



Sorption properties of the activated carbon-zeolite composite prepared from coal fly ash for Ni²⁺, Cu²⁺, Cd²⁺ and Pb²⁺

Vinay Kumar Jha¹, Motohide Matsuda, Michihiro Miyake*

Department of Material and Energy Science, Graduate School of Environmental Science, Okayama University, Tsushima-Naka, Okayama 700-8530, Japan

ARTICLE INFO

Article history:

Received 5 January 2008
Received in revised form 26 February 2008
Accepted 26 February 2008
Available online 6 March 2008

Keywords:

Coal fly ash
Zeolite
Composite materials
Retention of metals
Toxic metal ions

ABSTRACT

Composite materials of activated carbon and zeolite have been prepared successfully by activating coal fly ash (CFA) by fusion with NaOH at 750 °C in N₂ followed by hydrothermal treatments under various conditions. Uptake experiments for Ni²⁺, Cu²⁺, Cd²⁺ and Pb²⁺ were performed with the materials thus obtained from CFA. Of the various composite materials, that were obtained by hydrothermal treatment with NaOH solution (ca. 4 M) at 80 °C (a composite of activated carbon and zeolite X/faujasite) proved to be the most suitable for the uptake of toxic metal ions. The relative selectivity of the present sorbents for the various ions was Pb²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺, with equilibrium uptake capacities of 2.65, 1.72, 1.44 and 1.20 mmol/g, respectively. The sorption isotherm was a good fit to the Langmuir isotherm and the sorption is thought to progress mainly by ion exchange with Na⁺. The overall reaction is pseudo-second order with rate constants of 0.14, 0.17, 0.21 and 0.20 Lg/mmol min for the uptake of Pb²⁺, Cu²⁺, Cd²⁺ and Ni²⁺, respectively.

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1. Introduction

Global developments directed towards making human life increasingly comfortable have greatly increased industrialization and urbanization. However, this trend has damaged the environment alarmingly, mainly due to the generation of a large amount of hazardous waste and the pollution of both usable surface water and the atmosphere.

Resource recovery technology of solid waste is of great importance for ensuring sustainable development, and has resulted in many recent studies on the recovery of waste resources. For example, incineration wastes containing Si and Al, such as fly ash, coal fly ash, paper sludge, etc., have been converted into tobermorite (calcium silicate hydrate), zeolitic compounds [1–10], gehlenite and anorthite [11–13], and used as raw materials for cement [14,15]. Preparation of active carbon from waste newspaper [16,17], tobermorite from chaff [18] has also been investigated. However, there are many areas that have fallen behind in resource recovery technology.

Many millions of tonnes of coal fly ash (CFA) are discharged from coal-fired boilers throughout the world every year. According to a

report, the global recycling rate of CFA during the 9th decade of the 20th century was as low as 15%, excluding processes such as recycling the CFA as cement fillers and lining materials for hazardous material dumps [19]. Most of the reutilized coal fly ash is used in construction-related applications, including cement and concrete manufacture, production of bricks and lightweight aggregates and additives for the ceramic industry. There still remains a large amount of unutilized CFA.

Environmental-friendly utilization of CFA is an important subject because of measures needed for the prevention of environmental pollution. Although zeolite synthesis from fly ash is a minor application, it has begun to attract more attention because zeolites are useful materials for environmental remediation. Hydrothermal treatment with NaOH solution is a promising technique for the conversion of CFA into zeolites [3–8]. Further approaches involving hydrothermal treatment, such as the two-step method (fusion followed by hydrothermal treatment [20–22]) and the dry or molten-salt method [23] have been developed in order to achieve high synthesis efficiency and/or high crystallinity. The application of microwave synthesis has also been shown to be effective in reducing the reaction time [24,25].

Surface water pollution, which is rapidly increasing with industrialization and urbanization, has become a global environmental problem. In particular, severe problems arise from contamination of water by heavy metal ions and ions such as ammonium and phosphate which cause eutrophication. Wastewaters discharged by industries that process non-ferrous metal ores and concentrates

* Corresponding author. Tel.: +81 86 251 8906; fax: +81 86 251 8906.

