



Application of grass char for Cd(II) treatment in column leaching test

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ABSTRACT

Various adsorbents as well as toxicants have been investigated regarding the adsorption behaviors and mechanisms. However, most of these reports were based on batch test. The discrepancy in adsorption behaviors between batch test and column test has been recognized recently. This study was to investigate the sorption behavior of Cd(II) in a novel adsorbent made from Reed char. Batch adsorption test and column leaching test were both conducted. Various influence factors including confining pressure, pH, velocity, concentration and ionic strength were studied. The velocity was found to have negligible effect on the breakthrough of Cd(II). The adsorption affinity was observed for the first time to decrease from a high value ($R_d = 130.00$) to a negligible one ($R_d = 1.20$) with increasing confining pressure from 0 to 100.00 kPa. The breakthrough of acid Cd(II) solution was earlier for solutions with less pH and higher ionic strength. The Cd(II) laden adsorbent was reclaimed by flushing chelants through the column. The recycled adsorbent appeared to be applicable in the following adsorption treatment. Suggestions were provided regarding the potential engineering applications.

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1. Introduction

Heavy metal pollution is common in many areas of the world with the development of local economies and industries [1,2]. Although various routines were observed responsible for the transport of heavy metals in the environment, anthropogenic wastewaters containing heavy metals remain to be a main source of pollution in developing countries [3].

Cadmium is not a necessary nutritional element for living things and thus can cause severe toxicant effect at comparatively low doses to other heavy metals [3,4]. The maximum allowable concentration of Cd(II) in drinking water is strictly legislated in most countries worldwide. This toxicant also appears to be mobile in soil strata and estuary, and can be enriched in seeds of plants such as rice and aquatic livings such as fish, respectively [1,2]. Although most of the metals were retained in the upper few centimeters of the soil columns, cadmium was reported to be present in the column effluent by modeling investigations [5]. Once polluted, it will cost many following years to get remediated naturally or intentionally.

Various materials have been reported to remove heavy metals from wastewaters. Natural soils [6,7], minerals [3,8], tailing wastes and biomasses [9–14] were widely investigated using both the original form and the modified forms. As a kind of chemically active and unstable matters, biomass always appeared to have strong adsorp-

tion affinity and high adsorption capacity towards heavy metals. On the other hand, one major concern about biomasses was their tendency to be decomposed biologically, which limits the applicability of such materials in the long run view point.

Previous studies have shown the potential of biomass in heavy metal contained wastewater treatment after pyrolysis at increased temperature [6,8,15–17,9]. The sorption affinity and capacity of pyrolysed biomass, which are determined by batch test, appears to be higher than most of the reported sorbents [18]. However, little information is available about the sorption performance of these materials in column test. In environmental engineering, the pollution of groundwater far away from the point source could only be treated on site. In such conditions, permeable reaction wall has proved to be an effective and convenient choice for treatment of various pollutants. For heavy metals, installation of mineral in the PRW has been reported to be involved with precipitation by adjusting the pH of water or providing dissolvable ions such as PO_4 or S^{2-} , CO_3^{2-} that can react with heavy metals.

The partitioning behavior of solute between solution and solid phase is dependent on solid–solution ratio, as indicated by previous studies. The sorption parameters obtained from batch test could not be used to predict the transport of solute in compacted porous media. Therefore, it is necessary to conduct column leaching test to check the barring behavior of the pyrolysed biomass towards heavy metals, even though some batch sorption tests have been carried out.

This paper is aimed to reveal the sorption performance of pyrolysed grass char (GC) towards Cd(II) in compacted columns. A kind of grass was transformed into grass char by pyrolysing at 250 °C.

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The effects of initial concentration, confining pressure, infiltration velocity, solution pH and ionic strength on the leaching of Cd(II) through GC column have been evaluated to determine the suitable conditions for engineering practice. The breakthrough curves were analyzed by advective-diffusion models to calculate the partition coefficient of Cd(II) on GC. The possibility of application of GC in treatment of Cd(II) laden wastewater was discussed.

2. Theoretical background

The transport of solute in homogenous porous materials could be modeled with the following governing equations.

$$R_d \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} - \lambda C \quad (1)$$

$$C = C_0, \quad x = 0 \quad (2)$$

$$\frac{\partial C_e}{\partial x} = 0, \quad x = L \quad (3)$$

$$C_i = 0, \quad t = 0 \quad (4)$$

where C_e is the concentration of solute in exit of the soil column (M); C_0 is the solute concentration of the infiltration liquid (M); the C_i is the initial concentration in pore liquid (M); D is the diffusion coefficient (m^2/s); L is the column length (m); R_d is the retardation coefficient; t is the diffusion time (s); v = infiltration velocity of pore liquid (m s^{-1}); and λ is the reaction kinetic constant, which is identical to the physical meaning of that constant used in pseudo-first order kinetic models [19].

