

# Removal of inorganic pollutants in rainwater by a peat-derived porous material

Yunchul Cho · Sungpyo Kim · Heesoo Park ·  
Sridhar Komarneni · Yongsuk Hong

Published online: 28 January 2014  
© Springer Science+Business Media New York 2014

**Abstract** Although roof-top runoff water has been considered as an alternative water resource, the harvested rainwater needs to be treated for further use because it usually contains various contaminants such as heavy metals and microbes. The degree of the harvested rainwater quality depends upon its end use such as drinking water and irrigation. Especially, when harvested rainwater is to be used as gray water, a cost effective treatment system is required. Accordingly, the main purpose of this study was to examine the adsorption characteristics of peat, cost-effective biosorbent, for various inorganic pollutants such as ammonium, copper, cadmium and lead from roof-top runoff water. As part of efforts to investigate the sorption properties of peat, batch isotherm tests were carried out under various pH conditions. The characterization of peat was carried out with powder X-ray diffraction, Brunauer–Emmett–Teller, and scanning electron microscope measurements. Both heat-treated peat and non-treated peat appeared to have high sorption capacity for all inorganic

contaminants ( $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ ). An interesting finding is that the amount of  $\text{NH}_4^+$  sorbed on the sorbents was slightly higher compared to the other cations. Also, the sorption capacity of the peat sorbents increased with an increase of pH. On the other hand, kinetic data were well described by pseudo-second kinetic model, indicating that removal mechanism of cations by peat-derived sorbents is likely due to chemisorptions. The results of this study suggested that peat-derived porous materials can be used as effective sorbents for removal of cationic inorganic contaminants from harvested rainwater.

**Keywords** Heavy metals · Rainwater · Purification · Reuse · Ammonium · Biosorbent

## 1 Introduction

Recently the needs for conserving public water supplies and finding alternative water resources have continued to increase throughout the world due to an increase in water demand for industrial and residential use. This demand makes rainwater harvesting an alternative to traditional water supply sources. A roof-top rainwater harvesting is of great interest among a number of rainwater harvesting systems in many countries [1]. Recently, several researchers have examined the roof runoff water quality for the potential water resource [2–5]. These studies have reported that roof runoff contained heavy metals, organic compounds, and microbes [2, 6–8]. Among those contaminants, inorganic contaminants, such as ammonium, copper and lead, were commonly found in roof runoff and varied by types of roofing materials and airborne pollutants. For example, Chang et al. [6] reported that the mean value of lead concentrations for runoff from four different

Y. Cho  
Department of Environmental Engineering, Daejeon University,  
62 Daehak-ro, Dong-gu, Daejeon 300-716, Republic of Korea

S. Kim · H. Park · Y. Hong (✉)  
Department of Environmental Engineering, College of Science  
and Technology, Korea University, Sejong 339-700, Republic of  
Korea  
e-mail: yhong@korea.ac.kr

S. Kim · Y. Hong  
Program in Environmental Technology and Policy, Korea  
University, Sejong 339-700, Republic of Korea

S. Komarneni  
Department of Ecosystem Science & Management and Material  
Research Institute, The Pennsylvania State University,  
University Park, PA 16802, USA

roof materials was in the range of 0.034–0.049 mg/L. On the other hand, Huston et al. [7] reported that average concentrations of lead in rainwater tanks was 0.28 mg/L. Those values exceed the current WHO drinking water standard value for lead, which is 0.01 mg/L [9]. Therefore, harvested rainwater from roof runoff needs proper treatment for further various usages.

For the removal of heavy metals and ammonium from aqueous phase [10, 11], one of various technologies such ion exchange and sorption, chemical precipitation, and filtration might be chosen. Among these, sorption has been widely used to treat heavy metals from surface water and wastewater because of its simplicity. Various sorbents were proposed for treatment of heavy metals from water and wastewater [12–14]. Peat has been used as cost effective biosorbent for purification of water contaminated with heavy metals [15] since the peat was reported to show high affinity for cationic heavy metals (copper, cadmium and nickel) as well as anionic metal such as chromium [16–18].

Accordingly, as part of efforts to examine the potential of peat-derived porous materials as cost effective biosorbents for the use of harvested rainwater as gray water, sorption characteristics of heat-treated peat with ammonium ( $\text{NH}_4^+$ ) and three heavy metals ( $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ) was investigated. For this purpose, sorption isotherms were constructed from batch tests at various pH conditions. Also, the sorbent material was characterized by Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques to identify the removal mechanism of those cations with heat-treated peat.

## 2 Experimental

### 2.1 Preparation and characterization of sorbents

Two peat sorbents (natural peat and its heat-treated product) were used in this study. A natural peat (*Sphagnum*) was purchased from Demetra (Russia). The natural peat was air-dried at room temperature (non-treated peat), and the other was prepared by heat treatment of the natural peat in a tube furnace (Lindberg/Blue M, Asheville, NC) at heating rate of 10 °C/min to a final temperature of 550 °C for 1 h under a flow of  $\text{N}_2$  gas with 200 mL/min flow rate (heat-treated peat), and then followed by cooling at a rate of 10 °C/min to room temperature. They were then stored in a desiccator at a room temperature prior to use.