E-mail addresses: vinayj2@yahoo.com (V.K. Jha), mmiyake@cc.okayama-u.ac.jp (M. Miyake).

¹ Permanent address: Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal.

are usually polluted with heavy metal ions such as Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , etc. [26]. Many industries involved in metal finishing, mining and mineral processing, coal mining and oil refining, have problems associated with heavy metal contamination of process and runoff waters. The development of new approaches and technologies is therefore needed for both the removal and recovery of valuable metals from process and wastewaters [27].

Zeolites are crystalline aluminosilicates with uniform cavities and cation exchange capacity whereas activated carbon is highly porous carbon material and its amorphous skeleton consists of microcrystallites with a graphite lattice. Composite of activated carbon-zeolite formed by the zeolite growth on porous carbon supports can possess the bifunctional properties of both carbon and zeolite, which can have potential applications in air purification, wastewater treatment, filters in compressed air and gas purification, and many other applications in catalysis and separation [28].

Artificial zeolites prepared from CFA can have high cationic exchange capacities, large surface areas and high residual carbon contents and have been investigated for applications such as the removal of heavy metals from wastewater [29,30], $\text{NH}_4\text{-N}$ and COD [29,31–34] and the immobilization of heavy metals in polluted soils [35]. In the present study, an attempt has been made to prepare composites of activated carbon-zeolite from waste coal fly ash, and determine their uptake properties for the heavy metal ions Ni^{2+} , Cu^{2+} , Cd^{2+} and Pb^{2+} for possible environmental applications.

2. Materials and methods

2.1. Sample preparation and characterization

The two types of coal fly ash (CFA) used in this study were obtained from the Chugoku Electric Power Company Limited, Okayama, Japan. Table 1 shows their chemical compositions. A two-step process, i.e., fusion and hydrothermal treatment, was used to convert the CFA into composites of activated carbon and zeolite. One gram of CFA was mixed with 2.0 g NaOH and fired at 750 °C for 1 h in an N_2 atmosphere. After the NaOH fusion treatment, the mixture was ground and suspended in 12 ml deionized water then stirred and aged for 2 h at room temperature. The use of 12 ml water resulted in an NaOH concentration of ca. 4 M. The slurry was sealed in a Teflon-lined autoclave and kept at either 80 °C or 100 °C for 24 h. Finally the sample was filtered, washed several times with deionized water until it becomes neutral, dried at 50 °C overnight and then used in the sorption experiments.

The samples are designated C, indicating CFA, followed by percentage of carbon, followed by F, indicating NaOH fusion, followed by the amount of water (ml), followed by the hydrothermal treatment temperature (°C), followed by treatment time (h). For example, CFA with 8% carbon content fused with NaOH, treated with 12 ml water and hydrothermally treated at 80 °C for 24 h is

Table 1
Chemical composition of two types of coal fly ash and C8F128024 and C12F128024 products

Component	Content (mass%)			
	CFA type 1 (C8)	CFA type 2 (C12)	C8F128024	C12F128024
SiO_2	44.9	51.8	38.7	39.9
Al_2O_3	24.1	14.4	20.9	22.9
CaO	5.0	2.4	8.1	3.4
Carbon	8.0	12.0	3.0	8.6
Fe_2O_3	10.4	11.6	15.5	13.1
TiO_2	2.8	3.5	4.4	4.0
MgO	1.4	0.4	1.2	0.6
Na_2O	0.5	0.2	6.7	6.2
K_2O	1.1	1.9	0.3	1.1
Others	1.9	1.8	1.2	0.4

designated C8F128024, while as-received CFA with 8% carbon is designated C8.

The chemical compositions of the CFA starting materials, C8F128024 and C12F128024 were analyzed by X-ray fluorescence (ZSX-100s, Rigaku Japan). The carbon content was determined by differential thermal and thermo gravimetric analysis (TG-8120, Rigaku Japan). Powder X-ray diffraction (XRD) patterns were obtained using a diffractometer (RINT2100/PC, Rigaku, Japan) with monochromated $\text{Cu K}\alpha$ radiation and SEM micrograph was obtained from scanning electron microscopy (JMS-6380A, JEOL, Japan).