The adsorption of solute on sorbents is always involved with kinetic processes. The sorption can be divided into several stages, including fast sorption at the beginning within a very short duration and a sequential gradual sorption lasting for a long time [6,9,20]. This dynamic process could be fitted by an exponential equation such as pseudo-first order kinetics [21]. In such cases, a decaying transport theory as shown in Eq. (1) could be applied to model the breakthrough curves. The solution to this equation for the special boundary conditions has been obtained in the form of [18]:

$$\frac{C_e - C_0}{C_i - C_0} = \frac{1}{2} e^{P_L/2} \left[e^{-\sqrt{P_L^2/4 + P_L \times CT \times \lambda}} \operatorname{erfc} \left(\frac{1}{2} \sqrt{\frac{R_d \times P_L}{T}} - \sqrt{\frac{P_L \times T}{4R_d} + \frac{T \times CT \times \lambda}{R_d}} \right) + e^{\sqrt{P_L^2/4 + P_L \times CT \times \lambda}} \operatorname{erfc} \left(\frac{1}{2} \sqrt{\frac{R_d \times P_L}{T}} + \sqrt{\frac{P_L \times T}{4R_d} + \frac{T \times CT \times \lambda}{R_d}} \right) \right] \quad (5)$$

where P_L means column Peclet number; T means number of pore liquid; CT means unit column time; and R_d is the retardation coefficient. The relevant expressions are shown as:

$$P_L = \frac{vL}{D} \quad (6)$$

$$T = \frac{vt}{L} \quad (7)$$

$$CT = \frac{L}{v} = \frac{t}{T} \quad (8)$$

When the kinetic sorption is negligible, i.e., $\lambda = 0$, the analytical solution of Eq. (1) at the exit boundary is written as [22]:

$$\frac{C_e - C_i}{C_0 - C_i} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{LR_d - vt}{2\sqrt{DtR_d}} \right) + e^{vL/D} \operatorname{erfc} \left(\frac{LR_d + vt}{2\sqrt{DtR_d}} \right) \right] \quad (9)$$

These equations could be used to predict the parameters of solute transport on the basis of BTCs that are determined experimentally.

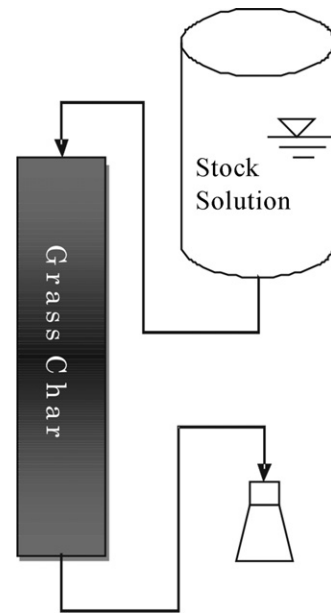


Fig. 1. Sketch of the test facility.

3. Materials and methods

The Reed was sampled from Kamo Gawa in Kyoto City, in December 2009. The stem was cut into short pieces less than 5 cm in length. Mud and gravel was removed from the sample. For preparing the adsorbent, the reed was heated anaerobically at 250.00 °C for 1.00 h and then cooled to room temperature. The obtained char was pulverized, screened through 500.00 μm sieves, and stored in Ziploc sealed bags for further test. The microscopy picture of GC was taken by SEM facility (JEOL, Japan). The chemical composition of GC was determined by EDX (EDX 720, Shimadzu, Japan). The specific surface area (SSA) of GC was analyzed by N_2 adsorption test (Belsorp18plus-HT, BEL Japan, Osaka, Japan). The sample was dried, ground and screened by mesh 75 μm before subjected to the X-ray analysis.

Fig. 1 shows the sketch of the operating system. A liter of CdCl_2 solution at predetermined concentrations (69.50, 695.00, 100.00 mg L^{-1} etc.) was prepared and filled into the upper tank to act as the stock solution. The grass char was filled into the chamber (1.50 cm in diameter, 8.00 cm in length) by shaken compaction. The density of the GC was determined to be 0.21. Both the inlet and outlet of the chamber was restrained by plastic filter stops. The water head of the fluid was controlled by changing the vertical distance between the water level and the top of the GC chamber, in order to control the infiltration velocity. A conical flask was connected to the outlet of the GC chamber to take the leachate samples, which were further subjected to ICP analysis to determine the Cd concentration (ICPS, Shimadzu, Japan). Atomic emission spectroscopy (AES) was used for elemental detection. The breakthrough curve of Cd in GC column was figured with elapsed time. The electrical conductivity and solution pH of the leachate were periodically determined by EC and pH meter.

For the samples with higher density, a tri-axial shear testing apparatus was used to apply the confining pressure. The GC was filled in the rubber membrane that was originally sized at ($D \times H = 6.00 \times 6.00 \text{ cm}^2$). The confining pressure was supplied by air pressure at 100.00 kPa. The final size of the GC column was measured ($D \times H = 5.53 \times 4.69 \text{ cm}^2$) after the test was stopped. The other parameters were kept identical to the previous studies. The room temperature was adjusted at 25 °C by air conditioner throughout these tests.

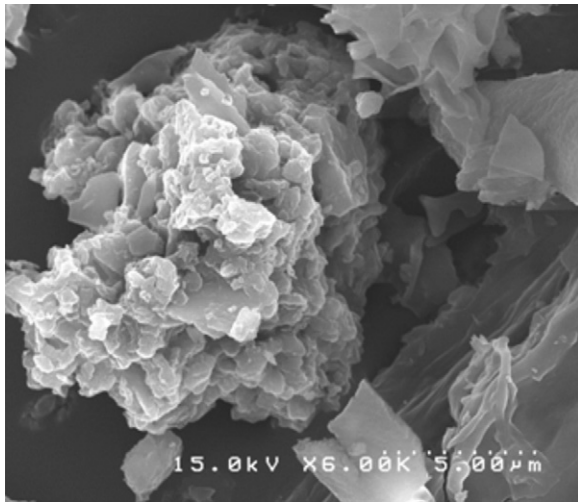


Fig. 2. SEM photo of the obtained grass char.

