-1}$ can be assigned to -OH stretch from carboxylic groups (-COOH and -COH). The peaks at $\sim 1,700$ and $1,566 \text{ cm}^{-1}$ are associated with the carboxylic acid and carboxylate anion stretch mode, and the adsorption band at $\sim 1,412 \text{ cm}^{-1}$ assigned to lactones [21]. The band at $\sim 2,900 \text{ cm}^{-1}$ is attributed to C-H stretching mode. The spectra (B) of Fig. 2 show the changes in the spectrum of LiAC15 after the adsorption of nickel. The peak at $3,433 \text{ cm}^{-1}$ has shifted to $3,428 \text{ cm}^{-1}$ and the peak at $1,566 \text{ cm}^{-1}$ has shifted to $1,560 \text{ cm}^{-1}$ after nickel adsorption. The peak for lactones seems to be overlapped by the shifted peaks. Thus, it can be reasonably concluded that the oxygen atom should be the main adsorption site for nickel attachment on LiAC15. The oxygen-containing functional groups can provide numerous chemical sorption sites for the nickel adsorption.

2. Metal Ion Removal

The experimental results depicted in Fig. 3 indicated that Ni(II) ion adsorption is in the order: LiAC15 (151.3 mg/g) > LiAC10 (149.1 mg/g) > KAC15 (136.7 mg/g) > KAC10 (133.7 mg/g) \geq NaAC15 (133.3 mg/g) > NaAC10 (127.9 mg/g) > GAC (122.1 mg/g). The addition of carboxylic functional groups at the surface of the activated carbon leads to an increase in metal ion removal because of the high affinity of the carboxylic functional group for metal ions [17]. Percentage of nickel was found to be 7.79% (GAC), 8.42% (NaAC15), 9.21% (KAC15) and 16.43% (LiAC15) by energy dispersive X-ray (EDX-KeveX Superdry). Due to the higher adsorption efficiency of LiAC15, this was used for all the other experimental studies. By increasing the Ni(II) ion concentration from 100 mg/L to 1,000 mg/L, the amount adsorbed increased from 19.7 mg/g to 151.3 mg/g at

Table 1. BET analysis for activated carbons

Physical parameters	GAC	NaAC15	KAC15	LiAC15
Specific surface area (m^2/g)	937.66	774.29	764.44	835.38
Langmuir surface area (m^2/g)	1,380.91	1,137.15	1,127.72	1,155.58
Micropore volume (mL/g)	0.3928	0.3292	0.3248	0.3327
Micropore area (m^2/g)	748.04	634.11	622.32	687.75
External surface area (m^2/g)	189.62	140.19	142.11	147.62
Average pore diameter (\AA)	24.08	25.94	26.79	28.21

