Augmenting granular activated carbon with natural clay for multicomponent sorption of heavy metals from aqueous solutions

Nuhu Dalhat Mu’azu, Mohammed Hussain Essa and Salihu Lukman

ABSTRACT

Multicomponent adsorption of Cd, Cr, Cu, Pb and Zn onto date palm pits based granular activated carbon (GAC) augmented with highly active natural clay at different proportion was investigated. The effects of the initial pH and the adsorbents mixed ratio on the removal selectivity sequence of the metals evaluated. Batch adsorption experiments were undertaken at initial pH 2, 6 and 12. At initial pH 2, both the percent removal and the metals adsorptive capacity decreased with increasing GAC to clay ratio (from 0 to 1) with the percentage removal of Cd, Zn and Cr ions dropping from 68, 81, 100% to 43, 57 and 70%, respectively. At both pH 6 and 12, the percentage removals and adsorption capacities of all the heavy metal ions are higher than at pH 2. Selectivity sequences for pH 2, 6 and 12 followed the order Pb > Cr > Cu > Zn > Cd; Pb > Cr > Cu > Cd > Zn and Cd > Cr > Cu > Pb > Zn, respectively. The adsorption trends were analyzed in relation to point of zero charge and ζ-potential and the metals ions speciation at different pH. These results will help better understand the feasibility of augmenting GAC with natural clay minerals during fixed bed column test which is more beneficial for practical industrial applications.

Key words | augmenting GAC with clay, distribution coefficient, heavy metals adsorption, point of zero charge, zeta potential

INTRODUCTION

Heavy metal ions pollution has been gaining attention currently due to their toxicity to both humans and aquatic animals at elevated levels in the environment. They are usually stable and non-biodegradable within the ecosystem. As a result, they tend to bioaccumulate in living tissues, thereby causing some serious health concern (Jiang et al. 2010; Sen & Gomez 2011). Simultaneous contamination of soils by several heavy metals has been reported (Calabrese et al. 1997; Kock & Rotard 2001; Serrano et al. 2005; Xiong et al. 2005). As such, competitive adsorption of these trace metals becomes of paramount importance for the determination of their availability to plants and mobility/movement within the environment. Depending upon their leachability and fixation characteristics, groundwater may be at risk of being contaminated (Zhang & Zheng 2007). Thus, assessment of the competitive adsorption of these heavy metals will give an insight into the leachability, potential toxicity and bioavailability of heavy metals in geosphere (Serrano et al. 2005). It will also help in the determination of soil capacity to respond to the introduction of heavy metals into the soil system (Reddy & Dunn 1986; Srivastava et al. 2005; Moreno et al. 2006; Zhang & Zheng 2007). Zhang & Zheng (2007) highlighted that the soil properties correlated with the uptake and movement of heavy metals in soil include pH, cation exchange capacity (CEC), soil organic matter (SOM), specific surface area and mineralogical composition of the clay minerals. Different soils exhibit different characteristics in controlling heavy metal retention and mobility which, in turn, depends on potential partitioning between soil-liquid interface determined by their distribution coefficients (Gomes et al. 2001). A number of physico-chemical techniques have been used for the removal of heavy metals in water and wastewater. One of the commonest techniques is adsorption on active solid surfaces. Efforts are still ongoing for discovery of cheap and efficient adsorbents for removal of heavy metals such as granular activated carbon (GAC) produced from agricultural/industrial wastes and natural/synthetic clay minerals.
and sediments. In recent times, clay minerals have been attracting attention due to their inherent natural characteristics for effective sorption of heavy metal removal from aqueous systems (Uddin 2017). This owes to their higher ion-exchange capacity and complexation potentials with the heavy metals (Srivastava et al. 2005; Bekkouche et al. 2012; Uddin 2017). Several studies related to competitive adsorption in the literature onto raw natural clay minerals focused on batch test with very few works carried out in continuous flow systems (Guerra et al. 2010, 2013; Gupta & Bhattacharyya 2012; Wongkoblap et al. 2013). This could be attributed to the low permeability of natural clay minerals that render the fixed bed adsorption tests practically difficult. Hence, in a few cases where column tests were undertaken using natural clay, the columns were very small bench-scale columns and the minerals were either mixed with sand (Wongkoblap et al. 2013) or were sieved and larger more porous particles were used (Guerra et al. 2010, 2013) in order to provide adequate column flow. However, there are clear merits of continuous process (column studies) over batch type operations for (i) achievable higher adsorption capacity and (ii) larger industrial applications are based on the continuous process. This renders fixed bed study more beneficial compared to the widely reported batch study. In contrast, GAC are very porous materials that allow fixed column test to be undertaken more conveniently and effectively. Considering the high capacity of the clay minerals used in this study, it was suggested that the clay mineral could augment the performance of the GAC used, thereby rendering the GAC-clay mixture employable for column tests. Hence, this study investigates the ability of natural clay to augment the adsorption capacity of GAC locally produced from date pits for simultaneous removal of multi-component of Cd, Cr, Cu, Pb and Zn in aqueous systems.

