Short Communication

High-capacity adsorption of Cr(VI) from aqueous solution using a hierarchical porous carbon obtained from pig bone

Shaochen Wei, Dongtian Li, Zhe Huang, Yaqin Huang*, Feng Wang*

State Key Laboratory of Chemical Resource Engineering, The Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, 15 Beisanhuan East Road, Beijing 100029, PRC, China

ARTICLE INFO

Article history:
Received 21 November 2012
Received in revised form 12 February 2013
Accepted 14 February 2013
Available online 22 February 2013

Keywords:
Pig bone
Hierarchical porous carbon
Adsorption
Hexavalent chromium
Equilibrium isotherms

ABSTRACT

A hierarchical porous carbon obtained from pig bone (HPC) was utilized as the adsorbent for removal of Cr(VI) from aqueous solution. The effects of solution pH value, concentration of Cr(VI), and adsorption temperature on the removal of Cr(VI) were investigated. The experimental data of the HPC fitted well with the Langmuir isotherm and its adsorption kinetic followed pseudo-second order model. Compared with a commercial activated carbon adsorbent (Norit CGP), the HPC showed an high adsorption capability for Cr(VI). The maximum Cr(VI) adsorption capacity of the HPC was 398.40 mg/g at pH 2. It is found that a part of the Cr(VI) was reduced to Cr(III) on the adsorbent surface from desorption experiment data. The regeneration showed adsorption capacity of the HPC can still achieve 92.70 mg/g even after fifth adsorption cycle.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Hexavalent chromium (Cr(VI)) has a severe future impact on environment and must be removed before being discharged to the aquatic system because of its toxic to livings (Sud et al., 2008). Adsorption is considered to be one of the most effective methods for treating Cr(VI) from aqueous effluents. But since the advantage of adsorption is achieved by well performing adsorbents, the choice of appropriate materials as an adsorbent is a quite important starting point. In this respect, a variety of materials have been developed as the adsorbent to remove Cr(VI) from wastewater, including activated carbon (AC), fiber, polymer, and so on (Jusoh et al., 2011; Vincent and Guibal, 2001; Gang et al., 2010). Despite carbon’s extensive use to treat Cr(VI) from effluent, it remains expensive and the demand for AC are a great. Improved and tailor-made materials are sought. Substitutes should be easily available, cheap and, above all, be readily regenerated, providing quantitative recovery (Mohan and Pittman, 2006).

Recently, the AC obtained from natural materials has attracted great attention of researchers as they can be available in an easy way and are green renewable. Numerous by-products of plants and animals have been used for preparation of AC, including coir pith, bamboo charcoal, corn stalk, Palm shell (Sukasbye et al., 2007; Wang et al., 2011; Chen et al., 2012; Mojdeh et al., 2010).

Among them, bone, as one kind of food industry byproducts, is very cheap and environment friendly with abundant production. And one kind of bone charcoal (Ghanizadeh et al., 2012) prepared from cow bone had been as an adsorbent material for the removal of Cr(VI), and the amount of adsorption was 2.2 mg/g. However, to improve the adsorption capacity is worthy of our further exploration. It is necessary to develop a new type and highly efficient bone-based adsorbent material.

Based on this, our research group prepared a hierarchical porous carbon based on the pig bone, which had high surface area and the hierarchical porous structure (Huang et al., 2011). Here, we speculate that the following points may be in favor of making the HPC an ideal candidate for chromosome-containing treatment: (i) the prepared carbon possess high surface area and well developed pore structure, which could provide more adsorption site; (ii) a mount of effective functional groups is existed on the surface of HPC; (iii) the preparation of HPC is based on easy operation because the pig bone is a kind of natural organic/inorganic composite material without synthesis and disperses of the template.

In this research, a novel hierarchical porous carbon obtained from pig bone (HPC) as the adsorbent was studied to evaluate its adsorption potential for Cr(VI) from aqueous solutions. The data were compared with the commercial carbon (Norit CGP). The effects of solution pH value, metal ions concentration, and temperature on the removal of Cr(VI) were investigated in a series of experiment. And desorption was investigated and the underlying mechanism for Cr removal by the adsorbents was elucidated.