2.2. Metal ion uptake experiment

All the metal ion solutions were prepared separately, containing ppm concentrations of analytical-grade metal chlorides. The composite samples were subjected to Ni^{2+} , Cu^{2+} , Cd^{2+} and Pb^{2+} uptake experiments by a batch method under the following conditions: temperature 25 °C (room temperature), solid/solution ratio 0.1 g/50 ml, initial metal ion concentrations 20–500 ppm of Ni^{2+} , Cu^{2+} and Cd^{2+} and 100–2000 ppm of Pb^{2+} , and treatment time 24 h. The kinetic experiments were performed at constant metal ion concentrations (500 ppm for Ni^{2+} , Cu^{2+} and Cd^{2+} and 1000 ppm for Pb^{2+}) for times of 0.5–6 h. Metal ion uptake experiments were also carried out in various solutions containing mixtures of two and three different metal ions. The pH values were measured immediately after placing the sample into the solution (pH_i) and after the uptake was complete (pH_e). After the uptake experiments, the solid samples were filtered, washed several times with deionized water and dried at 50 °C overnight. An atomic absorption spectrophotometer (AA-6800, Shimadzu, Japan) was used to determine the concentrations of metal ions in the solutions before and after the uptake experiment and converted from ppm to millimoles per liter.

3. Results and discussion

3.1. Characterization of products

The chemical compositions obtained by XRF show that the major components of the CFAs are SiO_2 , Al_2O_3 and carbon while those of and C8F128024 and C12F128024 are SiO_2 , Al_2O_3 , Na_2O and activated carbon (Table 1). The XRD traces (Fig. 1) show that the major

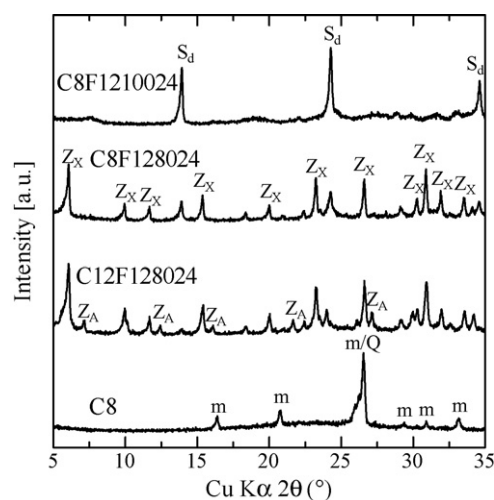


Fig. 1. XRD patterns of as-received CFA and resulting materials (C12F128024, C8F128024 and C8F1210024) from CFA fused with NaOH and hydrothermally treated at two different temperatures. Symbols are as: m – mullite; Q – quartz; Z_x – zeolite X; Z_A – zeolite A; and S_d – sodalite.

crystalline phases are α -quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), together with amorphous components.

The major components (SiO_2 and Al_2O_3) along with unburned carbon were activated by NaOH fusion treatment at 750°C in a N_2 atmosphere. The treatment temperature was based on the activation temperature for preparation of activated carbon [36]. With increasing temperature, the α -quartz and mullite in the CFA are decomposed by NaOH fusion and become amorphous. Fig. 1 shows the XRD patterns of the products of fusion and hydrothermal treatment, together with the as-received CFA. The XRD patterns of C8F128024 and C12F128024 show the formation of well-crystallized faujasite-type zeolite (zeolite Na-X) and a small amount of sodalite in both samples (comparatively more in C8F128024). A small amount of zeolite A is also formed from the CFA with the higher carbon content. We have already reported that either with increasing NaOH concentration and/or hydrothermal treatment time, zeolite A transformed to zeolite X [37]. This small amount of zeolite A in the case of C12F128024 may be due to two factors. The first may be due to higher amount of carbon which may have offered resistance for the complete transformation by partial blocking of reactants and second factor may be due to the difference in the SiO_2 and Al_2O_3 contents of CFA [38]. The XRD pattern of C8F1210024 indicates that zeolite Na-X is transformed to sodalite at the higher hydrothermal treatment temperature. The presence of activated carbon can be seen in the SEM micrograph of C8F128024 sample shown in Fig. 2. Further, we have already reported the detailed information regarding the presence of activated carbon; the microporous and mesoporous characteristics; BET sorption–desorption properties and impacts of NaOH concentration, time and temperature of the activated carbon-zeolite composite [22].