MATERIALS AND METHODS

Reagents

Throughout the study, analytical grade reagents were used. The heavy metal ions standard solutions were prepared from their respective nitrate salts having concentration of 1 g/L each. Ultra-pure deionized water was used for stock solution preparation and dilution purposes. Solutions of multi-component metal ions were prepared at the same concentration (20 mg/L each). pH adjustments to the desired values (2, 6 and 12) were achieved using 0.1 N HCl or 0.01 M NaOH solution. All glassware were cleaned with dilute HNO₃ (10% v/v) and oven dried (Isotemp oven, Fisher Scientific) at 120 °C before use.

Preparation and characterization of adsorbents

The natural clay was sampled from natural clay deposit of Al-hassa oasis in Eastern Province of Saudi Arabia. Lukman et al. (2013a) earlier reported its physicochemical and mineralogical characterization methods and results. The GAC was produced locally from date palm pits using phosphoric acids whose characteristics were reported elsewhere (Lukman et al. 2013b; Mu’azu et al. 2017). The point of zero charge (pHₚzc) for both clay and GAC were determined using pH drift method according to Rivera-Utila et al. (2001), while the zero potential (ξ-potential) was measured using Zetasizer nano series (Malvern, UK).

Adsorption experiments

The clay mineral was powdered using a wooden pestle and sieved through 200 mesh to obtain finer grains (i.e. <75 μm). The resulting clay powder was washed with nitric acid and oven dried at 110 °C. These adsorbents were mixed at different GAC percent compositions or ratios (0, 0.2, 0.4, 0.8, 1). The GAC ratio is defined as the mass of GAC to the total mass of the adsorbant (GAC plus clay). In each case, a total of 5 g mass of the adsorbant was mixed with 100 mL of mixed heavy metal ions containing Cd, Cr, Cu, Pb and Zn (each 20 mg/L), and the resulting suspension pH was adjusted to the desired value (2, 6 or 12). Batch adsorption experiments were conducted at constant room temperature of 20 °C. Solutions containing the heavy metal ions and adsorbents was agitated on a rotary shaker (New Brunswick Scientific Co., Inc., USA) for 20 h. The suspension was filtered twice; first using 0.45 μm, 150 mm Φ Whatman membrane, then by suction filtration with a finer size membrane having pore size of 0.2 μm and 47 mm Φ. The filtrates were collected in PTFE capped vials and heavy metals analysis followed immediately. US EPA Method 200.2, a procedure prepared by Martin et al. (1994) for spectrochemical, was adopted for determination of heavy metals concentration in the supernatant.

