

## Adsorption of aqueous metal ions on cattle-manure-compost based activated carbons

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### ARTICLE INFO

#### Article history:

Received 26 December 2008

Received in revised form 7 April 2009

Accepted 19 May 2009

Available online 22 May 2009

#### Keywords:

Activated carbon  
Adsorption isotherm  
Cattle-manure-compost  
Copper  
Lead  
Solution pH

### ABSTRACT

The objective of this study is to examine the suitability and performance of cattle-manure-compost (CMC) based activated carbons in removing heavy metal ions from aqueous solution. The influence of ZnCl<sub>2</sub> activation ratios and solution pH on the removal of Cu(II) and Pb(II) were studied. Pore texture, available surface functional groups, pH of point zero charge (pH<sub>PZC</sub>), thermogravimetric analysis and elemental compositions were obtained to characterize the activated carbons. Batch adsorption technique was used to determine the metal-binding ability of activated carbons. The equilibrium data were characterized using Langmuir, Freundlich and Redlich–Peterson models. It was found that the uptake of aqueous metal ions by activated carbons could be well described by Langmuir equation. It is suggested that the increase of surface area and mesopore ratio as a result of increasing activation ratios favored the removal of Cu(II), while activated carbon rich in acidic groups showed selective adsorption towards Pb(II). The preferable removal of Cu(II) over Pb(II) could be due to the rich nitrogen content as well as the higher mesoporous surface area in the CMC activated carbons. The impregnated CMC activated carbons also showed a better performance for Cu(II) removal at varying solution pH than Filtrasorb 400 (F400), while a similar performance was observed for Pb(II) removal.

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### 1. Introduction

The presence of aqueous metal ions in effluent from various related industries has been proven hazardous and poses a threat to the environment. The aqueous metal ions are known toxic in nature, non-biodegradable and more likely to accrue in human body, thus causing a number of health problems, diseases and disorders. Among the toxic and hazardous metal ions are copper, lead, mercury, cadmium and chromium [1]. Stringent contaminant limit has been put into practice by World Health Organization (WHO) to counter this predicament. Permissible concentrations for copper and lead in drinking water for instance, should be as low as 2 and 0.01 ppm, respectively [1].

Common techniques such as electrochemical method and chemical precipitation through pH adjustment are only feasible when dealing with high concentration of metal ions, but still unsatisfactorily to remove the metal species to a lesser degree. The utilization of activated carbon in solid–liquid phase separation has undoubtedly been one of the preferable techniques to remove the remaining trace metal ions from water. The success of this method relies upon the quality and the characteristics of activated carbon, i.e.

huge specific surface area, availability of surface functional groups, chemically stable and durable.

Nowadays, the depleted source of price, which can reach as high as US\$ 25/kg. The separation process thus becomes less economic because of this scenario. This has triggered a search for alternative activated carbon from abundant and inexpensive sources.

Several efforts to convert carbonaceous materials into activated carbon particularly for heavy metals remediation have been reported in literature [2]. And to name but just a few, coconut shell [3], sawdust [4], corncob [5], apricot stone [6] and pecan shell [7]. In most cases, one-step chemical activation is a method of choice by researchers in this area to activate the carbonaceous materials. Activating agents such as H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, ZnCl<sub>2</sub>, KOH and NaOH are known to produce a larger surface area and high yield [2]. Among others, ZnCl<sub>2</sub> was reported to give a higher yield [8]. The use of steam, CO<sub>2</sub>, etc. as a mean of physical activation, however, is not as popular as chemical activation due to the aforesaid reasons.

In addition to that, little information is published concerning the exploitation of animal waste for the same purpose [9,10]. Lima and Marshall [10] utilized activated carbon prepared from broiler manure using steam activation to remove Cu(II) from aqueous solution. Low commercial value of waste manure and a higher price–cost margin that may involve for clean disposal and further treatment make it a potential alternative of activated carbon.

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Taking these aspects into account, the present study was aimed to characterize the metal-binding ability of activated carbons derived from cattle-manure-compost (CMC), a waste residue of methane generation. Adsorptive capacity of the produced carbons was compared with the commercial coal-based activated carbon, Filtrasorb 400 (F400). The effects of activation ratios and solution pH on the removal of aqueous metal ions were examined and discussed.