To investigate the material characteristics of the sorbents, XRD, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS) and BET analyses were carried out. The crystalline structure was

determined by XRD using a D8 Advanced diffractometer (Bruker, USA) with  $\text{CuK}\alpha$  radiation. SEM–EDS analyses were performed with LEO SUPRA 55 (Carl Zeiss, Germany). The specific surface area of the sorbents was determined by BET  $\text{N}_2$  method using an ASAP 2010 analyzer (Micromeritics Instrument Corp, USA).

### 2.2 Determination of sorption isotherms and kinetics

Batch isotherm tests were carried out to determine sorption capacities of the sorbents for cationic contaminants. Five gram of sorbent was reacted with 25 mL of different solutions containing different cations ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{NH}_4^+$ ). The isotherm test was conducted in the initial concentration range of 1–20 mg/L (1, 2, 3, 5, 10, and 20 mg/L). After equilibration for 48 h, solid–liquid separation was carried out by centrifugation (Mega21R, Hanil Corp.) at  $1,000\times g$  for 5 min. The remaining concentrations of different cations in aqueous phase were analyzed using an atomic absorption spectrometer (AA-6300, Simadzu, Japan). Additionally, the effect of pH on different sorption capacity of two sorbents was investigated under various initial pH conditions (pH = 4.5, 5.5 and 6.5).

Kinetic experiments were conducted with the same manner of the isotherm test. A 5 g of sorbent was placed in a glass vial containing 25 mL of a solution with 1 mg/L of different cations ( $\text{NH}_4^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$ ). Then the batch tests were carried out for 30 min, 1, 2, 6, 12, 18, 24, and 48 h. The initial pH of the solutions was set to 6.5 using 0.1 N HCl solution to prevent precipitation of metal cations. All the experiments were performed in triplicate.

### 2.3 Sorption isotherm and kinetic models

Langmuir and Freundlich models were widely used to describe sorption of various cationic metals onto different sorbents including biomass [12, 16, 19]. A common linear form for the Langmuir model can be expressed as Eq. (1)

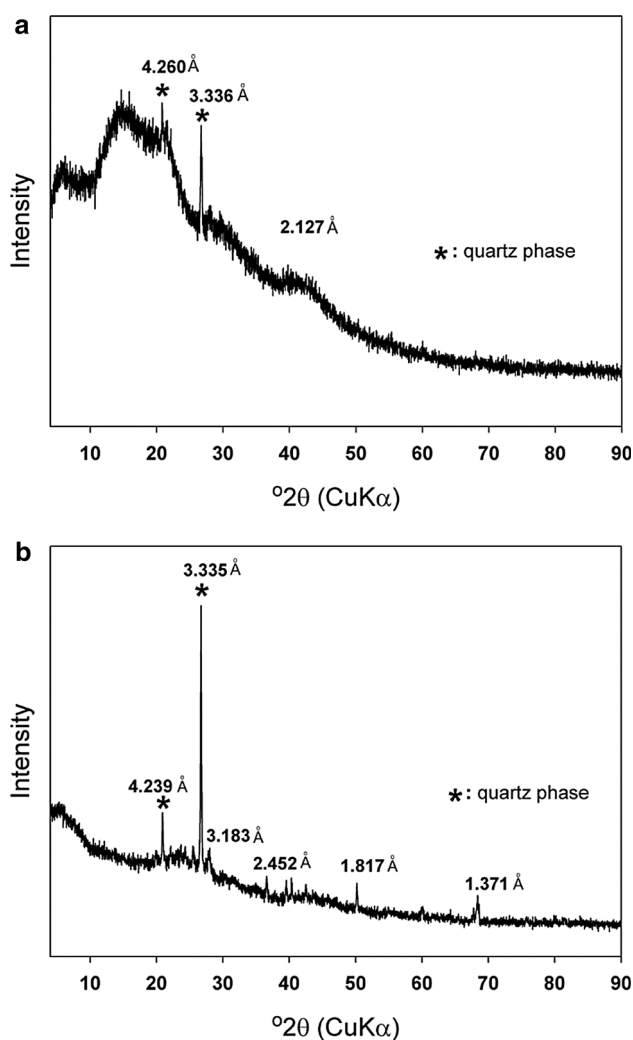
$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L} \frac{1}{C_e} \quad (1)$$

where  $q_e$  is the amount of cations taken up by sorbent at equilibrium (mg/kg),  $q_{\max}$  is the maximum sorption capacity (mg/kg),  $C_e$  is the equilibrium concentration of cations in the solution (mg/L), and  $K_L$  is Langmuir constant, respectively.

On the other hand, a linear form for Freundlich model [Eq. (2)] is expressed as follows:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (2)$$

where  $q_e$  is the amount of cations taken up by sorbent at equilibrium (mg/kg),  $K_f$  is the Freundlich empirical constant [(mg/kg) $^{(1-1/n)}$ ],  $C_e$  is the equilibrium concentration



**Fig. 1** XRD patterns of non-treated peat (**a**) and heat treated peat (**b**)

of cations in the solution (mg/L), and  $1/n$  is the Freundlich exponent.