4. Results and discussion

4.1. Characterization

The structural morphology and configuration of fine particle of GC was shown in Fig. 2. The surface of GC was irregular in shape and was composed by pits with varied depth and geometrical appearance. Because the treatment temperature is low, the grass may not be completely carbonized.

Table 1 shows the chemical composition of GC that was determined by EDX. The main chemical composition is found to consist of many different elements, including Si, Ca, Fe, K (the top 4 in mass ratio) and some other elements in minor content, e.g., S, Al, Ti and P. The high values in mass percent of silicate and calcium were easy to understand since these elements are abundant in soils. But it is surprising that the mass percents of iron and potassium even reach 16.00% in oxide form. High percent of iron could give rise to the stability of the adsorbent and the available adsorption sites on the particle surface. The potassium and calcium might act as active sorption sites in terms of equivalent ion exchange capacities. It is noteworthy that the compositions of carbon and amine were not available in this study. However, their contributions to the adsorption of heavy metals should not be neglected in the mechanism analysis. The specific surface area of the grass char was determined at 8.100 m²/g. This value is consistent with our previous results on leaf char [15].

Table 1
Chemical composition and SSA of Reed GC determined by EDX and N₂ BET test.

Composition	Mass ratio %
SiO ₂	38.197
CaO	17.123
Fe ₂ O ₃	16.255
K ₂ O	16.150
SO ₃	3.856
Al ₂ O ₃	3.395
TiO ₂	1.836
P ₂ O ₅	1.288
MnO	0.947
ZnO	0.467
CuO	0.213
SSA (m ² /g)	8.100
R ²	0.999

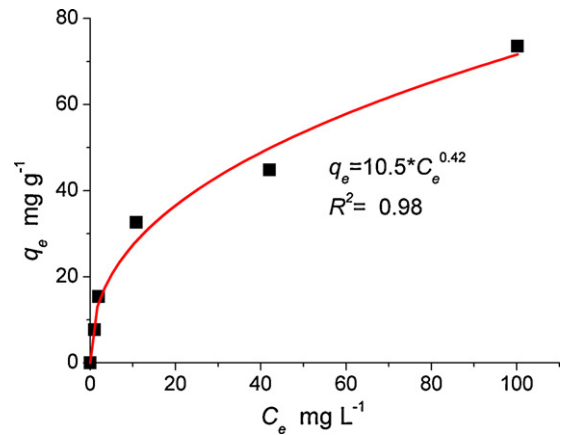


Fig. 3. Adsorption isotherm of Cd(II) on GC (dosage at 1.0 g L⁻¹, temperature at 25 °C, equilibration duration at 24 h).

4.2. Isothermal adsorption in batch test

Fig. 3 shows the adsorption isotherm of Cd(II) on GC in batch studies. The sorption isotherm was designated a Freundlich isotherm. The adsorption amount increased rapidly from 0 to 16.0 mg g⁻¹ with increasing equilibrium solute concentration from 0 to 2.0 mg L⁻¹. Further increase in solute concentration was likely to result in consistent increase in adsorption amount q_e , but the slope appeared to be much less than the initial stage. The isotherm could be well fitted by Freundlich model with determination coefficient at 0.98.

4.3. Breakthrough curve of Cd in GC column

4.3.1. Rigid-wall column test

The GC column was compacted to the largest density by seismic shaking. The outlet solution was sampled and further subjected to ICP test to determine the concentration of Cd(II). Fig. 4 shows the breakthrough curves of Cd(II) in these columns. It is obvious that the BTCs with different velocities are identical to each other before the breakthrough of Cd(II). The concentration in the outlet before breakthrough was found to be very low, close to the detection limit of the analysis apparatus. After breakthrough of the injected fluid, the BTCs separated from each other for columns with different infiltration velocities. The BTC of column with higher velocity possess a higher slope than the other curve. The baring capacity of the GC could be exhausted at a higher rate at higher injection velocity. These curves were fitted by advective-diffusion transport theory

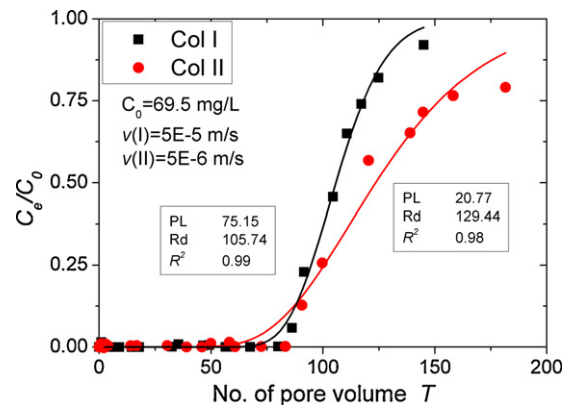


Fig. 4. BTC of Cd(II) on GC column at various velocity and initial concentration ($C_0 = 69.5 \text{ mg L}^{-1}$; $L = 6.0 \text{ cm}$, $V = 8.0 \text{ cm}^3$).