## 2. Material and methods

All analytical-reagent grade chemicals were purchased from Kanto Chemical Co., Inc. F400 activated carbon was obtained from Calgon Mitsubishi Chemical Corporation. Stock solutions of simulated wastewater containing metal ions were prepared by dissolving desired weight of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{PbCl}_2$  in de-ionized water.

### 2.1. Preparation of activated carbon

Procedures to convert CMC into activated carbon have been described by Qian and co-workers [11]. CMC was procured from JFE Corporation, Japan. Three activated carbons of different  $\text{ZnCl}_2$ :CMC activation ratios were prepared, i.e. 0, 1 and 2; designated as CZ0, CZ1 and CZ2 accordingly. Carbonization was progressed using a tubular electric furnace at  $500^\circ\text{C}$  for 1 h under the  $\text{N}_2$  flow of 300 mL/min. CZ0 can be regarded as a product of physical activation while the impregnated ones are those of chemical activation. The produced carbons and F400 were soaked overnight in hydrochloric acid and concentrated hydrofluoric acid, successively in order to eradicate the possible influence by minerals and ash. Then, they were decanted and thoroughly washed with de-ionized water to remove residual acids until the solution pH was consistent. To ensure that the ash is completely removed, the carbons were calcined in air at  $750^\circ\text{C}$  for 2 h to burn out carbon materials. Finally, the carbons were dried in oven prior the adsorption experiments.

### 2.2. Batch adsorption experiments

Adsorption of Cu(II) and Pb(II) was carried out at  $25^\circ\text{C}$  for 48 h in a stirred batch system. Fixed amount of the adsorbent (30 mg) was added to the conical flasks containing 50 mL of simulated wastewater with known concentration. The initial pH of the solution was varied between 2.6 and 6.3, and adjusted using either 0.1 M HCl or 0.1 M NaOH. For isotherm studies, the solution pH was left unadjusted, and was measured as  $5.2 \pm 0.3$ . Triplicate experiments were done to confirm the good reproducibility of data. The amount of metal ions adsorbed,  $q_e$  (mmol/g) was calculated as  $q_e = (C_0 - C_e) \times (V/m)$ , where  $C_0$  and  $C_e$  are respectively the initial and equilibrium concentration in mM,  $V$  (L) the volume of solution and  $m$  (g) is the mass of carbon. Few drops of 0.1 M HCl were added to the supernatant to stabilize the metal ions and the concentration was measured using atomic absorption spectroscopy (AAS) model Rigaku novAA 300.

**Table 1**  
Elemental composition and surface chemistry of activated carbons.

Carbon	Elemental analysis (wt%, daf)				Surface functional groups (mmol/g)			
	C	H	N	O <sup>a</sup>	Carboxylic	Lactonic	Phenolic	Basic groups
CZ0	74.3	2.20	2.20	21.3	0.545	0.197	0.840	0.120
CZ1	87.1	1.59	2.03	9.32	0.125	0.168	0.650	0.401
CZ2	84.9	1.70	1.89	11.5	0.125	0.138	0.698	0.378
F400	91.9	0.43	0.33	7.33	0.103	0.048	0.477	0.397

daf: dry ash free.

<sup>a</sup> Calculated by difference.

### 2.3. Characterization of activated carbon

Surface functional groups of activated carbon were estimated using methods described by Boehm [12]. Briefly, different batches of 300 mg carbon were brought into contact with 15 mL solutions of  $\text{NaHCO}_3$  (0.1 M),  $\text{Na}_2\text{CO}_3$  (0.05 M), NaOH (0.1 M) and HCl (0.1 M), and were allowed to equilibrate for 48 h. The aliquots were back-titrated with either HCl (0.05 M) for acidic groups or NaOH (0.1 M) for basic groups, at which the neutralization points were observed using the universal pH indicators.