To determine the rate of sorption reaction and interpret sorption mechanism of cations on the peat, pseudo-second order kinetic models were used in this study. Pseudo-second order model has been widely used to describe adsorption characteristics of heavy metals onto various organic sorbents [20, 21]. This model assumes that chemisorption is the rate limiting step in the sorption process. The linear expression of pseudo-second order kinetic model can be Eq. (3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

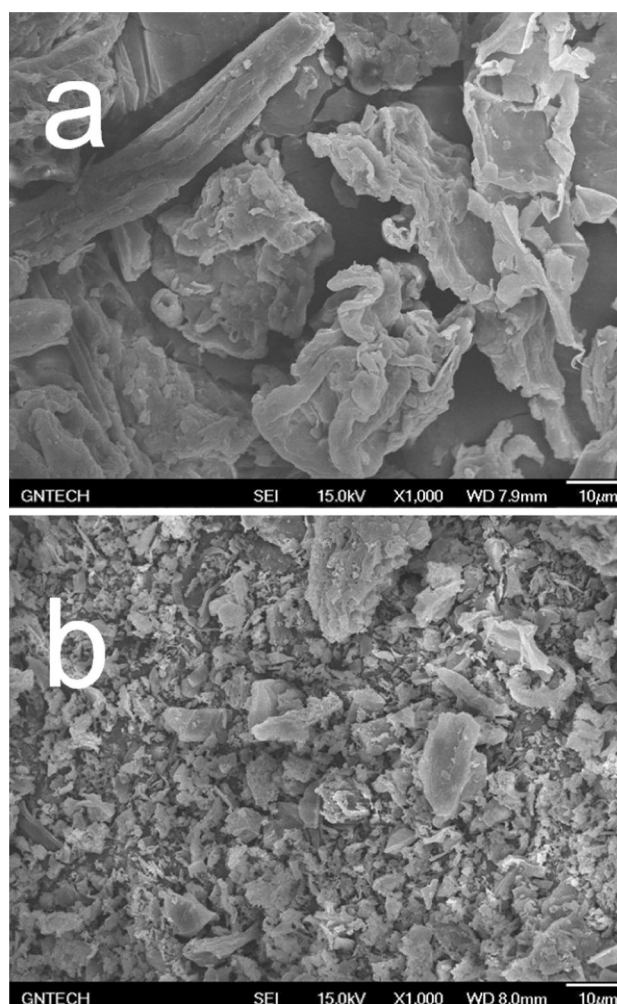
where  $q_e$  and  $q_t$  is the amount of cations taken up by the sorbent at equilibrium and at time  $t$  (min), respectively (mg/kg),  $k_2$  is the rate constant of the pseudo-second order model (kg/mg min).

### 3 Results and discussion

#### 3.1 Characterization of non-treated peat and heat-treated peat

XRD patterns of two peat sorbents (non-treated peat and heat-treated peat) are shown in Fig. 1. The XRD pattern of non-treated peat showed a low-intensity hump around 17° 2-theta and some minor peaks (4.260 and 3.336 Å) related to quartz phase (Fig. 1a). This XRD pattern suggests non-treated peat is amorphous solid phase with small amount of quartz mineral [22]. For heat-treated peat, sharp and high intensity peaks (4.239 and 3.335 Å) present in the XRD pattern are attributed to quartz. This increase in the peak intensities corresponding to quartz phase is likely due to the relative increase of the inorganic portion as a consequence of loss in volatile organic matter by the heat treatment.

Figure 2 shows SEM images of the peat sorbents. The non-treated peat has different shapes such as rod and sheet,

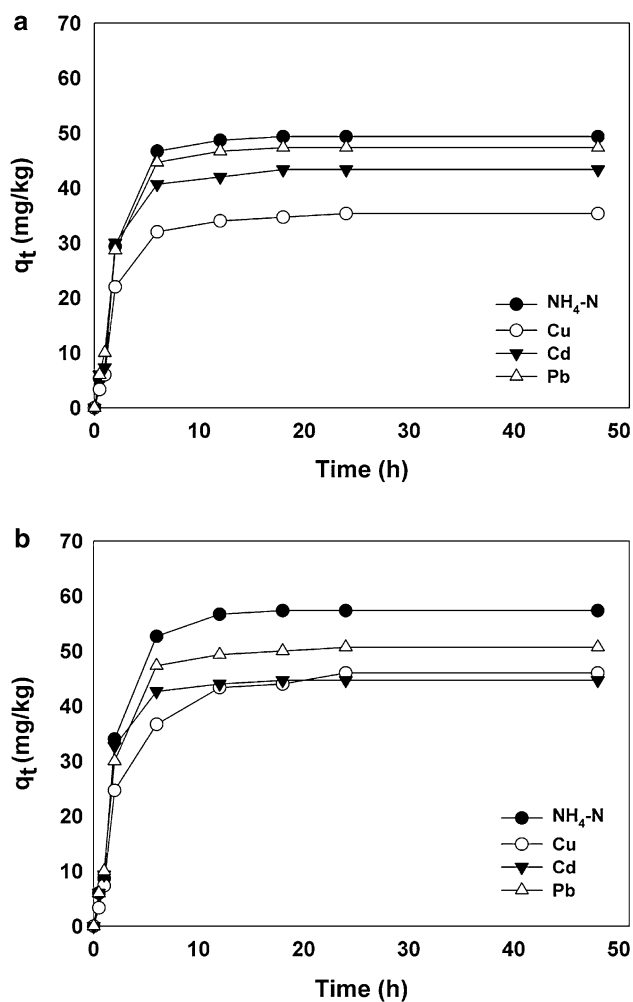


**Fig. 2** SEM images of peat (**a** non-treated peat, **b** heat-treated peat)

**Table 1** Major elemental composition of peat

Sample	Elemental composition (wt%)						
	C	O	Si	Ca	Fe	Zr	Na
Non-treated peat	54.87	41.95	1.06	0.38	0.35	–	–
Heat-treated peat	62.72	27.23	2.85	–	–	1.83	1.24