3.2. Sorption isotherms

The metal chlorides were preferred as the aqueous environment due to their easily soluble nature in water. The uptake of M^{2+} ($\text{M} = \text{Ni}, \text{Cu}, \text{Cd}$ and Pb) by the various materials obtained from CFA was determined after a contact time of 24 h, since the sorption kinetics (below) suggested that this time is sufficient to achieve

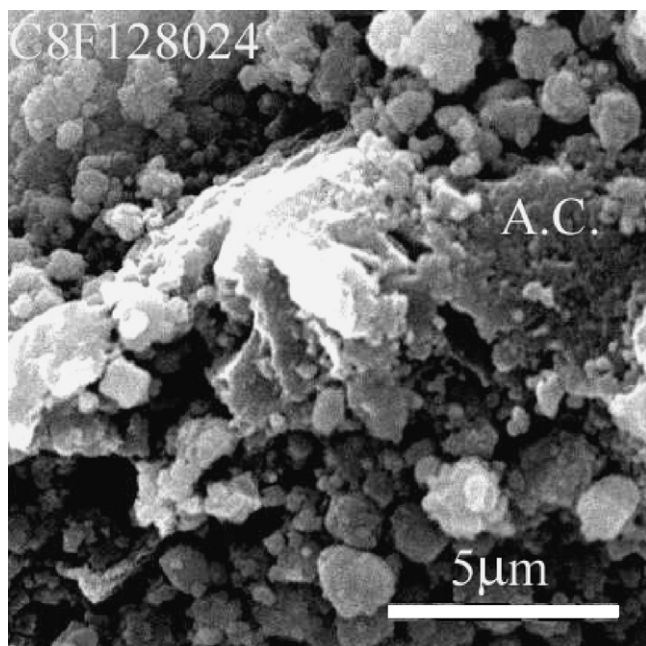


Fig. 2. SEM micrograph of C8F128024 sample where A.C. stands for activated carbon.

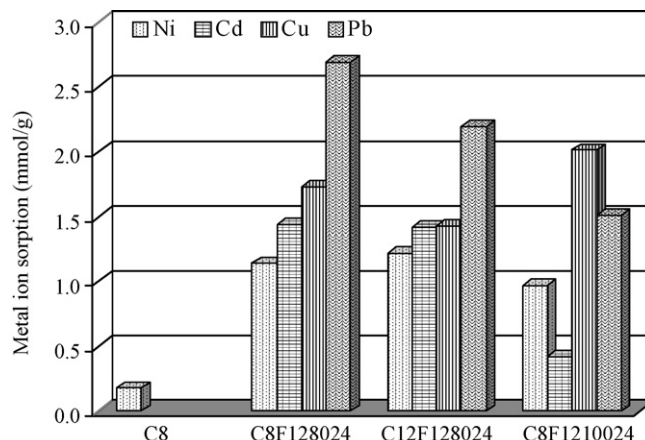


Fig. 3. Metal ion sorption of various products prepared from CFA.

equilibrium. The amount of uptake is shown in Fig. 3. As-received CFA takes up hardly any Ni^{2+} , while C8F1210024 (sodalite) shows different uptake behavior from C8F128024 and C12F128024, especially for Cu^{2+} . The difference in the uptake capacities of present metal ions between C8F128024 and C12F128024 is expected to be due to mainly the difference in activated carbon content. The sorption isotherm experiments were carried out using C8F128024 and C12F128024. The plots of the release of Na^+ vs. metal ion sorption (Fig. 4) show that the uptake reactions for these metals progress principally by cation exchange, because the molar ratio of $\text{M}^{2+}/\text{Na}^+$ is approximately 2.