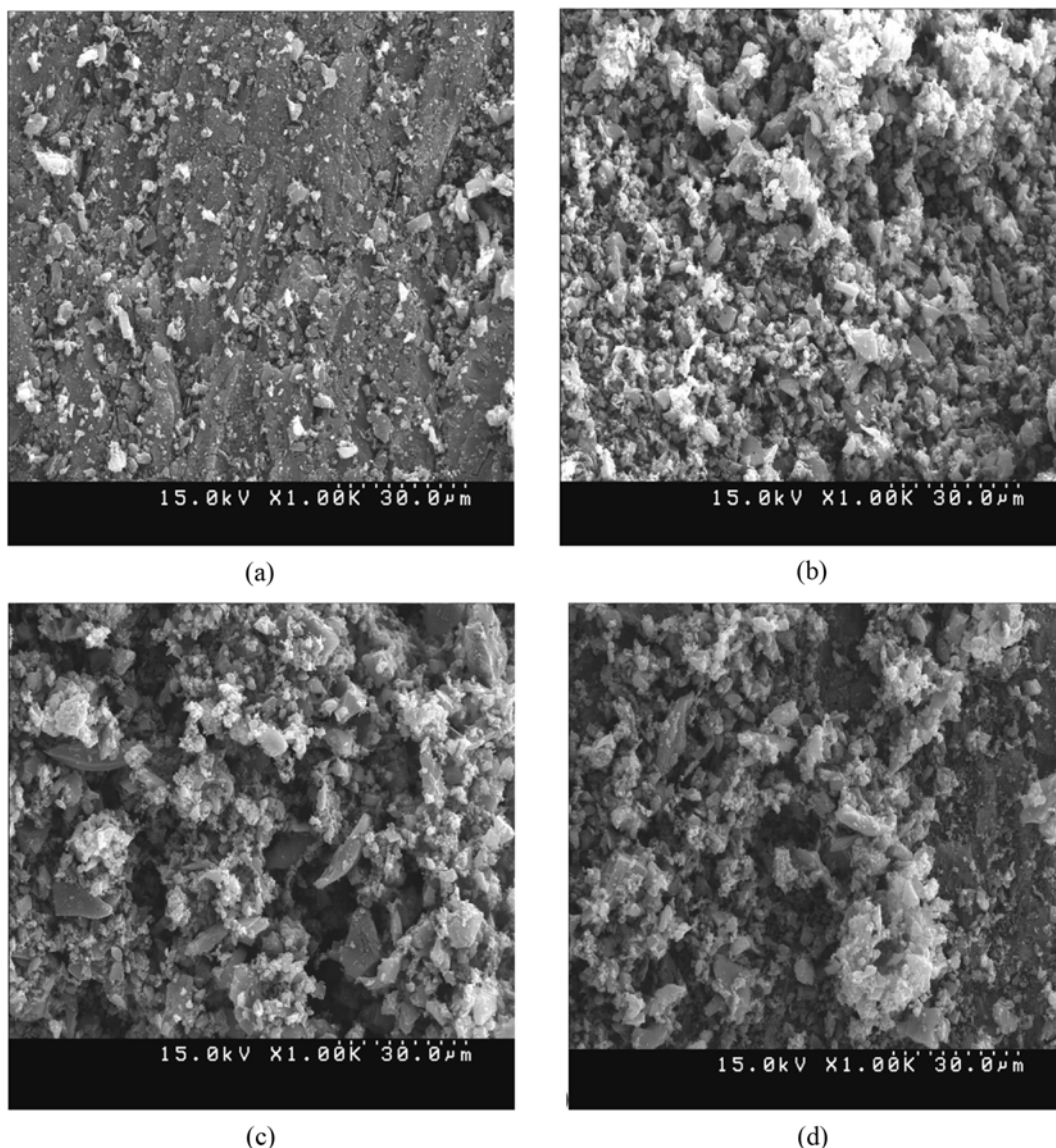


Fig. 1. SEM images of the surface of the carbons: (a) GAC (b) NaAC15 (c) LiAC15 (d) LiAC15 after adsorption with Ni(II) ion.

pH 4.5; however, the percentage of Ni(II) ion removal decreased from 98% to 76% for LiAC15.

The experimental results obtained from nickel ion adsorption by LiAC15 under different initial pH conditions are shown in Fig. 4. LiAC15 dosage (500 mg/L), nickel ion (1,000 mg/L) and agitation speed (185 rpm) were kept constant in all experiments. The Ni(II) ion adsorbed by LiAC15 was sensitive to pH variation over the examined range of 2 to 5. The adsorption amount increased with increasing pH to reach a maximum at pH 4.5. At pH < 4.5, H^+ ions compete with Ni(II) ions for the surface of the adsorbent, which would restrict the approach of Ni(II) ions due to the repulsion [22]. Hence, the metal removal is the lowest amount presumably due to the enhanced competition of proton with nickel ions for ligand binding sites and complex formation. The condition of pH > 4.5, noted in adsorption decrease, may be attributed to precipitation of the nickel ions as hydroxides [22]. For this reason, the optimal pH value was selected to be 4.5.