The value of  $\text{pH}_{\text{PZC}}$  of each activated carbon was determined using the pH drift method [13]. Different batches of 100 mg carbon were brought into contact with 50 mL NaCl (0.1 M) of different initial pH. The initial pH of the solution was adjusted between 2 and 12 by adding 0.1 M HCl or 0.1 M NaOH. The suspensions were allowed to equilibrate for 24 h at  $25^\circ\text{C}$  and 100 rpm. The value of  $\text{pH}_{\text{PZC}}$  was determined when the equilibrium pH is equal to the initial pH.

Pore characteristics of activated carbons were determined using liquid nitrogen at 77 K in Beckman Coulter SA3100 surface area analyzer (USA). Elemental compositions of activated carbons were measured twice using a Perkin–Elmer PE2400 microanalyzer. Thermogravimetric analysis was performed using a Seiko EXSTAR6000 TG/DTA6200 instrument under a helium flow of 150 mL/min and heating rate of  $10^\circ\text{C}/\text{min}$  up to  $1100^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Properties of activated carbon

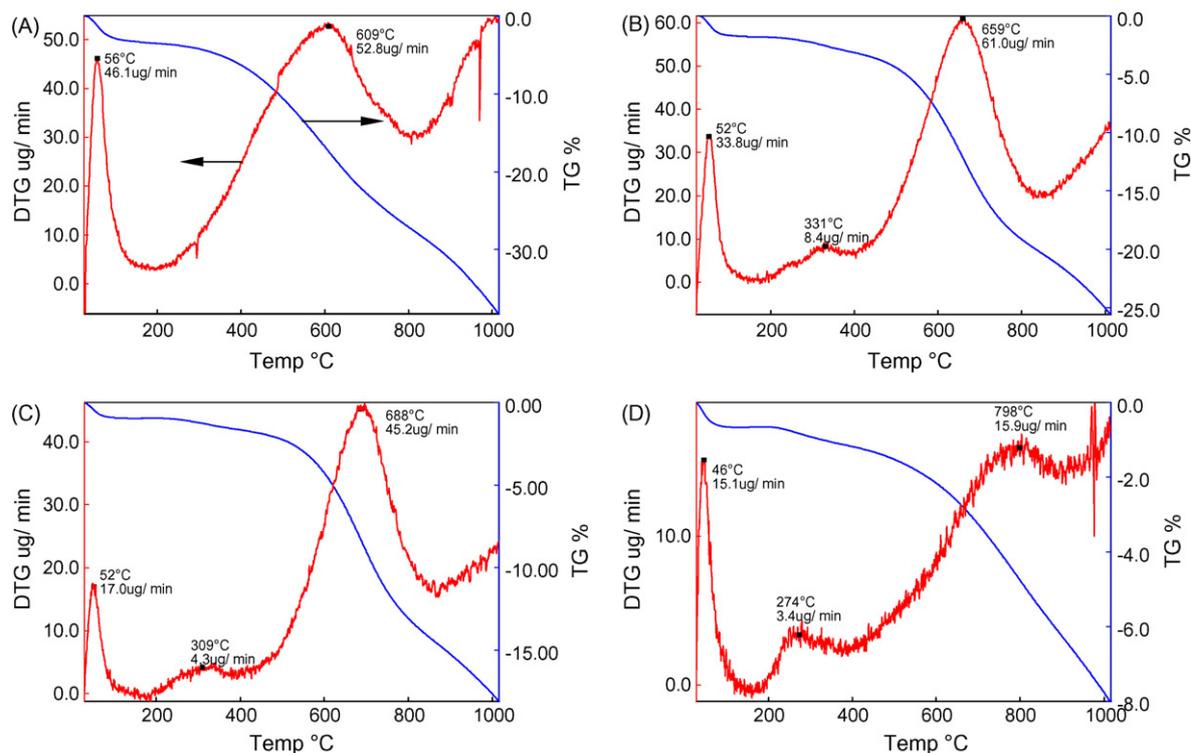
Characterization of activated carbon is important to understand the properties that may affect the removal of aqueous metal ions. Results of elemental composition and functional groups are tabulated in Table 1. It is clear that, the use of activating agent for carbonization increased the percentage of carbon about 10%. The percentage of nitrogen in CMC activated carbons is about six times higher than that of reference activated carbon. CZ0 shows a higher amount of total acidic groups as compared to the other activated carbons, and similar concentration of functional groups is revealed by both CZ1 and CZ2.