The sorption isotherms of M^{2+} were simulated by the mathematical equations of Langmuir [39] and Freundlich [40]. The Langmuir model assumes that the removal of metal ion occurs on a homogeneous surface by monolayer sorption, and predicts a linear relation between (C_e/Q_e) and C_e .

$$\left(\frac{C_e}{Q_e}\right) = \left(\frac{1}{Q_{\max}}\right) C_e + \left(\frac{1}{Q_{\max}b}\right) \quad (1)$$

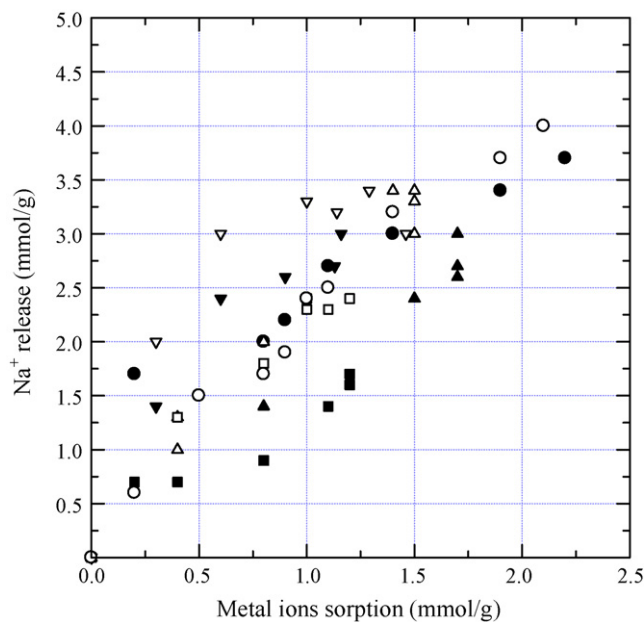


Fig. 4. Relationship between released Na^+ from the samples and sorbed metal ions to the samples. Symbols are as follows: (●) C8F128024- Pb^{2+} ; (○) C12F128024- Pb^{2+} ; (■) C8F128024- Ni^{2+} ; (□) C12F128024- Ni^{2+} ; (▲) C8F128024- Cu^{2+} ; (△) C12F128024- Cu^{2+} ; (▼) C8F128024- Cd^{2+} ; (▽) C12F128024- Cd^{2+} .

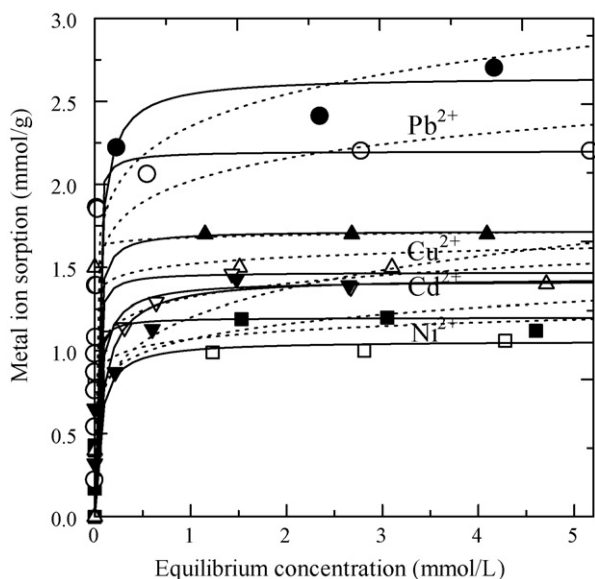


Fig. 5. Sorption isotherms of Ni^{2+} , Cu^{2+} , Cd^{2+} and Pb^{2+} by the composite materials obtained from CFA. Solid and dot lines represent predicted data obtained from Langmuir and Freundlich parameters. Symbols are shown in Fig. 4.

where C_e (mmol/L) is the equilibrium concentration, Q_e (mmol/g) is the amount sorbed at equilibrium, Q_{max} (mmol/g) is the monolayer sorption capacity and b (L/mmol) is the Langmuir constant.

On the other hand, the Freundlich model, which assumes the surface heterogeneity and exponential distribution of active sites, provides an empirical relationship between the adsorption capacity and equilibrium constant of the adsorbent. The mathematical representation of this model is

$$\log Q_e = \frac{1}{n} \log C_e + \log K_f \quad (2)$$

where K_f (mmol/g) and n (g/L) are the Freundlich constants related to the sorption capacity and sorption affinity of the sorbent, respectively. Q_e and C_e are similar as Eq. (1).