– not significant (&lt;0.01 %)

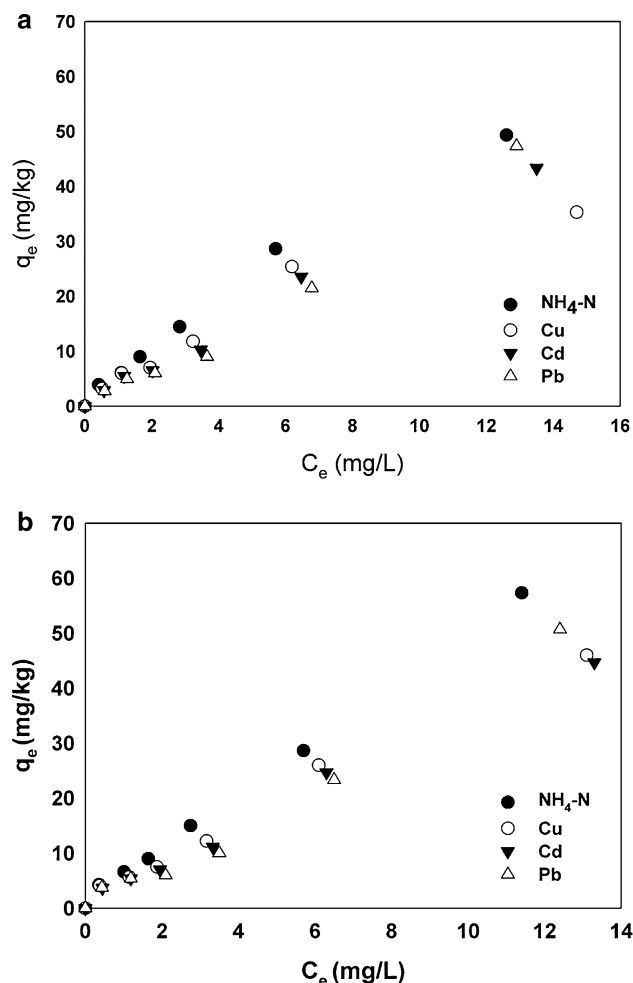
**Fig. 3** The amount of various cations sorbed by peat as a function of time (**a** non-treated peat, **b** heat-treated peat) at pH 6.5

while heat-treated peat has flake-like shape. The heat treatment at 550 °C resulted in morphological changes and size reduction. Also, the heat treatment caused changes in the chemical composition of peat. EDS analysis of peat sorbents indicated that non-treated peat mainly contained carbon (54.87 wt%), oxygen (41.95 wt%), silicon (1.06 wt%), calcium (0.38 wt%) and iron (0.35 wt%) (Table 1). In case of heat-treated peat, main elements were carbon (62.72 wt%), oxygen (27.23 wt%), silicon (2.85 wt%), zirconium (1.83 wt%), and sodium (1.24 wt%). The carbon

content was increased from 54.87 to 62.72 wt% after the heat treatment. This increase in carbon content may be due to the carbonization process during heat treatment. On the other hand, for comparing surface area of two peat sorbents, the specific surface area was estimated via BET surface area measurement. The specific surface area of the non-treated peat was 0.82 m<sup>2</sup>/g, which was slightly lower than the reported value of 0.99 m<sup>2</sup>/g [23]. For heat-treated peat, the specific surface area was 70.48 m<sup>2</sup>/g, having almost two orders of magnitude greater than that of the non-treated peat. This result clearly showed that heat treatment contributed to size reduction of peat, resulting in an increase in the specific surface area (Fig. 2).