Analytical method

All filtrates from the adsorption studies were analyzed for the heavy metals (i.e. Cd, Cr, Cu, Pb and Zn) using inductively coupled plasma optical emission spectrometry.
(ICP-OES; Spectro Ciros Vision model) (Ortega 2002). Other quality control measures stipulated in the US EPA Method 200.7 (Martin et al. 1994) and Method 200.8 (Creed et al. 1994) were adhered to. All tests were run in triplicates and the average was used for the analysis of results. The amount of heavy metals removed (adsorbed) at equilibrium was analyzed and interpreted using adsorptive capacity, $q$, percentage adsorbed onto the clay soil, $R$, and distribution coefficient, $K_d$. These parameters were computed using Equations (1)–(3), respectively.

$$q = \frac{(C_0 - C_e)V}{M}$$

(1)

$$R = \frac{C_0 - C_e}{C_0} \times 100$$

(2)

$$K_d = \frac{C_a}{C_e}$$

(3)

where $q =$ adsorptive capacity (mg/g), $C_0 =$ initial liquid-phase concentration of sorbate (mg/L), $C_e =$ equilibrium liquid-phase concentration of sorbate (mg/L), $C_a =$ equilibrium solid-phase adsorbed concentration of sorbate (mg/kg); $M =$ is the adsorbents mass (g); $V =$ volume of solution (mL); $R =$ percent pollutant adsorbed (%); and $K_d =$ distribution coefficient of the sorbate (L/kg).

RESULTS AND DISCUSSION

Characteristics of the adsorbents

The detailed physico-chemical properties of the clay sample obtained from the numerous analyses carried out as outlined have been reported earlier (Lukman et al. 2013a). The clay employed in this study composed of 4.3% SOM. Even at this low level, the SOM could play prominent role in the sorption of heavy metal ions (Sparks 2003) as they are characterized by high specific surface area as well as CEC (Stevenson 1982). The EC of the clay sample is 5617 milli Siemens per meter which implies that it has high dissolvable salts components (Sparks 2003; Grisso et al. 2009). The clay surface area (42 m$^2$/g) will give it ability to adsorb heavy metals on its surface. The plastic and liquid limits are 25.95 and 44.71, respectively. Figure 1 depicts a micrograph of the clay soil that clearly revealed the surface texture and porosity of the clay soil. The holes and smaller openings visible on the clay surface indicate that during adsorption, the clay would enhance the contact area and facilitate pore diffusion. Availability of the large surface area makes it possible for the clay soil to accommodate heavy metals on its active sites through ion exchange and complexation. The dominant elements are O and Si whose percentage compositions are 53% and 18%, respectively. Other elements present in lesser quantities are Ca, Al, Fe, Na, Cl, K and Mg. The mineralogical composition using X-ray diffraction (XRD) revealed that the clay is mainly composed of montmorillonite; quartz and calcite are also present in lesser quantities. Montmorillonite possesses a 2:1 layer structure with octahedral sheets separable by water molecules with properties rendering a good adsorbent (Reddi & Inyang 2000).

Competitive adsorption and selectivity sequence

Bekkouche et al. (2012) observed that ionic forms of heavy metals and ionization state of the surface functional groups of adsorbents enable pH to play the most significant role in adsorption studies. Variations of the percentage removal with GAC ratio at different pH are shown in Figure 2 for all the metal ions. Figure 3 shows the variations of the adsorption capacities of the different mixed adsorbents with the GAC ratio. It is evident from Figure 2 that Cu, Pb and Cr were adsorbed to much greater extents than Cd and Zn at pH 2. As the percentage of GAC increases in the adsorbent mixture, remarkable reduction in the percentage removal of Cd and Zn was noted, from 68 to 43% and 81 to 57%, respectively. In addition, adsorption of Cr dropped sharply in the absence of the clay minerals (i.e. 100% GAC). From Figure 2, adsorptive capacity for all the metal ions are observed to be decreasing with increasing GAC ratio at pH 2. Highest selectivity for Pb, Cr and Cu was noted from their respective higher distribution coefficients at pH 2 as shown in Table 2. Generally, the values of the distribution coefficients presented in Table 1 increases
with increasing selectivity of clay for the heavy metals and vice versa. The least selective metal ions were Cd and Zn whose distribution coefficients are 33.8 and 35.08 L/Kg, respectively. It may be difficult to arrive at a specific selectivity sequence at pH 2 because of complete adsorption of Pb ions at GAC ratio 0.8. This complete removal of Pb makes its equilibrium concentration to be zero and distribution coefficient to approach infinity. However, the following sequence may be deduced from Table 2 at pH 2: Pb > Cr > Cu > Zn > Cd.