M^{2+} uptake experiments were performed with initial M^{2+} concentrations ranging 0.3–10 mmol/L. The resulting sorption isotherms are shown in Fig. 5. The parameters calculated from the Langmuir and Freundlich equations using the experimental data are listed in Table 2. The solid and broken curves in Fig. 5 are calculated from the resulting Langmuir and Freundlich parameters. The correlation coefficient values indicate the superiority of Langmuir model over Freundlich model. The resulting Q_{max} values decrease in the order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$.

This metal ion uptake series is consistent with and higher than those previously reported for fly ash [41], Na-A [42], Na-P1 [43] and clinoptilolite [27,44,45]. Pb^{2+} and Cd^{2+} have zero-ligand-field sta-

Table 2

Langmuir and Freundlich parameters for metal sorption by composites of activated carbon and zeolite synthesized from coal fly ash

Sorbent	Me^{2+}	Langmuir model				Freundlich model		
		Q_{max}	b	R^2	ΔG	K_f	n	R^2
C8F128024	Ni^{2+}	1.20	85	0.9994	-28	1.07	15.5	0.8524
	Cd^{2+}	1.44	12	0.9974	-23	1.20	5.2	0.8722
	Cu^{2+}	1.72	50	0.9998	-27	1.68	83.3	0.4173
	Pb^{2+}	2.65	24	0.9979	-25	2.35	8.8	0.8303
C12F128024	Ni^{2+}	1.06	18	0.9988	-24	1.07	8.5	0.6477
	Cd^{2+}	1.42	22	0.9989	-25	1.32	11.5	0.8630
	Cu^{2+}	1.47	72	0.9998	-28	1.52	27.0	0.8881
	Pb^{2+}	2.20	110	0.9999	-29	2.02	10.6	0.7212

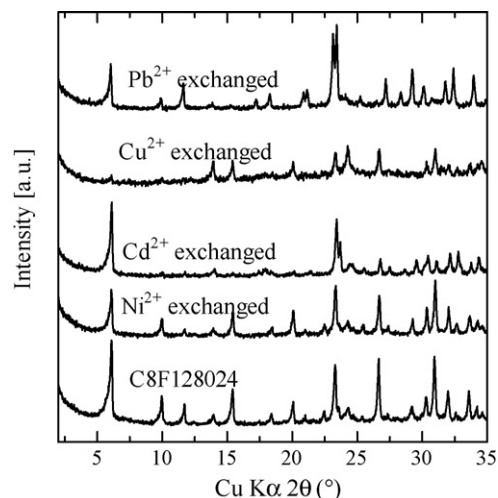


Fig. 6. XRD patterns of C8F128024 before and after metal ions exchanged samples.

bilization in octahedral aqua complexes, because their electronic configurations are d^{10} . Thus, they interact strongly with the zeolite framework during the metal ion uptake process [42], compared to Ni^{2+} , whose electronic configuration is d^8 . The d^9 electronic configuration of Cu^{2+} produced unique uptake behavior; the XRD patterns of the samples after Cu^{2+} uptake showed that the zeolitic structure was partly destroyed (Fig. 6), suggesting the occurrence of other phenomena such as precipitation, in addition to cation exchange. The equilibrium pHs of the solution were in the ranges of 6.7–10.0 for Ni^{2+} and Cd^{2+} , 5.5–8.9 for Cu^{2+} and 7.4–10.4 for Pb^{2+} . The solubility product of $\text{M}(\text{OH})_2$ shows that $\text{Cu}(\text{OH})_2$ is precipitated in the pH range $\geq ca. 5.2$ when the concentration of Cu^{2+} is 0.01 mol/L, and $\text{Cu}(\text{OH})_2$ is more insoluble than $\text{Ni}(\text{OH})_2$, $\text{Cd}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$. Therefore, precipitation probably causes an increase in the amount of Cu^{2+} removed.