### 3.2 Sorption of different cations with peats

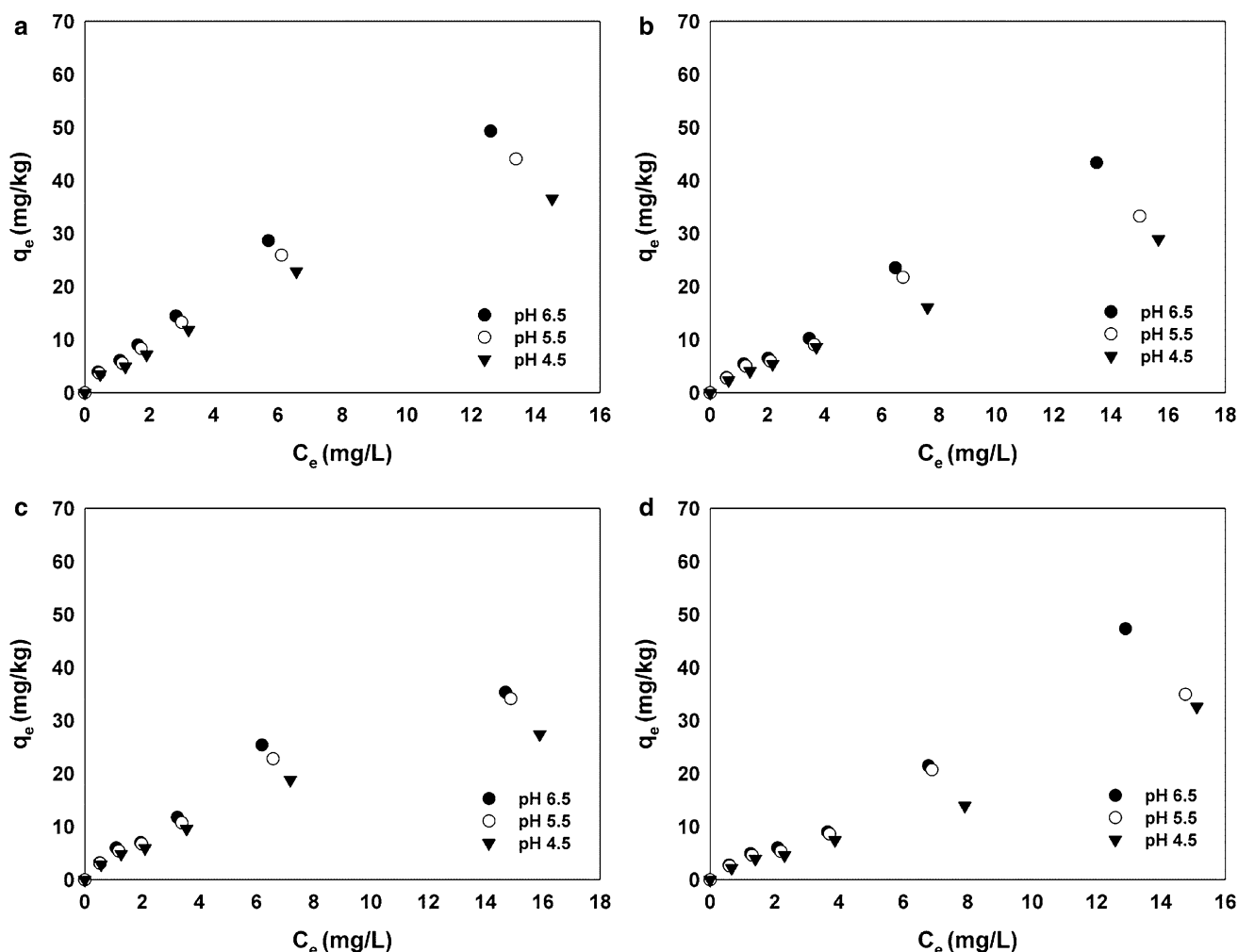
Figure 3 shows the sorption capacities of two peat sorbents for different four cations (Cd<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, and NH<sub>4</sub><sup>+</sup>) at pH 6.5. The sorption of NH<sub>4</sub><sup>+</sup> by non-treated peat was rapid in the initial stage of the sorption process (Fig. 3a).

**Fig. 4** Sorption isotherms of four different cations with peats (**a** non-treated peat, **b** heat-treated peat) at pH 6.5

After 12 h sorption reaction, non-treated peat could not take up cations anymore and the isotherm showed plateau. Similar trends were found for heavy metal cations ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$ ). On the other hand, the sorption capacity of non-treated peat for four cations followed the order:  $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . Like non-treated peat, the sorption process of four different cations by heat-treated peat was a rapid process in the initial stage followed by a very slow process. For heat-treated peat, the order of sorption capacity for four different cations was as follows:  $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Cd}^{2+} \approx \text{Cu}^{2+}$  (Fig. 3b).