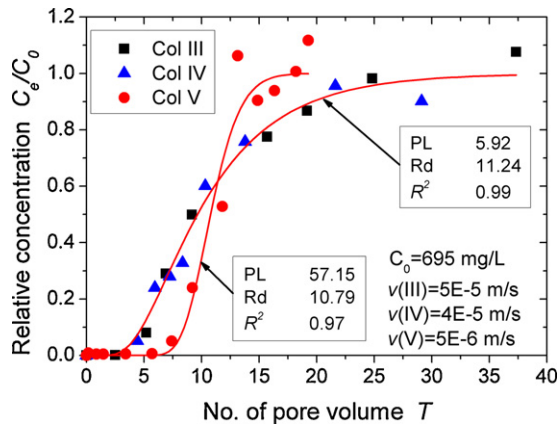


Fig. 5. Effect of infiltration velocity on BTC of Cd in GC column ($C_0 = 695 \text{ mg L}^{-1}$).

using least square root regression method. The retardation coefficient R_d was found to decrease with increasing infiltration velocity.

Fig. 5 shows the BTCs of columns with higher initial Cd(II) concentrations. Ten times higher Cd(II) concentration (695.00 mg L^{-1} vs 69.50 mg L^{-1}) resulted in brought forward BTC. The number of pore volume required to get the column broken through was reduced from 83.00 to less than 5.70 when initial concentration was changed from 69.50 to 695.00 mg L^{-1} . The infiltration velocity was likely to have a more significant influence on BTC in case of influent with higher initial solute concentration. Increase in infiltration velocity by 7–9 times resulted in shortened breakthrough times by a half from 5.70 to 2.90 pore volumes. The BTCs of columns with similar velocity at 5.00 and $4.00 \text{ E}^{-5} \text{ m s}^{-1}$ were coincident to each other, indicating the experimental results were reliable and convincing.

The highest solute concentration in the effluent was found to be higher in column with less infiltration velocity (Col V). The maximum Cd(II) concentration was determined to be 1.12 times of the initial concentration in the influent. Fluctuation in C_e/C_0 was also observed in BTC of Col V after the complete breakthrough of the column. This feature is different from the normal trend observed in other tests. The heterogeneous adsorption as well as the heterogeneity of fabrics in the column might be related to this behavior. As observed in adsorption isotherm of Cd(II) on GC in Fig. 3, the adsorption amount does not increase linearly with the increase in equilibrium solute concentration. With the increase in solute concentration, the partition coefficient of Cd(II) between solution and solid decreased correspondingly. The Cd(II) in the influent was fixed in the GC column before breakthrough. With the slowly developed migration of Cd(II) in the GC column, the concentrated Cd(II) front in the pore liquid would transport from the inlet to the outlet gradually. Because Col V has accumulated more Cd(II) than Col III and Col IV before the breakthrough occurred, the concentration of Cd(II) in the penetrating solute front might be higher in Col V than the others. When the column was finally broken through, the stored Cd(II) near the solute front in the column would be released once again. And thus the solute concentration appeared to be higher in Col V with less infiltration velocity than the other columns and even higher than the initial value (C_0).

4.3.2. Column performance of GC under confining pressure

Fig. 6(a) shows the BTC of Cd(II) leaching from a compacted GC column under high confining pressure (100.00 kPa). The BTC was well fitted with the advective-diffusion transport model. The determination coefficient was determined at 0.992. The transport parameters, i.e., retardation coefficient R_d and Peclet number, PL , were determined separately at 1.76 and 10.62. The retardation factor was close to the critical value at 1.00 which indicates a negligible

adsorption between solute and sorbent. The sharp edge in BTC confirmed this speculation. The solute concentration was chosen as a comparable value to the previous tests as shown in Fig. 6. However, the retardation factor deviated from each other greatly even with the similar conditions (solute concentration, velocity, sorbent fillings) except for the presence of confining pressure in this test. The great decrease in Cd(II) adsorption capacity by GC could be ascribable to the effect of static compression resulted from the confining pressure. In the test, the compression made the GC column more compact in density and much less in permeability. The pore volume was calculated from the difference between the volume changes in the confining liquid. The permeability was greatly decreased ($6.00\text{E}^{-8} \text{ m s}^{-1}$) compared to those without confining pressure ($\approx 5.00\text{E}^{-5} \text{ m s}^{-1}$).

Previous studies showed that the adsorption of solute on adsorbent in aqueous systems was dependent on sorbent dosage or solid solution ratio [15,23]. The unit adsorption amount was found to decrease with increasing sorbent dosage while the adsorption constant K_d decreased correspondingly. The increase in column density will increase the solid-solution ratio in the sorbent-solution system in the limited pore space of the column. This could be responsible to the decrease in the adsorption affinity as indicated by the retardation factor R_d . The decrease in porosity will affect the permeation mode of pore liquid in the porous media. In loosely filled column, the permeation of pore liquid might consist of turbulent dispersion which could greatly increase the homogeneity of the interface between sorbent and solution during the permeation. For compact column, the pore liquid might be characterized by advective flow where the interface between solution and