The mechanism of metal ion adsorption may be explained based

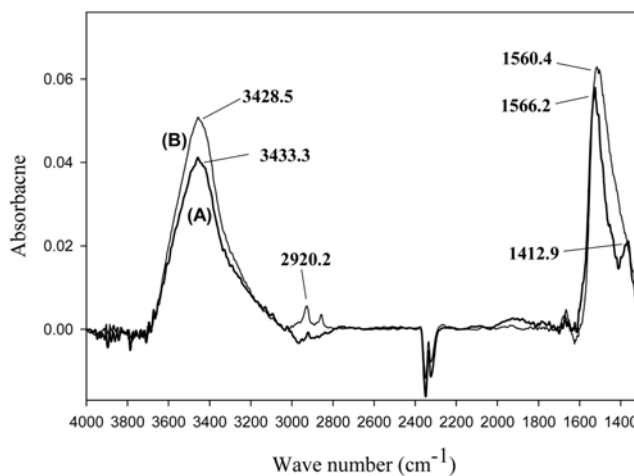


Fig. 2. FT-IR spectra of the activated carbons: (A) LiAC15 and (B) LiAC15 after adsorption with Ni(II) ion.

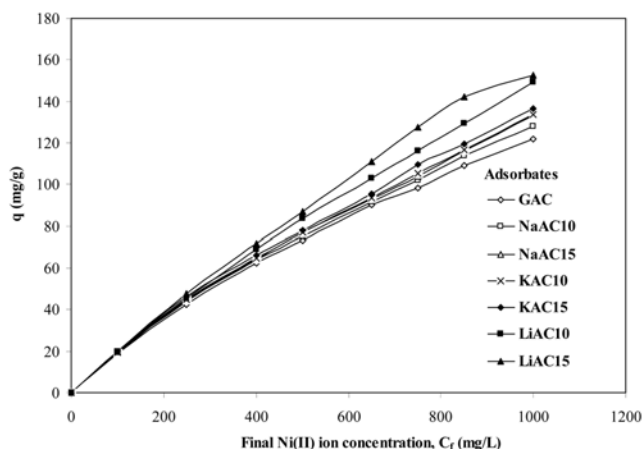


Fig. 3. Adsorption amounts of Ni(II) ion on various acetate-modified activated carbons: adsorbent dosage=500 mg/L and pH=4.5.

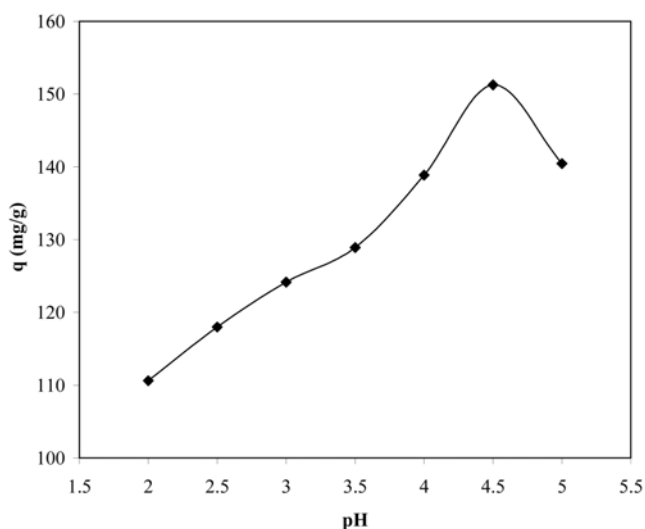


Fig. 4. Effect of pH on Ni(II) ion (1,000 mg/L) adsorption by LiAC15 (500 mg/L of adsorbent dosage).

on ion exchange model. In activated carbon, carbon-oxygen complexes and other oxygen complexes are present. The surface oxygen complexes are hydrolyzed by water molecules as shown below:



This is confirmed by decreasing the final pH of the solution. This obviously shows that the concentration of H^+ increases during the uptake of more metal ions.

Since carbon is modified with acetates of Na^+ , K^+ , Li^+ , these metal ions exchange with H^+ in the aqueous medium as follows:



While increasing the nickel ion concentration, the reaction is as follows:



From the Eqs. (2), (3) and (4), the -OH group is involved for the adsorption of metal ions.