Table 2 lists the yield and physical characteristics of activated carbons. Carbonization without chemical activation was found to give smaller yield than that with  $\text{ZnCl}_2$  activation. A much lower value of  $\text{pH}_{\text{PZC}}$  of CZ0 is directly corresponding to its greater amount of acidic groups, which easily hydrolyze the protons to create extra acidity in solution. A slightly higher value of  $\text{pH}_{\text{PZC}}$  of F400 is in accordance with its lesser acidic groups than CMC activated carbons. Apparently, the increase of surface area and pore volume of CMC activated carbons are associated with the increase of  $\text{ZnCl}_2$  activation ratios. Activation ratio 1 gives textural characteristics identical with F400, while activation ratio 2 produces a 100% mesoporous activated carbon. Amount of  $\text{ZnCl}_2$  used for activation is expected to widen the present micropores due to its dehydrating effect, thereafter enlarging the surface area, pore volume and mesopore content. The average pore widths of all activated carbons

**Table 2**  
Yield and physical characteristics of activated carbons.

Carbon	Yield (%)	pH <sub>PZC</sub>	Pore structure				
			S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>meso</sub> (m <sup>2</sup> /g,%)	V <sub>tot</sub> (mL/g)	V <sub>meso</sub> (mL/g,%)	D <sub>avg</sub> (nm)
CZ0	25.1	4.3	320	111 (34.7)	0.218	0.126 (57.8)	2.73
CZ1	40.3	5.3	1395	424 (30.4)	0.742	0.318 (42.9)	2.13
CZ2	40.6	5.8	1752	1752 (100)	1.360	1.360 (100)	3.10
F400	NA	6.4	1099	222 (20.2)	0.680	0.290 (42.6)	2.47

S<sub>BET</sub>: BET surface area, S<sub>meso</sub>: mesopore surface area, V<sub>tot</sub>: total pore volume, V<sub>meso</sub>: mesopore volume, D<sub>avg</sub>: average pore width.



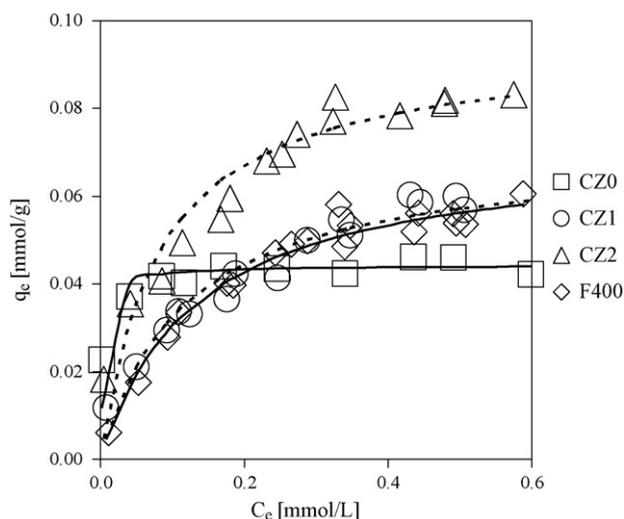
**Fig. 1.** TG and DTG curves of activated carbons. A: CZ0; B: CZ1; C: CZ2; D: F400.

are within the lower limit of mesopores varying between 2.1 and 3.1 nm.

The thermogravimetric profiles of the respective activated carbons are shown in Fig. 1. All activated carbons used in this study display a peak below 50 °C, due to the removal of physisorbed moisture. It can be seen that, CZ0 reveals a peak of high intensity, and the intensity of the peak gradually decreases with the increase of activation ratios. This can be inferred by the fact that the amount of ZnCl<sub>2</sub> used for activation decreases the hygroscopic nature of CMC activated carbons. Another common feature in all samples is a peak at temperatures between 600 and 800 °C which corresponds to the decomposition of functional groups and volatiles. Different from other activated carbons, CZ0 depicts a missing low intensity peak at temperatures ranging from 270 to 340 °C, indicating that no tar was remained after the physical activation. This low intensity peak could also be partly due to the decomposition of carboxylic groups. As compared with F400, CMC activated carbons show a less rigid structure, and the weight loss decreases with increasing activation ratios.