Numerous competitive adsorption results onto soils and activated carbons revealed that Pb, Cr and Cu have higher selectivity than Zn and Cd with the selectivity sequence varying from one adsorbent to another (Gomes et al. 2001; Bansal & Goyal 2005; Covelo et al. 2008; Usman 2008). Comparable studies corroborated this as they reported that Cd and Zn ions are generally more difficult to remove from solution using adsorption compared to others such as Cr, Pb and Cu which possess high sorptive capacity for clay minerals (Srivastava et al. 2005; Covelo et al. 2007; Zhang & Zheng 2007; Usman 2008; Jiang et al. 2010; Bekkouche et al. 2012).

Adsorption preference of clay sorbents for Pb ions over most heavy metals could be attributed to its (i) greater first hydrolysis constant, (ii) higher atomic weight, (iii) greater ionic radius, and, subsequently, smaller hydrated radius (Shaheen et al. 2013). These characteristics make Pb most preferred element for both electrostatic as well as complexation reaction compared to the other cohabiting metal ions (Gomes et al. 2001; Usman 2008). At pH 6, Figure 2 shows that Cr and Cu ions have the highest percentage removal, while Cd and Zn are the least adsorbed at pH 2. The percentage removals of all the metal ions at pH 6 and 12 are higher than at pH 2 (Figure 2), while their adsorptive capacities fluctuate with GAC ratio except for Cr, whose adsorptive capacity shows a decreasing trend with increase in GAC ratio. This observation may be attributed to the creation of acidic surface functional groups on GAC which ionize in

Figure 2 | Percentage removal of the heavy metals at different pH and GAC-clay ratio.
solution to produce $H^+$, thus, leaving behind negative adsorption sites for positive cations (Bansal & Goyal 2005). Highest selectivity for Pb, Cr and Cu was also noted at pH 6 as shown in Table 2. The least selective metal ion was Zn, followed by Cd, Zn and Cd exchanging position in the selectivity sequence which is not unusual as corroborated by the results of Gomes et al. (2001) and Usman (2008). Nonetheless, the following sequence may be deduced from Table 2 at pH 6: Pb $>$ Cr $>$ Cu $>$ Cd $>$ Zn. This sequence is, to a greater extent, similar to trends as reported by other authors (Gomes et al. 2001; Bansal & Goyal 2005; Covelo et al. 2008; Usman 2008). However, under an alkaline condition (pH
12), Cd and Pb exhibited entirely different behaviors. Cd was adsorbed more than any other metal ion (Figure 2), while Pb was least adsorbed after Zn. Throughout the investigated pH range, Zn was the least adsorbed, which means it has the highest mobility in solution. Remarkable removal of metals ions at pH 12 may be attributed to the change in GAC surface functional group from positive, in the acidic pH, to negative in the alkaline condition with subsequent increase in the electrostatic attraction between metal ionic species in the solution and negative adsorption sites on the GAC surface. Highest selectivity for Cd, Cr and Cu were observed at pH 12 (Table 2). The least selective metal ions were Zn, followed by Pb. Onwu and Ogah (Onwu & Ogah 2013) also reported higher adsorption of Cd ions than Pb ions in alkaline pH using powdered African white star apple seeds as adsorbent. At pH 12, the following sequence could be deduced from Table 2: Cd > Cr > Cu > Pb > Zn. Corroboration of this sequence may also be found in other related studies (Gomes et al. 2001; Bansal & Goyal 2005; Covelo et al. 2008; Usman 2008).