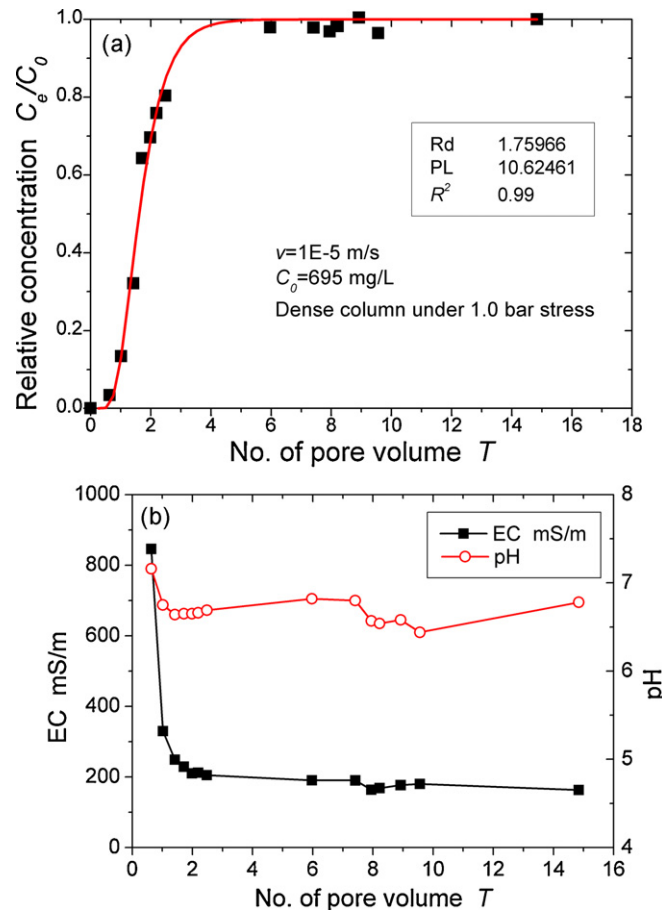


Fig. 6. BTC of Cd(II) (a) and solution properties (b) in GC column under confining pressure (100 kPa pressure loading).

sorbent is hard to get complete disturbance. This means that the solute would have less chance to access the surface of the sorbent. And thus the adsorption would be less likely to take place during the permeation process.

This observation is noteworthy since the density of the adsorbent should be taken into consideration when designing a similar filter adsorption facility for wastewater treatment. These results also notify us that the in situ application of adsorbents in groundwater treatment in terms of reactive barring wall should be very careful since the barring performance of the adsorbent might deviate significantly from that obtained from batch test. Measures, such as maintaining a moderate density of the filling materials, should be taken to adjust the sorption capacity of the sorbent in these situations.

Fig. 6(b) shows the solution properties of the leachate from GC column. The electrical conductivity was found to consistently decreasing from the beginning of Cd(II) infiltration. The astonishingly high EC at the first sample was about 846.00 mS m^{-1} . This could be explained by the cation exchange reaction between Cd(II) and active sorption sites on GC surface. The solution was checked and the main composition of the leached cations is potassium. At the beginning of infiltration, the sorption of Cd(II), although very limited in capacity, did take place regarding the observed BTC and EC. Change in EC was gradually equilibrated and the residual value was around $163.00\text{--}190.00 \text{ mS m}^{-1}$, indicating the total breakthrough of Cd(II) in the column. The change in pH also had the similar decreasing trend to that of EC. The solution pH decreased from the alkaline state from the beginning to the weak acidic state afterwards. However, the decreasing trend stopped later and the solution pH was found to range from 6.44 to 6.78.

4.4. Leaching of Cd by tap water

In order to investigate the long term stability of the toxicant laden adsorbent in simulated underground environment, a leaching test with tap water was conducted in this study. Fig. 7 shows the BTC of Cd(II) leached by tap water. The column was the same to the one in the above test. The difference is that the column was used sequentially for this test. After the complete breakthrough of the GC column by Cd(II), the source solution was replaced by tap water and all the other conditions were kept to be identical.

The BTC was characterized by a peak and a tailing. The maximum Cd(II) concentration in the leachate was determined at 201.60 mg L^{-1} which is much less than the initial input value ($C_i = 695.00 \text{ mg L}^{-1}$). This might be caused by the gradual adsorption process with equilibration time.

The residual Cd(II) concentration was 12.30 mg L^{-1} which is much higher than the tap water ($C_0 = 0.00 \text{ mg L}^{-1}$). This observation showed that the adsorbed Cd(II) on compact GC column was not stabilized on the sorbent in presence of diluted clean water. The previously fixed Cd(II) by GC in the presence of concentrated Cd(II) solution was released once again into the solution when the pore liquid was replaced by tap water which did not contain Cd(II). Previous studies using batch method have confirmed the gradual desorption of solute from adsorbent when the equilibrium concentration in solution decreased [18]. Successive leaching experiments prove that a lead complex sorbed on the surface of Fe colloid or FeOOH polymers could be leached out from the solid ashes [24]. This study further proved the negative effect of fluctuation in solute concentration in pore liquid.