### 3.2. Adsorption experiments

Equilibrium removal of tested metal ions by CMC activated carbons and F400 are illustrated in Figs. 2 and 3. In general, the removal of Cu(II) and Pb(II) by CZ1, CZ2 and F400 falls on the category of L-



**Fig. 2.** Equilibrium removal of Cu(II) by activated carbons. Lines were predicted from Langmuir equation, dashed: CZ1 and CZ2; solid: CZ0 and F400.

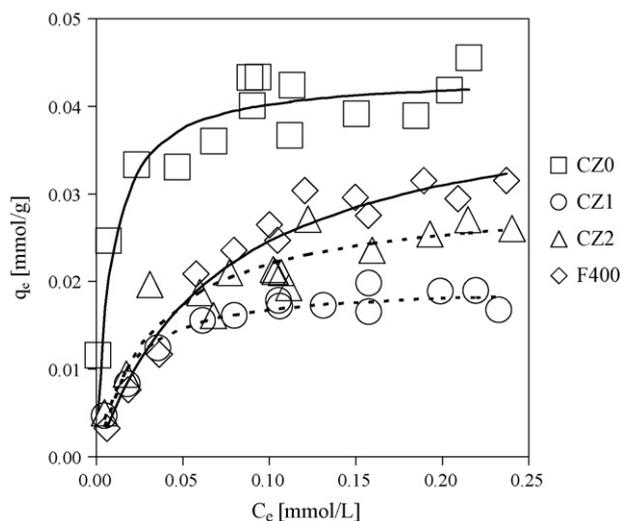


Fig. 3. Equilibrium removal of Pb(II) by activated carbons. Lines were predicted from Langmuir equation, dashed: CZ1 and CZ2; solid: CZ0 and F400.

shape isotherm according to Giles classification [14]. The convex upward trend by these three activated carbons exhibits a strongly favorable adsorption. The uptake by CZ0, on the other hand, is distinguished by H-shape isotherm [14]. High value of slope at low initial concentration signifies the high affinity of adsorption.

From Fig. 2, both CZ0 and CZ2 display a greater removal of Cu(II) at equilibrium concentration below 0.09 mM. Yet, the uptake by CZ0 thereafter immediately reaches a plateau, while it continues to rise for CZ2. The former could be attributed to the abundant acidic functional groups, whereas the latter probably caused by a higher surface area and mesopore content. Clearly CZ1 and F400 show similar amount of adsorption capacity along the increase of equilibrium concentration. This can be explained by their similar physical characteristics as indicated in Table 2. It can be noticed that, the maximum uptake of Cu(II) increases with increasing surface area of activated carbons, because the higher the surface area the more interaction probabilities can take place in the solution.

Unlike in Fig. 2, CZ0 displays a greater removal of Pb(II) in comparison with other activated carbons as shown in Fig. 3. Although having the smallest surface area amongst the tested activated carbons, large concentration of acidic groups does provide the advantage for CZ0 in the adsorption of Pb(II). Considerable effect of surface area could also be observed from a greater removal of Pb(II) by CZ2 above CZ1. Nevertheless, both impregnated CMC activated carbons showed a lesser removal of Pb(II) as compared to F400 at equilibrium concentration above 0.06 mM.

Clearly in Figs. 2 and 3, the impregnated CMC activated carbons showed a greater removal of Cu(II) over Pb(II) in comparison with F400. It is believed that the impregnated surface with rich nitrogen content could be a possible reason for the preferable uptake of Cu(II). This is in agreement with the findings by a number of researchers [15–17]. It is suggested that the adsorption of Cu(II) onto the nitrogen rich surface is through a coordination mechanism [15,16].