**Effect of pH change on metal ions adsorptive behaviors**

The metal ions had the maximum adsorptive capacity when the low GAC ratio was low. These suggest the clay minerals surface charges as well the metals speciation favors adsorption onto the clay minerals compared to the GAC. Generally, depending on the solution pH, clay minerals

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH 2</th>
<th>pH 6</th>
<th>pH 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>Cd^{2+}</td>
<td>Cd^{2+} Cr(OH)^{2+}</td>
<td>Cd^{2+}; CdOH^{+}; Cd(OH)<em>{2} (aq); Cd(OH)</em>{3}; Cd(OH)_{4}^{2-}</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr^{3+}; Cr(OH)^{2+}</td>
<td>Cr_{2}(OH)<em>{3}^{+}; Cr^{3+}; CrOH^{2+}; Cr(OH)</em>{3} (aq); Cr_{2}(OH)_{3}^{2+}</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Cu^{2+}</td>
<td>Cu^{2+}; Cu_{3}(OH)<em>{2}^{2+}; CuOH^{+}; Cu</em>{2}OH^{3+}; Cu_{2}(OH)_{2}^{2-}</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>Pb^{2+}</td>
<td>Pb^{2+}; PbOH^{+}</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Zn^{2+}; ZnOH^{+}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Zero equilibrium liquid phase concentration.

**Table 1** Distribution coefficients of heavy metals at different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>GAC ratio</th>
<th>Distribution coefficients, K_d, L/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>42.02 522.01 1,823.32 780.00 83.36</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>34.41 51,741 1,632.89 798.00 40.73</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>46.95 3,519.82 1,682.13 2,701.09 38.02</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>38.01 2,777.20 1,542.50 4,020.40 26.79</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>26.31 1,592.90 1,388.45 HIGH* 13.91</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>15.11 44.82 534.02 298.22 7.64</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>33.80 2,271.93 1,433.88 – 35.08</td>
</tr>
</tbody>
</table>

12  | 0         | 362.78 19,027.62 HIGH* 283.03 |
|    | 0.2       | 308.14 14,794.81 HIGH* 196.68 |
|    | 0.4       | 148.56 7,387.41 HIGH* 179.00 |
|    | 0.6       | 292.74 4,577.70 2,577.40 627.25 18.63 |
|    | 0.8       | 339.71 4,631.16 1,599.43 2,375.21 115.09 |
|    | 1         | 932.38 3,616.36 2,560.65 744.82 31.53 |
| Average |          | 397.39 9,005.84 2,565.66 – 137.33 |

12 | 0         | HIGH* HIGH* 3,056.92 479.38 43.30 |
|    | 0.2       | 39,980.00 5,777.10 HIGH* 147.60 |
|    | 0.4       | HIGH* 6,329.21 4,020.40 448.93 217.53 |
|    | 0.6       | HIGH* 5,777.10 4,631.16 747.75 218.95 |
|    | 0.8       | 2,857.70 3,369.83 2,682.70 647.78 241.10 |
|    | 1         | HIGH* 3,056.92 2,375.21 1,287.19 141.81 |
| Average |          | – – 3,832.73 729.48 237.21 |

**Table 2** Visual Minteq speciation results for 25 mg/L initial concentration of each heavy metal in solution and temperature 25°C

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH 2</th>
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<th>pH 12</th>
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<tbody>
<tr>
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</tr>
<tr>
<td>Cu</td>
<td>Cu^{2+}</td>
<td>Cu^{2+}; Cu_{3}(OH)<em>{2}^{2+}; CuOH^{+}; Cu</em>{2}OH^{3+}; Cu_{2}(OH)_{2}^{2-}</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>Pb^{2+}; PbOH^{+}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Zn^{2+}; ZnOH^{+}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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are known to possess two types of surface charges; a net permanent surface charge and a variable charge can be +ve, positive -ve or zero at the point of zero charge (i.e. pH_{pzc}) (Polati et al. 2006; Sponza et al. 2013). Based on the pH drift method (Rivera-Utrilla et al. 2001), the pH_{pzc} is the point when pH_{final} = pH_{initial} which corresponds to the point of the intersection of line that passes through the origin and the plot of the pH_{final} vs pH_{initial} as depicted in Figure 4(a). Accordingly, the pH_{pzc} of clay and GAC of 9.72 and 6.65 indicates that the surface of clay and GAC switched from positive to negative at pH > 9.72 and pH > 6.65, respectively. Moreover, the negative ξ-potential drop across the clay (−0.47–56 mV) and GAC (−25–42 mV) solid/liquid double layer throughout pH 2–12 range (Figure 4(b)) suggests the surfaces of both sorbents were suitable for sorption of the ions regardless of the initial suspension pH (Hunter & James 1992; Zadaka et al. 2010). The high value of pH_{pzc} for the clay which could be attributed to presence of oxide or hydroxides of aluminium and iron in the mineral is comparative to those reported in literature (Polati et al. 2006; Sponza et al. 2013; Vhahangwele & Mugera 2015). Consequently, above these pH_{pzc} values, it was expected that the electrostatic attraction of metal ions on both the clay and GAC surfaces would increase, thereby leading to improved removal efficiency of the metal ions. Hence, at pH of 2 and 6, both the clay minerals and the GAC surface are positively charged which was susceptible to result in repulsion of positively charged metal ions in solution and, as a consequence, lowered the adsorption capacity (lower K_d values).