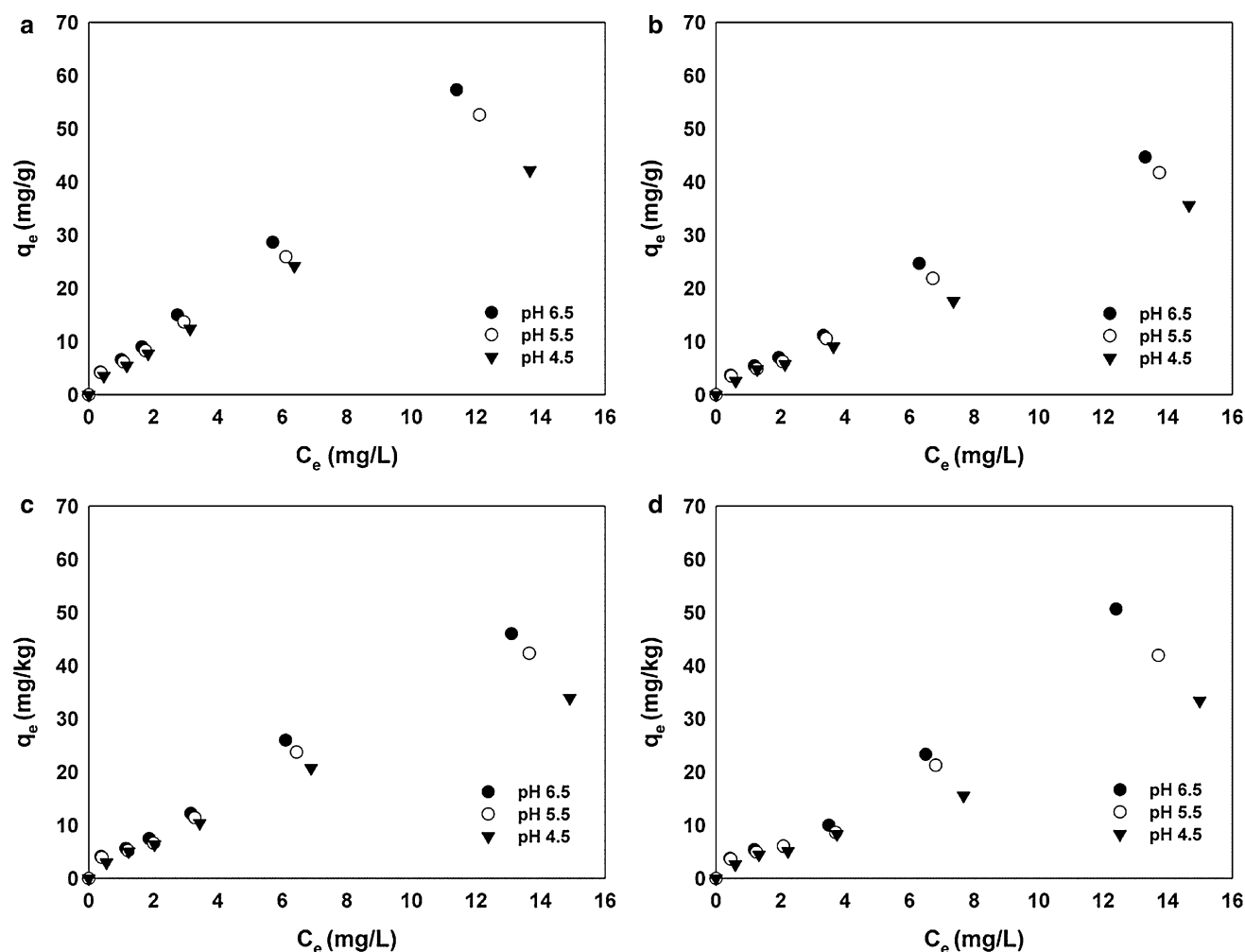
Sorption isotherms of different cations with two peat sorbents at the initial pH 6.5 were determined to describe their sorption behaviors (Fig. 4). For non-treated peat, all sorption isotherms showed a linear relationship between the amount of cation sorbed on the peat and the concentration of the cation in water. The amount of  $\text{NH}_4^+$  sorbed by non-treated peat was greater than other cations. In case of heavy metal cations ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and,  $\text{Cu}^{2+}$ ), the order of sorption capacity seemed to be in a good agreement with

the result ( $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$ ) reported by Kalmykova et al. [15]. They suggested that the sorption affinity of peat for cations could be related to dissimilar sorption mechanism, which might be caused by different functional groups (i.e., carboxylic, phenolic, and other nitrogen and sulfur containing groups) acting differently with various cations as a specific active site of the sorption, ionic potential and ionic size of cations, and etc. Like non-treated peat, the sorption isotherms of heat-treated peat showed a linear relationship. Similarly, the amount of  $\text{NH}_4^+$  sorbed by heat-treated peat was greater than other cations. The trend of the sorption capacity was found to be  $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Cd}^{2+} \approx \text{Cu}^{2+}$ , which was a little different from non-treated peat. It is interesting to note that the sorption capacity of heat-treated peat was slightly higher than non-treated peat for all cations although the specific surface area of heat treated peat was much higher than that of non-treated peat. These results suggest that various functional groups such as carboxylic and phenolic groups in natural peat [18] which played important roles in heavy



**Fig. 5** Effect of pH on the sorption of four different cations with non-treated peat (a  $\text{NH}_4^+$ , b  $\text{Cd}^{2+}$ , c  $\text{Cu}^{2+}$ , d  $\text{Pb}^{2+}$ )





**Fig. 6** Effect of pH on the sorption of four different various cations with heat-treated peat (**a**  $\text{NH}_4^+$ , **b**  $\text{Cd}^{2+}$ , **c**  $\text{Cu}^{2+}$ , **d**  $\text{Pb}^{2+}$ )

metal binding might be decomposed due to carbonization [24].