The desorption of solute is actually existing, and is time dependent as the leaching has a low rate. This means the leaching would last for a long time until the new equilibrium is obtained [25]. Even on "L" type adsorbent, the desorption is still present in column leaching test, indicating the potential risk of toxicant release in the long run. The monitoring works are needed when such kind

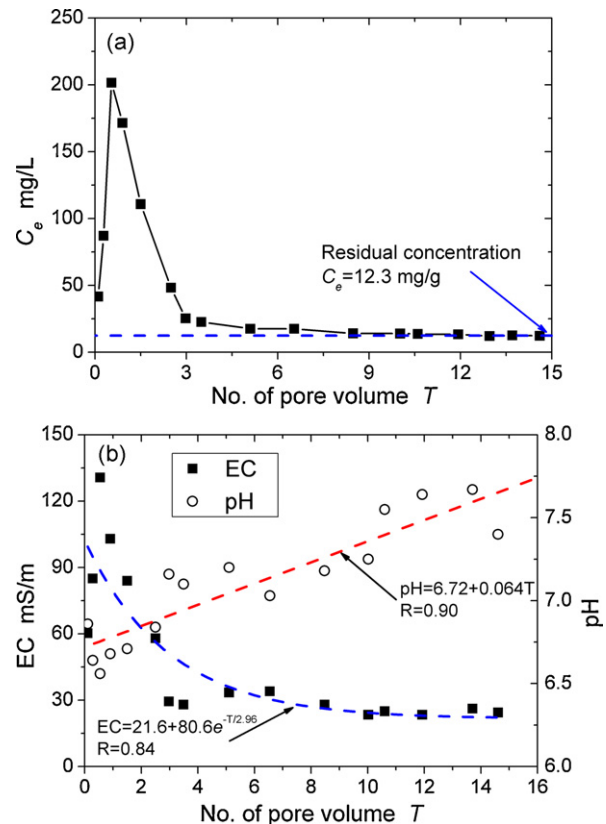


Fig. 7. BTC of Cd(II) (a) and solution properties (b) leached by tap water after the GC column was broken-through by concentrated Cd(II) solution (confining pressure 100 kPa ; $C_0 = 0 \text{ mg L}^{-1}$; $C_i = 695 \text{ mg L}^{-1}$; $v = 1.2 \text{E} - 5 \text{ m s}^{-1}$).

of reactive permeable wall is applied in practice. When the barring material was broken through, the filling adsorbents should be excavated and properly dealt with as soon as possible in order to prevent the leaching of toxicant from the solid to the pore liquid.

The EC in the leachate was found to decrease with the flush of the tap water while the pH increases. The change of EC could be fitted by an exponential equation, which is consistent with the above mentioned speculation of dynamic desorption of Cd(II) that is dependent on time. The pH was linearly dependent on elapsed time, indicating the gradual reclamation of the natural state of GC which has an alkaline property.

4.5. Effect of influent pH

Fig. 8 shows the BTCs of Cd(II) in GC column when permeated with acidic solution. The pHs of the infiltrated solution were ranged within 2.14–3.16. It is obvious that the BTC was located in the left side for solutions with lower pH which could breakthrough the column within a much less duration. For the tested four columns Col I–Col IV, the numbers of pore volume was determined at 9.10, 15.20, 27.70 and 37.40, separately, when the column was broken through. The maximum concentration of Cd(II) in the leachate was found to be much higher than that in the influent. The peaks in Cd(II) concentration for the four tested columns were ranged from 1.38 (Col IV) to 2.95 (Col III). The adsorption of cationic heavy metals has been found to be greatly decreased in acidic solution condition [8,15,25,26]. Our previous investigations on metal adsorption on various biomasses are also in agreement with this phenomenon [15,23].

The abnormally high value in Cd(II) concentration is likely to take place in the following processes: (1) neutralization of acid in the solute front in the column; (2) adsorption of Cd(II) on GC at

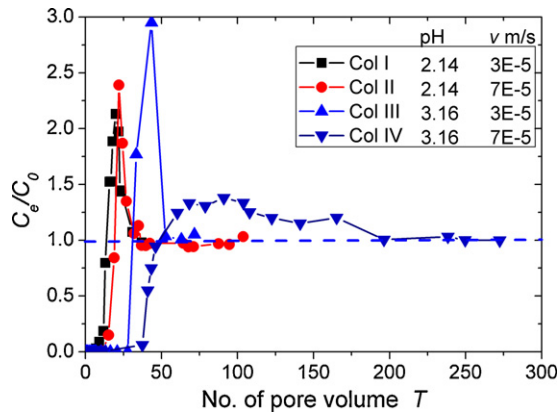


Fig. 8. BTCs of Cd(II) in GC column when permeated with acidic solutions ($C_0 = 100 \text{ mg L}^{-1}$).

comparatively neutral pH; (3) exhaustion of acid buffering capacity of GC in contact with influent with continuously increasing acidity; (4) release/desorption of previously adsorbed Cd(II) in the solute front when the pH of pore liquid was decreased. The finally released amount of Cd(II) include those previously accumulated in the GC. Therefore a peak in BTC was observed in the leaching test. Afterwards, the BTC returned to the normal level equivalent to the input value.

The permeating velocity was found to influence the BTC to some extent. The increase in velocity appeared to postpone the arrival of breakthrough of the column. This is reverse to the previous observation in neutral pHs as shown in Fig. 8. The discrepancies in BTCs between Col III and Col IV include the peak in C_e/C_0 and the equilibration duration. The increase in permeating velocity increased the equilibration time, not only in breakthrough time when $C_e > 0$, but also the final equilibration time when $C_e/C_0 = 1$. It is shown that the higher infiltration velocity is favorable for a better barring performance towards Cd(II).

4.6. Effect of ionic strength on Cd(II) leaching from GC column

Fig. 9 shows the effect of salinity on solute breakthrough curves. The solution with higher ionic strength appeared to breakthrough earlier. These BTCs were fitted by Eq. (9) using least square root method. The model constants were shown in Fig. 9. The coefficients of determination were both determined at $R^2 = 0.99$. The retardation factor R_d was determined at 72.51 and 60.48, respectively for solution at $I = 0.001$ and 0.01 M . The sorption capacity was found to decrease with increasing salinity. This is in agreement with other studies [6,16,25]. The increased ionic strength might introduce increased competition to the target toxicant about the adsorption sites on the adsorbent.