On the other hand, Table 2 shows the likely distribution of the species due speciation as a result of pH changes using Visual MINTEQ speciation modeling. Hence, it was expected that the different species in solution were predominantly (>99.94%) in cationic form under initial pH values of 2 and 6 while at pH 12 in anionic form. Also, according to Visual MINTEQ modeling, the saturation indices when the pH was increased to pH 12 were predominantly >0 suggesting possibility of precipitation of the metal ions to formation of their respective hydroxides (Table 2). Consequently, the anionic form of the species in solution, as well as the tendency towards precipitation, correlated well with the improved removal of the metal ions removal from the solution at pH 12 which would have resulted in the higher K_d values under pH 12 (Table 1). Acidic medium may not always favor removal of metal ions onto negative surfaces compared to basic medium due to disassociation of more anions, higher attraction forces and formation of hydroxides which would precipitate out of the medium at basic pH (Ismail et al. 2009). It is noteworthy to observe the fluctuation in Figures 2 and 3, which led to rapid decline in the adsorption, especially for Zn. Interestingly, this behavior was more pronounced at pH 6 which coincides with the point where there was drop in the ξ-potentials, especially for the clay (Figure 4(b)). Hunter and James (1992) postulated that at pH < pH_{pzc}, the ξ-potential could drop or even reversed to positive due to excessive protonation, increase in ionic strength resulting from increased dissolution of metal ions in the pore fluid and compression of the electrical double layer (Hunter & James 1992; Ismail et al. 2009). Obviously, other pH dependent mechanisms such as
speciation, redox and complexation reactions as well as co-metals ionic effects could have played dominant roles in the observed trends of the metal ions sorption (Fiol & Villaescusa 2009; Nurchi & Villaescusa 2011).

CONCLUSION

In this study, multicomponent adsorption of Cd, Cr, Cu, Pb and Zn onto natural clay mixed using date palm pits based GAC were conducted to investigate the effects of the initial solution pH and the adsorbents mixed ratio on the feasibility of augmenting the GAC for column adsorption tests. The main conclusions are as follows:

(1) Adsorption of the heavy metals onto the mixed adsorbents decreases with increasing in the GAC ratio.

(2) Pb ions possess the highest distribution coefficients at pH 2 and 6 and, hence, the highest adsorbed from solution. Pb selectivity decreased significantly in an alkaline condition.

(3) Conversely, Cd ions were the least adsorbed at pH 2. However, distribution coefficient of Cd ions increased from pH 6 to 12, thereby making them the most selective ions at pH 12.

(4) Selectivity sequences for pH 2, 6 and 12 are: Pb > Cr > Cu > Zn > Cd, Pb > Cr > Cu > Cd > Zn and Cd > Cr > Cu > Pb > Zn, respectively.

(5) Remarkable percentage removals for the heavy metals was observed at almost all the pH values, with some of the removals reaching up to 100%.

(6) These results will help better understand the feasibility of augmenting the performance of GAC produced from date palm wastes during a fixed bed column test, which is more beneficial for practical industrial applications.

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