A good adsorption process is designed upon the fundamental information of equilibrium isotherms. In this study, three generally used isotherm models were employed to characterize the adsorption data. The Langmuir isotherm can be represented as [18,19]:

$$q_e = \frac{C_e Q b}{1 + b C_e} \quad (1)$$

where  $Q$  and  $b$  represent the maximum monolayer uptake capacity and adsorption affinity, respectively. A linear line of  $C_e/q_e$  against  $C_e$  gives a slope of  $1/Q$  and an intercept of  $1/(Qb)$ . The Freundlich

isotherm is given by [20].

$$q_e = K_F C_e^{1/n} \quad (2)$$

where  $K_F$  and  $n$  are the Freundlich constants related to the uptake capacity and intensity, respectively. Values of  $n$  ranging from 1 to 10 are considered to represent surface heterogeneity and that of favorable adsorption conditions. A straight line can be obtained by plotting  $\log q_e$  versus  $\log C_e$ . The Redlich–Peterson isotherm which combines the features of the Langmuir and Freundlich equations can be described as follows [21]:

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (3)$$

$A$ ,  $B$  and  $g$  are all the Redlich–Peterson constants, where  $0 < g < 1$ . It is also useful to note that, when  $g$  equals to 0, the Redlich–Peterson equation becomes Henry's law equation, while it results in Langmuir equation when  $g$  is unity. These constants were solved using Solver add-in, given the condition where the sum of squared error is the least thus yield the optimum value of correlation of determination ( $r^2$ ).

Isotherm constants for aqueous metal ions together with the equilibrium values of solution pH are tabulated in Table 3. The adsorption data in this study can be well described by the three isotherm models, but it was found that the Langmuir plots were more fitted to linear approximation than the other two equations. This is also supported by some activated carbons showing  $g$  values close or equal to 1 in Redlich–Peterson model. The favorability of activated carbons for the removal of aqueous metal ions was further predicted using a separation factor of Langmuir equation,  $R_L$  as  $1/(1 + b C_0)$ . Under the concentration range studied, it was found that the values of  $R_L$  for all activated carbons lie between 0 and 1, indicating that they are favorable to adsorb the heavy metals.

Results shown in Table 3 are in agreement with the estimation by pure observation proposed by Giles and co-workers [14]. For the removal of both aqueous metal ions, CZ0 provides a bigger affinity in comparison with other activated carbons, which is caused by a significant amount of acidic functional groups. On the molecular basis, clearly CZ0 can accommodate similar maximum amount of Cu(II) and Pb(II), but the respective value of affinity for Cu(II) is about twice that of Pb(II). This suggests the preferable adsorption of Cu(II) over Pb(II) by CMC activated carbons. For Cu(II) removal, the greater surface area of CZ2 depicts a slightly larger affinity than CZ1.

Apart from that of CZ0, the values of adsorption affinity for Pb(II) removal are always higher than those for Cu(II). This phenomenon can be explained by the different size of aqueous metal ions. The values of non-hydrated ionic radii for Cu(II) and Pb(II) are 0.73 and 1.19 Å, while the hydrated ones are 4.19 and 4.50 Å, respectively [22]. It is noted that, the bigger the ionic radii the lesser the amount of energy is utilized for dehydration, thus the greater its affinity to occupy the adsorbent sites [23]. It is also presumed that the most functioning sites for the lower removal capacity of Pb(II) with larger affinity is acidic functional groups, whereas  $\pi$  of basal plane and lone pair of nitrogen are expected to be the active sites for the larger removal capacity of Cu(II) but lower affinity. As demonstrated in Table 3, the decrease of adsorption affinity of Pb(II) with increasing activation ratios implies the preferable dehydration of Pb(II) ion on the outer surface instead of inside the pore channels [24].

The decrease in solution pH below the value of  $\text{pH}_{\text{PZC}}$  upon the addition of activated carbons is due to the dissociation of protons from the ionizable functional groups.