The Langmuir constant b is related to the free energy change of sorption (ΔG , kJ/mol) according to the following formula [12]:

$$\Delta G = -RT \ln(1000b) \quad (3)$$

where R is the gas constant (8.314 J/(mol K)) and T is the temperature (K). The Gibbs free energy indicates the degree of spontaneity of the sorption process, negative values reflecting a more energetically favorable sorption process. The ΔG values obtained from Eq. (3) are listed in Table 2, confirming the feasibility of all the sorbents and the spontaneity of the sorption process.

3.3. Sorption kinetics

Fig. 7 shows the sorption of metal ions by the composite C8F128024 as a function of contact time. These plots indicate that the sorption progresses in two steps. The first step is the rapid sorption of the metal ion within 30 min, with a slower second step during which equilibrium is attained. This behavior, consisting of an initial rapid and quantitatively predominant sorption followed by a slower and quantitatively insignificant sorption has been extensively reported [46,47]. The rapid step is thought to be due to the abundant availability of active sites on the sorbent material, and as these sites become increasingly occupied, the sorption becomes less efficient and slower.

In order to investigate the rate law describing the metal ion sorption, the kinetic data obtained from the batch experiments were analyzed using three kinetic equations, namely, the first-order equations proposed by Lagergren and Svenska [48] and Eligwe and Okolue [49], and the pseudo-second order equation proposed by

Table 3
Kinetic data for the sorbent C8F128024 obtained from various equations

System	K_1 from Eq. (4)	K_1' from Eq. (5)	K_2 from Eq. (4)	Q_e (mmol/g) from	
				Eq. (4)	Eq. (6)
Ni	4.6×10^{-3}	3.1×10^{-4}	0.198	1.97	1.12
Cd	1.0×10^{-3}	2.5×10^{-4}	0.209	3.35	1.08
Cu	3.8×10^{-3}	2.4×10^{-4}	0.172	1.93	1.67
Pb	1.2×10^{-3}	2.1×10^{-4}	0.137	1.23	2.23

Ho et al. [50]. The equations were rearranged to obtain the linear forms, as follows:

$$\log_{10}(Q_e - Q_t) = \log_{10}Q_e - \frac{K_1}{2.303}t \quad (4)$$

$$\ln[C_i/C_e] = K_1't \quad (5)$$

$$\frac{t}{Q_t} = \frac{1}{(K_2Q_e^2)} + \frac{1}{Q_e}t \quad (6)$$

where Q_t is the amount sorbed (mmol/g) at time t (min), C_e and Q_e are as in Eq. (1), C_i is the initial concentration (mmol/L), K_1 , K_1' and K_2 are rate constants of Eqs. (4)–(6), respectively. Eqs. (4)–(6) yielded the rate constants (K_1 , K_1' and K_2) and the equilibrium metal ion sorption Q_e , presented in Table 3. The Q_e values obtained from the pseudo-second order Eq. (6) are comparable with the Q_{max} values obtained from the Langmuir Eq. (1) (Table 2), indicating the pseudo-second order reaction model is more appropriate for metal ion sorption by the present composite materials. Several other studies on the sorption of divalent metals on heterogeneous sorbents show that the kinetics generally follows a pseudo-second order rate law [49,51,52]. Furthermore, the kinetic data obtained from the metal ions uptake of present work will be helpful for mass transfer parameters in fixed-bed ion exchange columns, operating under non-equilibrium conditions.

3.4. Sorption in multi-component systems

The uptake amounts of metal ions in multi-component systems represented by the present samples C8F128024 and C12F128024 are shown in Table 4 and Fig. 8. Compared with the single-component system, the uptake of metal ions in the multi-component systems is decreased, which can be attributed to the

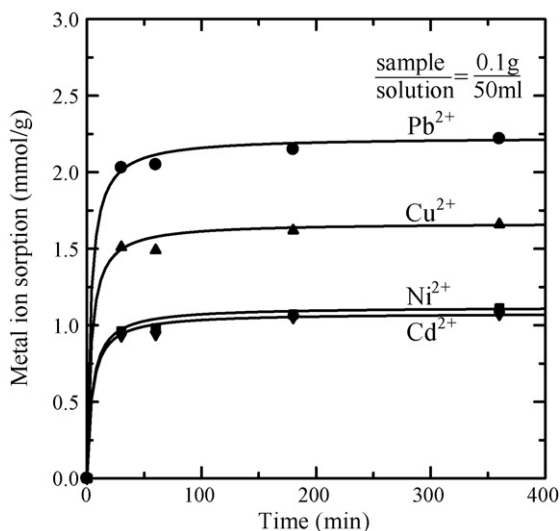


Fig. 7. Plots of metal ions sorbed on composite material C8F128024 prepared from CFA as a function of contact time. Solid lines represent predicted data by a pseudo-second order model.