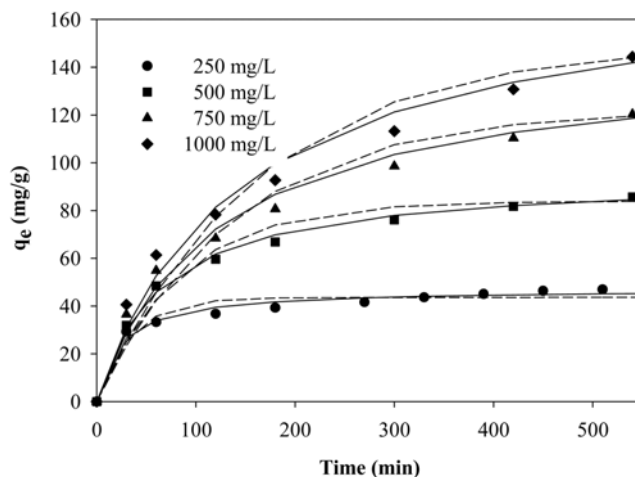


Fig. 5. Effect of contact time on adsorption of Ni(II) ion onto LiAC15 (500 mg/L of adsorbent dosage and pH 4.5): curves predicted by the pseudo-first order kinetic model (---) and the pseudo-second order kinetic model (—).

After the adsorption was completed, 0.05 M HCl was added to the adsorbent in order to elute the adsorbed metal ions. In the acid medium, protons (H^+ ions) compete with Ni^{2+} ions and displace the same. A 99.9% recovery of adsorbed metal ion was achieved. This is further evidence that ion exchange is involved in the adsorption process.

3. Adsorption Kinetics

Fig. 5 shows the effect of agitation time and initial concentration on removal of nickel ion by LiAC15 at pH 4.5. It is evident from Fig. 5 that the adsorption of nickel ion increases rapidly with time as well as with the increase of the initial ion concentrations. However, the time to reach the adsorption equilibrium takes longer with an increase in the concentration.

To investigate the mechanism of adsorption, kinetic models are applied to experimental data. The pseudo-first-order kinetic model can be expressed as [23]:

$$q = q_e (1 - \exp(-k_1 t)) \quad (5)$$

In addition, the non-linear form of the pseudo-second kinetic order model was also applied to the present study as follows:

$$q = q_e \left(1 - \frac{1}{1 + q_e k_2 t} \right) \quad (6)$$

where, q is the amount adsorbed (mg/g), q_e is the amount adsorbed at equilibrium time (mg/g), k is the adsorption rate constant (1/min) and t is the time (min). The pseudo-second order model is based on the adsorption capacity on the solid phase. Contrary to other well established models, it predicts the behavior over the whole range of studies and it is in agreement with the chemisorptions mechanism being the rate-controlling step [24].

The rate constants and predicted equilibrium amount at all the concentrations have been calculated and are summarized in Table 2. In the pseudo-first-order model, the calculated k_1 values decrease with increase in Ni(II) ion concentration (Table 2). The experimental and calculated values of q_e are very close; thus, the pseudo-first-order kinetic model is suitable for modeling the adsorption of nickel. However, as shown in Table 2 and Fig. 5, the calculated values of

Table 2. Kinetic constants for Ni(II) ion adsorption by LiAC15

Ni(II) ion concn (mg/L)	First order kinetic model				Second order kinetic model		
	q_e (exp) (mg/g)	k_1 (1/min) $\times 10^{-2}$	q_e (cal) (mg/g)	R^2	k_2 (g/mg/min) $\times 10^{-2}$	q_e (cal) (mg/g)	R^2
250	43.62	0.029	43.61	0.942	0.001	47.14	0.981
500	85.66	0.012	83.95	0.973	0.0002	94.46	0.996
750	123.7	0.007	122.1	0.969	0.00005	145.2	0.988
1000	148.2	0.006	149.6	0.972	0.00003	179.9	0.988

q_e in the pseudo-second-order kinetic model are more accurate for the experimental adsorption.