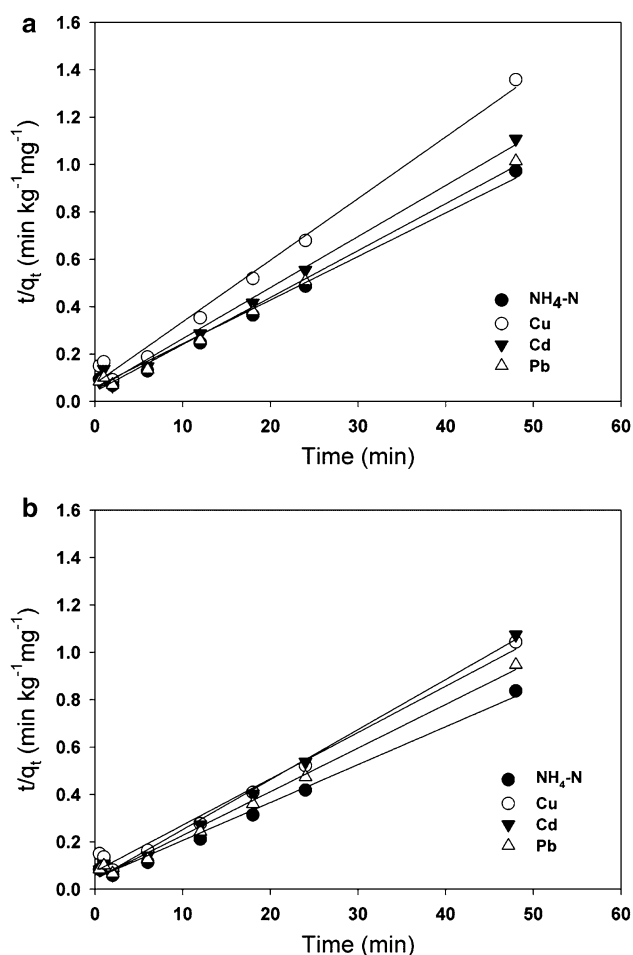
In order to investigate the effect of pH on sorption of four different cations by two peat sorbents, sorption isotherms were constructed at different initial pH values (4.5, 5.5 and 6.5) (Figs. 5, 6). The sorption capacities of non-treated peat for all of the cations increased as pH increased. The surface of non-treated peat is expected to have more negatively charged with an increase of pH because the  $\text{pH}_{\text{pzc}}$  (pH at point of zero charge) of peat moss was reported to be 3.9 [23]. Similarly, sorption capacities of heat-treated peat for the cations increased with the higher pH (Fig. 7).

### 3.3 Sorption isotherm and kinetic models

Langmuir and Freundlich models were used to interpret the sorption behavior of different cations on the peat. The model parameters and coefficient of determination ( $R^2$ ) obtained by fitting the isotherm data points were summarized in Tables 2

and 3. For non-treated peat, the isotherms were well described by both Langmuir and Freundlich models ( $R^2 > 0.93$  for all cases). For heat-treated peat, Freundlich model seemed to describe experimental data better than Langmuir model because  $R^2$  values for Freundlich model were higher than those for Langmuir model. This result suggests that the surface of heat-treated peat may be heterogeneous and the active site on the surface may have different sorption energies (Table 4).

On the other hand, pseudo-second order kinetic model was applied to understand sorption mechanism of different cations with peats. Based on high  $R^2$  values ( $R^2 > 0.98$ ) for all kinetic data, pseudo-second order kinetic model described both non-treated peat and heat-treated peat well. This result suggests that sorption process is mainly controlled by chemisorptions, which may involve the sharing/exchange of electrons between the sorbate and the surface of sorbent [20]. For non-treated peat, the theoretical amount of cations taken up by the sorbent at equilibrium ( $q_e$ ) followed the



**Fig. 7** Pseudo-second order model for the sorption of different cations by peat (**a** non-treated peat, **b** heat-treated peat) at pH 6.5

**Table 2** Langmuir and Freundlich parameters for the sorption of different cations by non-treated peat at pH 6.5

Cations	Langmuir model constant			Freundlich model constant		
	$q_{\max}$	$K_L$	$R^2$	$n$	$K_F$	$R^2$
$\text{NH}_4^+$	29.16	0.35	0.93	1.28	6.66	0.98
$\text{Cd}^{2+}$	34.84	0.15	0.97	1.16	4.24	0.97
$\text{Cu}^{2+}$	23.16	0.29	0.97	1.33	5.13	0.97
$\text{Pb}^{2+}$	28.33	0.17	0.96	1.10	3.71	0.96

**Table 3** Langmuir and Freundlich parameters for the sorption of different cations by heat-treated peat at pH 6.5

Cations	Langmuir model constant			Freundlich model constant		
	$q_{\max}$	$K_L$	$R^2$	$n$	$K_F$	$R^2$
$\text{NH}_4^+$	25.64	0.51	0.89	1.29	7.45	0.97
$\text{Cd}^{2+}$	19.92	0.46	0.87	1.29	5.27	0.96
$\text{Cu}^{2+}$	18.35	0.68	0.81	1.38	6.14	0.94
$\text{Pb}^{2+}$	16.21	0.62	0.79	1.28	3.21	0.89

**Table 4** Kinetic parameters of pseudo-second order kinetic model for sorption of different cations by peat sorbents at pH 6.5

Cations	Sorbents	$q_{e, \text{exp}}^*$ (mg/kg)	$q_e$ (mg/kg)	$k_2$ (kg/mgmin)	$R^2$
$\text{NH}_4^+$	Non-treated peat	49.33	54.35	$5.69 \times 10^{-3}$	0.98
	Heat-treated peat	57.34	62.50	$5.57 \times 10^{-3}$	0.99
$\text{Cd}^{2+}$	Non-treated peat	43.08	46.29	$9.54 \times 10^{-3}$	0.99
	Heat-treated peat	46.01	47.39	$1.09 \times 10^{-2}$	0.99
$\text{Cu}^{2+}$	Non-treated peat	35.68	38.46	$8.99 \times 10^{-3}$	0.98
	Heat-treated peat	44.67	51.28	$5.04 \times 10^{-3}$	0.98
$\text{Pb}^{2+}$	Non-treated peat	47.33	50.51	$9.33 \times 10^{-3}$	0.99
	Heat-treated peat	50.67	54.35	$7.82 \times 10^{-3}$	0.99

\*  $q_e$  obtained from kinetic experiments

order:  $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . This trend is similar to the order of sorption affinity. For heat-treated peat, the order was as follows:  $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ .

## 4 Conclusions

For both natural peat(non-treated peat) and heat-treated peat, the amount of  $\text{NH}_4^+$  sorbed on the sorbents was slightly higher than the other cations ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and,  $\text{Pb}^{2+}$ ). For non-treated peat, the sorption capacity for four cations followed the order:  $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . Similarly, heat treated peat showed the same order. Sorption affinity of heat-treated peat for all cations was higher than natural peat. This enhancement of sorption affinity is likely due to the increase of specific surface area during heat treatment. The sorption affinity of peats for cations increased with an increase of pH. For the sorption of  $\text{NH}_4^+$  by natural peat and heat-treated peat,  $\text{NH}_4^+$  uptake amount at pH 6.5 was 49.33 and 57.34 mg/kg, respectively. On the other hand, pseudo-second order kinetic model described kinetic data for both non-treated peat and heat-treated peat well. This result implies that chemisorption is main sorption process.

**Acknowledgments** This subject is supported by the Korea Ministry of Environment as “Eco Innovation Project” (Project No. 413-111-004).

## References

1. C. Vialle, C. Sablayrolles, M. Lovera, S. Jacob, M.-C. Huau, M. Montrejaud-Vignoles, *Water Res.* **45**(12), 3765 (2011)
2. G. Simmons, V. Hope, G. Lewis, J. Whitmore, W. Gao, *Water Res.* **35**(6), 1518 (2001)
3. J.Y. Lee, G. Bak, M. Han, *Environ. Pollut.* **162**, 422 (2012)
4. A. Teemusk, Ü. Mander, *Ecol. Eng.* **30**(3), 271 (2007)
5. S. Tsakovski, M. Tobiszewski, V. Simeonov, Z. Polkowska, J. Namieśnik, *Environ. Pollut.* **158**(1), 84 (2010)
6. M. Chang, M.W. McBroom, R.S. Beasley, *J. Environ. Manag.* **73**(4), 307 (2004)

7. R. Huston, Y.C. Chan, H. Chapman, T. Gardner, G. Shaw, *Water Res.* **46**(4), 1121 (2012)
8. P.S.M. Santos, M. Otero, R.M.B.O. Duarte, A.C. Duarte, *Chemosphere* **74**, 1053 (2009)
9. WHO, *Guideline for Drinking Water Quality*, 3rd edn. (World Health Organization, Geneva, Switzerland, 2008)
10. K. Athanasiadis, B. Helmreich, H. Horn, *Water Res.* **41**, 3251 (2007)
11. R.F. Moreira Neto, M.L. Calijuri, I.C. Carvalho, A.F. Santiago, *Resour. Conserv. Recycl.* **65**, 124 (2012)
12. S. Cetin, E. Pehlivan, *Colloids Surf. A* **298**(1–2), 82 (2007)
13. E. Lourie, E. Gjengedal, *Chemosphere* **85**(5), 759 (2011)
14. N. Sharma, K. Kaur, S. Kaur, *J. Hazard. Mater.* **163**(2–3), 1338 (2009)
15. Y. Kalmykova, A.-M. Stromvall, B.-M. Steenari, *J. Hazard. Mater.* **152**, 885 (2008)
16. P.A. Brown, S.A. Gill, S.J. Allen, *Water Res.* **34**(16), 3907 (2000)
17. B. Sen Gupta, M. Curran, S. Hasan, T.K. Ghosh, *J. Environ. Manag.* **90**(11), 954 (2009)
18. S. Babel, T.A. Kurniawan, *J. Hazard. Mater.* **B97**, 219 (2003)
19. B. Chen, C.W. Hui, G. McKay, *Water Res.* **35**(14), 3345 (2001)
20. Y.S. Ho, G. McKay, *Water Res.* **34**(3), 735 (2000)
21. M.A. Tofighy, T. Mohammadi, *J. Hazard. Mater.* **185**, 140 (2011)
22. A.P.S. Batista, L.P.C. Romão, M.L.P.M. Arguelho, C.A.B. Garcia, J.P.H. Alves, E.A. Passos, A.H. Rosa, *J. Hazard. Mater.* **163**, 517 (2009)
23. H. Šillerová, M. Komárek, V. Chrastný, M. Novák, A. Vaněk, O. Drábek, *J. Colloid Interf. Sci.* **396**, 227 (2013)
24. J.C.C. Freitas, T.J. Bonagamba, F.G. Emmerich, *Energy Fuels* **13**, 53 (1999)