Table 4
Metal ion sorption of C8F128024 and C12F128024 sorbents in multi-component system

Sorbent	M ²⁺	C _i (mmol/L)	C _e (mmol/L)	Q _e (mmol/g)			Total Q _e
				Cu ²⁺	Ni ²⁺	Cd ²⁺	
C8F128024	Cu ²⁺	4.18	0.73	1.73	–	–	2.10
	Ni ²⁺	6.62	5.88	–	0.37	–	
C12F128024	Cu ²⁺	4.18	1.15	1.52	–	–	1.91
	Ni ²⁺	6.62	5.84	–	0.39	–	
C8F128024	Cu ²⁺	2.81	0.14	1.34	–	–	2.28
	Ni ²⁺	4.46	3.71	–	0.38	–	
	Cd ²⁺	1.60	0.48	–	–	0.56	
C12F128024	Cu ²⁺	2.81	0.46	1.18	–	–	2.11
	Ni ²⁺	4.46	3.68	–	0.39	–	
	Cd ²⁺	1.60	0.52	–	–	0.54	

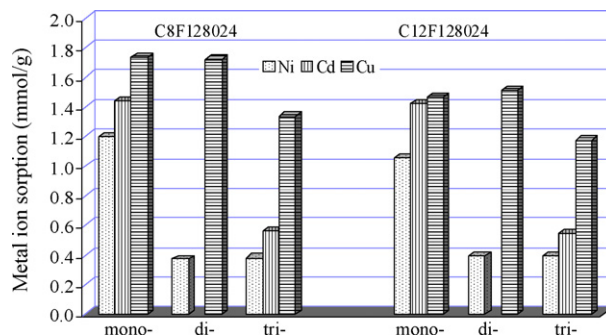


Fig. 8. Metal ion sorption by samples C8F128024 and C12F128024 in mono-, di- and tri-metal ionic solutions.

interference of other metal ions during the uptake process i.e., competitive reactions. Furthermore, Cu²⁺ uptake decreases in going from two to three-component solutions, but Ni²⁺ uptake hardly changes under these conditions. However, the total uptake of metal ions by these samples increases in going from one to two to three-component solutions, indicating that there are still more occupation sites available for the uptake of other metal ions even after the uptake of one type of ion by the samples, because not all the ions have the same occupation site within the solid samples.

4. Conclusion

The following conclusions result from the present study:

- Composites of activated carbon/zeolite can be prepared from coal fly ash.
- These composite materials have good sorption characteristics for heavy metals, with sorption isotherms of the Langmuir type.
- The equilibrium sorption capacity follows the order Pb²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺. The higher uptake of Pb²⁺ and Cd²⁺ is due to their zero-ligand-field stabilization by comparison with Ni²⁺ which has high ligand-field stabilization. The increased uptake of Cu²⁺ is due to the precipitation of Cu(OH)₂ due to

its lower pH precipitation range, by comparison with Ni(OH)₂, Cd(OH)₂ and Pb(OH)₂.

- The overall sorption is pseudo-second order with an initial rapid and quantitatively predominant sorption followed by a second slower and quantitatively insignificant sorption.
- Although the uptake amounts of metal ions in multi-component systems were decreased by competitive reactions, the total uptake was increased.

Acknowledgements

This work was supported by a Grant-in-Aid from Okayama Prefectural Government and Okayama Prefecture Industrial Promotion Foundation, and in part by a Grant-in-Aid from the Okayama University 21st Century COE program “Strategic Solid Waste Management for Sustainable Society”. We are thankful to Professor Dr. K.J.D. MacKenzie of Victoria University of Wellington, Wellington, New Zealand for critical reading and editing of the manuscript.

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