4. Adsorption Isotherm

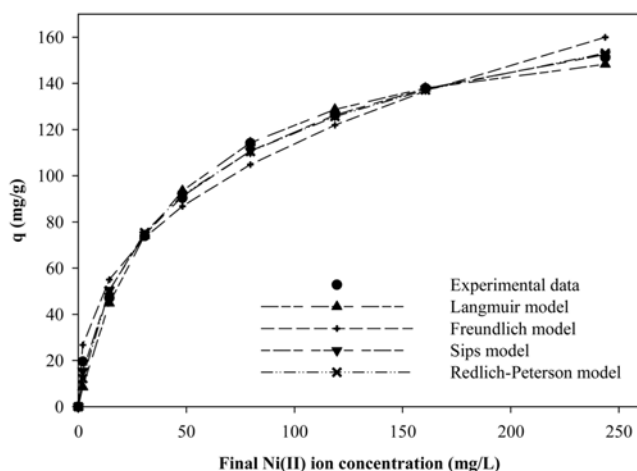


Fig. 6. Comparison of Langmuir, Freundlich, Sips and Redlich-Peterson models to experimental isotherm data obtained from Ni(II) ion adsorption by LiAC15 (pH 4.5, agitation speed=185 rpm, adsorbent dosage=500 mg/L).

To optimize the design of an adsorption system for the removal of metal from effluents, it is important to establish the most appropriate correlation for equilibrium curves. Experimental isotherm data acquired at different pH were fitted with the adsorption isotherm models with two or three parameters: Langmuir, Freundlich, Sips and Redlich-Peterson isotherm models [25]. Fig. 6 shows the application of all the isotherm models to experimental isotherm data of LiAC 15, which was measured at pH 4.5. And the isotherm parameters related to each model obtained from the experimental data are listed in Table 3.

The experimental data for various pH conditions were fitted with the Langmuir isotherm model:

$$q = \frac{q_{\max} b_L C_f}{1 + b_L C_f} \quad (7)$$

where q_{\max} is the maximum amount of metal adsorbed (mg/g), b_L the Langmuir equilibrium constant (L/mg) and C_f is the equilibrium concentrations (mg/L). The Langmuir model served to estimate the maximum amount of metal adsorbed values where they could not be reached in the experiments. The constant b_L represents the affinity between the adsorbent and adsorbate. Both q_{\max} and b_L increase with increasing pH from 2 to 4.5, while further increase in pH decreases both constants (Table 3). High values of b are reflected in the steep initial slope of an adsorption isotherm, indicating desirable

Table 3. Isotherm constant of two-and three- parameter models for adsorption of Ni(II) ion by LiAC15

Models		pH						
		2.0	2.5	3.0	3.5	4.0	4.5	5.0
Two parameter								
Langmuir	q_{\max} (mg/g)	132.7	146.6	157.7	159.8	167.8	173.3	165.8
	b_L (L/mg)	0.0101	0.0103	0.0106	0.0134	0.0168	0.0243	0.0211
	R^2	0.995	0.995	0.994	0.992	0.986	0.993	0.989
Freundlich	K_F (L/mg)	9.35	10.11	10.50	13.57	15.38	20.13	19.44
	n_F (L/mg)	2.42	2.38	2.33	2.51	2.49	2.65	2.75
	R^2	0.988	0.985	0.981	0.973	0.972	0.987	0.974
Three parameter								
Sips	K_S (L/mg)	3.292	3.133	2.968	3.071	4.875	9.747	7.339
	a_S (L/mg)	0.0198	0.0180	0.0165	0.0180	0.0245	0.0442	0.0376
	β_S (L/mg)	0.758	0.804	0.843	0.899	0.822	0.714	0.768
	R^2	0.998	0.998	0.996	0.993	0.989	0.998	0.992
Redlich-Peterson	K_{RP} (L/mg)	2.134	2.000	1.923	2.441	2.967	6.869	4.171
	a_{RP} (L/mg)	0.0539	0.0319	0.0203	0.0234	0.02430	0.1068	0.0389
	β_{RP} (L/mg)	0.809	0.865	0.918	0.930	0.940	0.825	0.925
	R^2	0.998	0.996	0.995	0.992	0.987	0.996	0.989

high affinity. Therefore, LiAC15 performed well in nickel adsorption at pH 4.5 compared to other pH values examined.