The surface of activated carbon becomes negatively charged thus favors the removal of metal ions. However, the amount of protons released accompanying the adsorption of metal ions by activated

**Table 3**  
Equilibrium pH and isotherm constants for Cu(II) and Pb(II) removal by activated carbons.

Carbon	Heavy metal	pH <sub>e</sub>	Langmuir model			Freundlich model			Redlich–Peterson model			
			Q (mmol/g)	b (mM <sup>-1</sup> )	r <sup>2</sup>	K <sub>F</sub>	1/n	r <sup>2</sup>	A (L/g)	B	g	r <sup>2</sup>
CZ0	Cu(II)	4.1 ± 0.1	0.0443	225	0.995	0.0503	0.113	0.902	41.9	906	0.950	0.942
CZ1		4.4 ± 0.1	0.0708	8.43	0.967	0.0782	0.403	0.980	4.39	56.5	0.639	0.961
CZ2		4.4 ± 0.1	0.0948	12.1	0.977	0.106	0.333	0.976	199	1852	0.662	0.958
F400		5.5 ± 0.1	0.0714	7.47	0.981	0.0922	0.553	0.946	0.527	7.30	1.00	0.971
CZ0	Pb(II)	4.1 ± 0.1	0.0435	123	0.984	0.0663	0.229	0.897	16.9	338	0.909	0.915
CZ1		4.6 ± 0.1	0.0196	58.7	0.981	0.0349	0.348	0.915	0.954	46.9	1.00	0.947
CZ2		4.7 ± 0.1	0.0297	28.6	0.964	0.0523	0.399	0.887	1.87	52.2	0.834	0.869
F400		5.5 ± 0.1	0.0418	14.3	0.966	0.0967	0.628	0.948	0.635	15.3	1.00	0.965

pH<sub>e</sub>: equilibrium pH.

carbons used in this study was not stoichiometrically identical. This can be inferred by the consistent values of equilibrium pH, as indicated in Table 3. Because of plentiful acidic functional groups, CZ0 released a great amount of protons for Cu(II) and Pb(II) removal. About 1.4 mM protons were in excess for every metal ions adsorbed by CZ0, thus implies the non-fully utilized surface sites for adsorption. It can be suggested that the removal mechanism for CZ0 could be due to ion exchange, while for other activated carbons, it also could be due, at least in part, to ion exchange.

### 3.3. Influence of solution pH

Distribution of metal species is strongly dependant on solution pH and metal concentration. Initial concentrations of 0.32 mM for Cu(II) and 0.24 mM for Pb(II) were selected because at these concentrations all activated carbons are expected to reach their saturation points. The upper pH value was adjusted at 6.3 in order to avoid the formation of precipitate complexes which can results in the decrease of aqueous metal ions concentration [25].

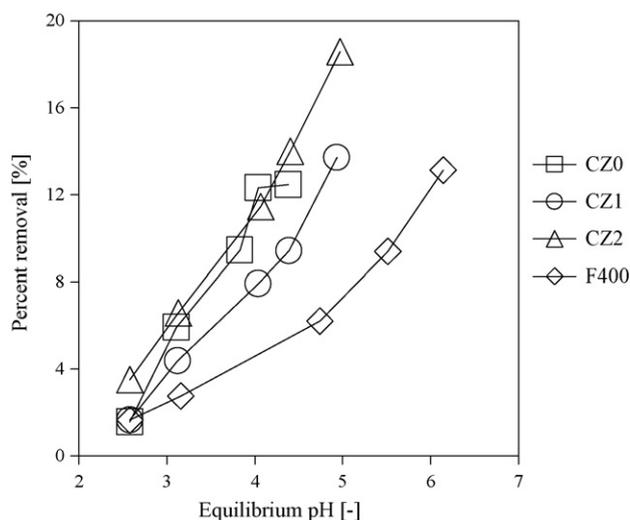
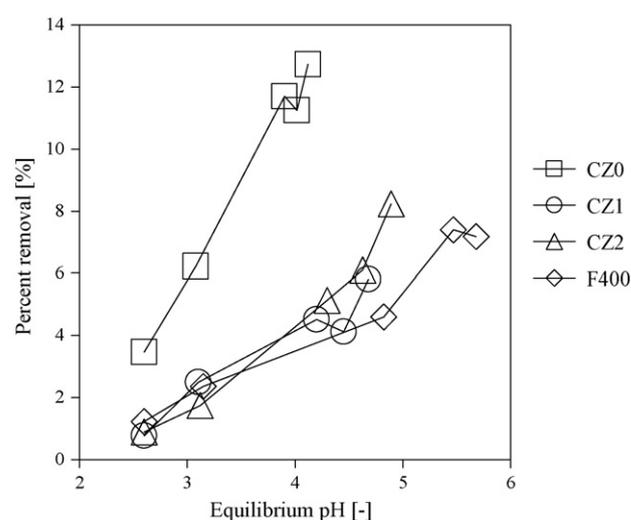
The pH profiles are given in Figs. 4 and 5. In both figures, obviously the removal of Cu(II) and Pb(II) by activated carbons increased with increasing alkalinity in solution.