The change of EC in the leachate was rapidly equilibrated by the influent. The ECs of the two columns were determined at 34.00 and 152.00 mS m^{-1} , separately. The pH was found to decrease with increasing infiltration time, ranging from 6.40 to 5.50. This trend is consistent with the change in Cd(II) concentration as shown in Fig. 9(a), and thus could be viewed as a result of solute–sorbent interaction.

4.7. Chelant enhanced desorption of adsorbed Cd(II) from GC column

The effects of two chelants NTA and EDTA were investigated in this section. Fig. 10 shows the BTC of Cd(II) in different conditions. The column was originated from the leaching test in the previous section when the effect of pH was accounted. The chelating

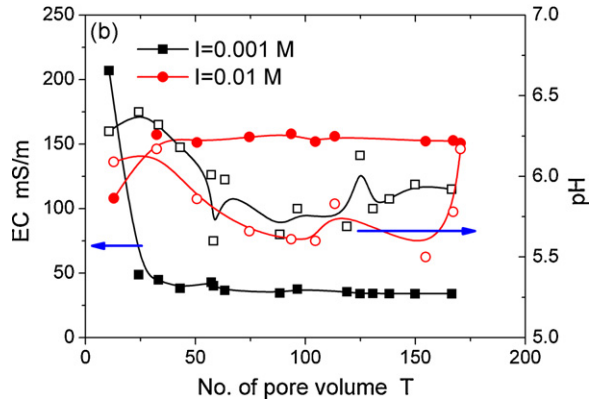
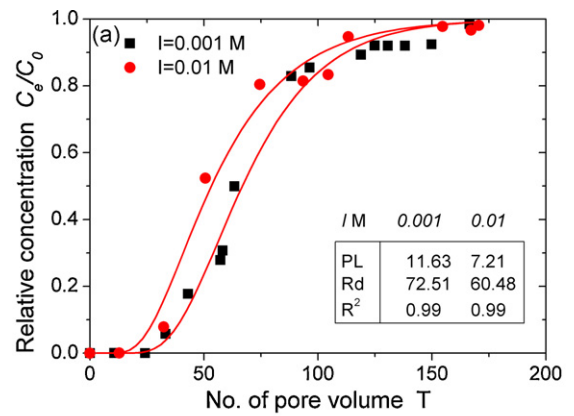


Fig. 9. Effects of ionic strength on BTC of Cd(II) (a) and the solution properties (b) in GC column ($C_0 = 100 \text{ mg L}^{-1}$; natural pH; $v = 1.2 \times 10^{-4} \text{ m s}^{-1}$. Solid symbol: EC; open symbol: pH).

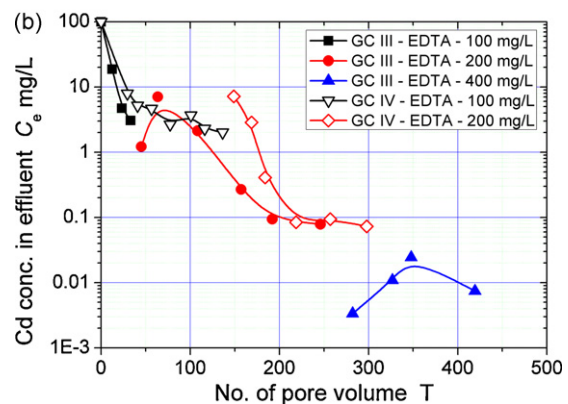
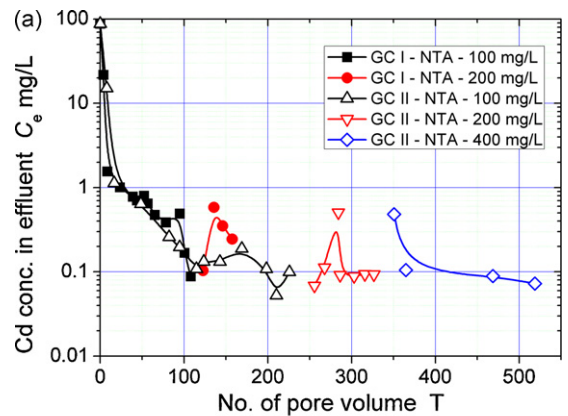


Fig. 10. BTC of Cd(II) in GC columns laden by Cd(II) using NTA (a) and EDTA (b) solutions ($v = 1.7 \times 10^{-4} \text{ m s}^{-1}$).