The Freundlich isotherm was originally empirical in nature, but was later interpreted as adsorption to heterogeneous surfaces. It is represented as follows:

$$q = K_F C_F^{1/n_F} \quad (8)$$

where q is the amount adsorbed at equilibrium (mg/g), K_F is the Freundlich constant (L/g), C_F is the equilibrium concentration (mg/L) and n_F is the Freundlich exponent. At pH 4.5, both K_F and $1/n_F$ reached their corresponding maximum values. This implies that the binding capacity reaches the highest value and the affinity between the adsorbent and nickel ions is also higher than other pH values. However, as shown in Fig. 6 and Table 3, the Freundlich isotherm showed relatively large deviation from the experimental data.

Sips or Langmuir-Freundlich isotherm has the following form:

$$q = \frac{K_S C_F^{\beta_S}}{1 + a_S C_F^{\beta_S}} \quad (9)$$

where q is the amount adsorbed at equilibrium (mg/g), K_S is the Sips model isotherm constant (L/mg), C_F is the equilibrium concentration (mg/L), a_S is the Sips model constant (L/mg) and β_S is the Sips model exponent. The exponent β_S values were close to unity as shown in Table 3. It means that nickel adsorption data obtained in this study is more of Langmuir form rather than Freundlich form, which is also confirmed in Table 3.

The Redlich and Peterson isotherm model is as follows:

$$q = \frac{K_{RP} C_F}{1 + a_{RP} C_F^{\beta_{RP}}} \quad (10)$$

where q is the amount adsorbed at equilibrium (mg/g), K_{RP} is the isotherm constant (L/mg), C_F is the equilibrium concentration (mg/L), a_{RP} is the constant (L/mg), and β_{RP} is the exponent in the Redlich-Peterson model. The exponent, β_{RP} , lies between 0 and 1. There are two limiting behaviors: Langmuir form for $\beta=1$ and Henry's law form for $\beta=0$.

The Redlich-Peterson isotherm constant, K_{RP} , and model constant, a_{RP} , increased with pH and reached maximum at pH 4.5. On the contrary, a reverse trend was observed with exponent β_{RP} , which was lowest at pH 4.5. And β_{RP} values were close to unity, i.e., the data approach to the Langmuir model.

CONCLUSION

The modification of activated carbon by acetates of sodium, potassium and lithium significantly improved the adsorption capacity of Ni(II) ion. FT-IR studies showed that the oxygen atoms in the hydroxyl groups on the activated carbon surface were involved in this adsorption process. Therefore, because more oxygen atoms could be available for nickel removal through modification, the adsorption efficiency of modified GAC was higher than that of the unmodified GAC by the following order: LiAC15>LiAC10>KAC15>KAC10>NaAC15>NaAC10>GAC. The overall adsorption rate was illustrated by the pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data obtained from this study was well presented by Langmuir, Sips, Redlich-Peterson isotherm models. However, the Freundlich isotherm had the largest deviation from

the experimental data among the applied isotherm models. These results demonstrate that lithium acetate modified GAC could be used as an effective adsorbent for the adsorption of nickel from aqueous solution. Further study is needed to evaluate other more selective modifiers and to evaluate the applicability of this technique in a large scale processes using granulated activated carbon.

ACKNOWLEDGMENT

The support of the 2006-E-ID-11-P-15-1-000-2008 and 2006-E-ID-11-P-19-1-000-2008 from the Korea Energy Management Corporation (KEMC) and the Ministry of Knowledge Economy (MKE) is gratefully acknowledged.

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