At a higher acidity, it is well understood that the surface of activated carbon is protonized by excessive amount of protons in solution. Consequently, the divalent cations are repelled from the positively charged surface due to the repulsive force. As the alkalinity increases, the ionizable surface groups are prone to lose their protons which results in the negatively charged surface. This later

enhances the capture of metal species due to the increase of electrostatic attraction.

From Fig. 4, as the equilibrium value of solution pH increases, clearly the removal of Cu(II) by CZ1 is superior than that of F400, even though the amount of uptake is somewhat comparable using the same initial values of solution pH. Apparently, all CMC activated carbons show a better performance than the commercial F400 activated carbon. At equilibrium pH 4.9 for example, CZ1 and CZ2 were able to remove 13.7 and 18.6% Cu(II), while only 9% was removed by F400. This implies the advantage of using CMC activated carbons for Cu(II) removal in acidic environment. A slightly higher removal of Cu(II) by CZ2 at equilibrium pH 2.5 could be due to its greater surface area, higher mesopore ratio and nitrogen rich surface, while that of CZ0 as high as CZ2 could be attributed to the surface acidic functional groups. The graphite basal plane could be estimated to largely contribute as the adsorption sites for the varying performance of CZ1, CZ2 and F400.

In Fig. 5, the performance by impregnated CMC activated carbons is shown comparable with F400 along the increase of equilibrium pH. Similar amount of Pb(II) could be removed by these activated carbons particularly at equilibrium pH below 4.7. For all initial values of solution pH studied, however, CZ0 still showed a greater removal of Pb(II) in comparison with other activated carbons, which is thought to be caused by a plentiful acidic groups. Identical performance by CZ1, CZ2 and F400 could be explained by their similar amount of acidic functional groups, mainly the carboxylic groups.

**Fig. 4.** pH profile for the adsorption of Cu(II) by activated carbons at 0.315 mM.**Fig. 5.** pH profile for the adsorption of Pb(II) by activated carbons at 0.241 mM.

#### 4. Conclusions

Conclusions that can be drawn from this study are listed as follows.

- (1) CZ0 possesses a richer amount of acidic functional groups than CZ1 and CZ2, yet suffers from low yield and a smaller BET surface area.
- (2) Copper uptake by CMC activated carbons increased with increasing surface area and mesopore content, which results from the increase of activation ratios.
- (3) Composition of nitrogen in the CMC activated carbons possibly play an important role for the selective removal of Cu(II) over Pb(II).
- (4) The equilibrium data were more fitted to, and could be satisfactorily described by Langmuir isotherm.
- (5) Performance of CMC activated carbons for Cu(II) removal at varying solution pH was somewhat better than F400.
- (6) CMC activated carbons have been proven feasible for solid–liquid phase separation process, and are foreseen to be a material of choice especially for Cu(II) removal from aqueous solution.

#### Acknowledgements

This work was funded in part by the Japan Society for the Promotion of Science (JSPS) under Grants-in-aid for Scientific Research (C) (No. 20510072). Financial assistance from Ministry of Higher Education Malaysia and Universiti Teknologi Malaysia is gratefully acknowledged. The authors wish to thank Dr. Masami Aikawa of Kisarazu National College of Technology for his fruitful discussion. Gratitude is also extended to Dr. Nagao Keiichi (Head) and Dr. Satoru Nakada of Safety and Health Organization, Chiba University for their encouragement and support on this work.

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