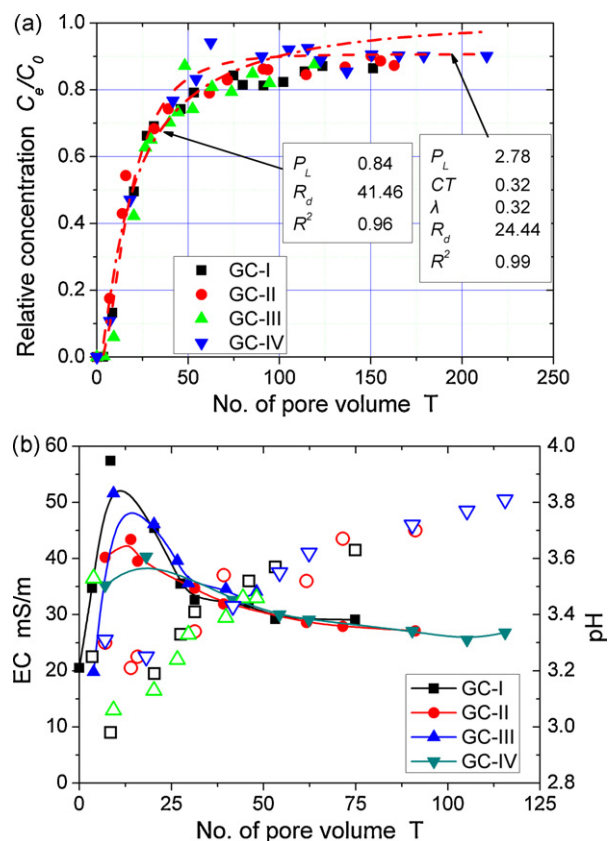


Fig. 11. BTC of Cd(II) in recycled GC column after flushed with chelant (a) and solution properties in leachate (b) ($C_0 = 100 \text{ mg L}^{-1}$; solid symbol: EC; open symbol: pH; the curves in figure (a) were fitted by solute transport models).

agents were dissolved in distilled water to required concentration and were permeated through the Cd(II) saturated columns Col I–Col IV. The BTC showed that the Cd(II) was effectively desorbed from GC by the chelant. The effect of EDTA appeared to be more effective than that of NTA because the residual concentration of Cd(II) in presence of EDTA was about ten times less than that of NTA. Increasing the concentration of chelant, the amount of removed Cd(II) was found to increase at beginning but quickly come to the same value to the previous stage. The gradual release of Cd(II) from the GC column indicated that the desorption was composed of rapid and slow reactions. The surface of GC is structured with various pits and pores. The adsorbed Cd(II) might be pertained in the micropores and thus might pose great difficulty in desorption. Recycling of Cd(II) laden GC appeared to be challenging by the chelant leaching method, although the results were encouraging. Because the GC is very cheap in cost, easy to prepare and abundant in the nature, the recycling of GC by expensive chemicals appears to be difficult and not to be cost effective. Direct burring or incineration might be more appropriate in practical viewpoint.

4.8. Barring effect of recycled GC for Cd(II)

Fig. 11 shows the BTCs of Cd(II) in recycled GC columns after flushed with chelating agents. These test data were found to distribute in the similar pattern within a narrow range. The BTCs were characterized with a gap between the plateau of the final Cd(II) concentration and the input value. The equilibrium Cd(II) concentration in the leachate did not reach the original concentration in the influent even after permeated with 220.00 pore volumes. The BTCs were fitted with two different transport models with Eq. (5) and without Eq. (9) adsorption kinetics, separately. The best-fit

curves and the calculated model constants were shown in Fig. 11(a). According to the determination coefficient, the model accounting for the adsorption kinetics was better to fit the BTCs ($R^2 = 0.99$). The predicted retardation coefficient R_d was found to be 24.44, much less than that obtained under similar condition in the test about ionic strength ($R_d = 60\text{--}72$). However, the adsorption of Cd(II) on chelant laden GC increased with increasing contact time in an exponential form, as indicated by the transport model.

The evaluation about the applicability of recycled GC column in Cd(II) adsorption appeared to be hard to give a confident conclusion. There existed two reverse features, increase in dynamic adsorption ($\lambda > 0$) and decrease in adsorption affinity (R_d). The former caused a decreased equilibrium Cd(II) concentration compared to the initial value in the influent. The latter resulted in an advance in breakthrough duration. After all, the GC could be successively reclaimed by chelating agents like NTA and EDTA. And the recycled GC appeared to possess reasonable capacity for Cd(II) adsorption. The adsorption effect was obviously demonstrated. But the applicability of these treatment methods should be further evaluated with regard to the cost effectiveness.

5. Conclusions

1. The prepared grass char was found to possess satisfying adsorption capacity and affinity towards Cd(II) in column leaching test. The infiltration velocity did not affect the breakthrough duration when the initial concentration was at medium level (69.50 mg L^{-1}), but did affect at high Cd(II) concentrations (695.00 mg L^{-1}).
2. The adsorption affinity (R_d) of GC towards Cd(II) decreased from 130 to 1.76 with increasing confining pressure from 0 to 100 kPa. This behavior was reported here for the first time. The adsorbed Cd(II) on GC under high confining pressure could be slowly desorbed by tap water with a tailoring effect (residual Cd(II) concentration at 12.30 mg L^{-1}). The application of GC in the underground circumstance should be carefully considered about this effect.
3. The breakthrough of acid Cd(II) solution was earlier for solution with less pH. The increase in permeating velocity and decrease in ionic strength were related to postponed breakthrough at pH 3.16.
4. The flush of Cd(II) laden GC column with NTA or EDTA solution ($C_0 \leq 200 \text{ mg L}^{-1}$) could remove most of the adsorbed Cd(II) within 200 pore volumes to achieve a leachate containing residual Cd(II) at $<0.01 \text{ mg L}^{-1}$.
5. The chelant flushed GC column could be further used to adsorb Cd(II) contained wastewater. The adsorption varies with the gradual elapse of permeation time.

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