* Corresponding authors. Tel./fax: +86 10 6443 8266.
E-mail addresses: huangyaqin9@gmail.com (Y. Huang), wangf@mail.buct.edu.cn (F. Wang).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.02.040
2. Methods

2.1. Adsorbents and reagents

HPC was prepared according to the method described in a previous study (Huang et al., 2011) and the commercial activated carbon NORIT CGP SUPER (Norit CGP) purchased from Norit company (Beijing). The stock solution of Cr(VI) in deionized water was prepared at a concentration of 1000 mg/L from water-soluble metallic salts (K₂Cr₂O₇). All water samples used in the adsorption experiment were diluted from this stock solution with deionized water. For pH adjustments to the water samples, 0.1 mol/L NaOH and 0.1 mol/L HCl were used.

2.2. Surface and structure characteristics of the adsorbents

Micromeritics ASAP 2020 instrument was used to characterize the surface area and pore-structure of the adsorbents using N₂ sorption at 77 K. The functional groups present in the adsorbent were characterized using the KBr translucent disc to prepare the HPC and Norit samples with a Fourier transform infrared spectrometer (FTIR, Nicolet 6700) over the wavelength region 4000–500 cm⁻¹. The surface of the Cr-loaded sample was analyzed using an ESCALAB 250 X-ray photoelectron spectroscopy (XPS). Boehm's titration method was used to quantify the basic and acidic surface functional groups of HPC and Norit (Arafat et al., 2004). The point of zero charge was carried out using the pH drift method (Babic et al., 1999).

2.3. Batch uptake studies

Adsorption equilibrium experiments were carried out in a temperature controlled thermostatic shaker operated at 130 rpm. All the Cr(VI) solutions required for experiments were freshly prepared by diluting the stock solution. The volume of Cr(VI) solution was 5 mL with initial concentration 100 mg/L and the dosage of adsorbent used was 5 mg. After 24 h of contact the adsorbent was separated from solution by filtration and the filtrate was analyzed for residual Cr(VI).

2.4. Desorption studies

For the desorption study, 0.1 g HPC adsorbents were added to 100 mL of Cr(VI) solutions (100 mg/L, pH = 2), and shaken at 130 rpm for 24 h at 27 °C. Thereafter the Cr(VI)-adsorbed HPC adsorbent was separated from solution by filtration, then shaken for 24 h in 100 mL of 1 M NaOH solution (130 rpm, 27 °C). After filtration, Cr(VI)-desorbed HPC adsorbent was separated and washed by distilled water to neutralize and followed by the oven drying.

2.5. Analytical methods

The concentration of Cr(VI) was analyzed spectrophotometrically by UV/Vis double beam spectrophotometer (UNIC-UV-2000) at 540 nm after using diphenylcarbazide complexing agent (Pehlivan and Cetin, 2009). The total chromium (Cr(VI) + Cr(III)) was measured by a graphite furnace atomic adsorption spectroscopy (AA 6300C, SHIMADZV, Japan). All experiments were conducted in several times (normally more than three times) and average values were considered.

3. Results and discussion

3.1. Structure and texture characterization

The textural characteristics of the HPC and Norit CGP calculated from nitrogen adsorption–desorption isotherms are listed in Table 1. In comparison with Norit CGP, the surface area and total pore volume of the HPC are much larger than that of Norit CGP, which means the HPC could provide more active adsorption sites and capacity for metal ions. To be specific, it is can be inferred from the nitrogen adsorption–desorption isotherm of HPC (Wei et al., 2011) that it has not only micropores in large quantities, but also possesses developed mesoporous and macroporosity structure. Meanwhile, for the Norit CGP, it showed the similar adsorption–desorption isotherm type IV (Fig. S1). The pore size distribution of HPC is consistent with nitrogen desorption isotherms and demonstrated that the pores of HPC are mainly distributed in three regions: micropores (<2 nm), mesopores (2–50 nm) and few macropores (>50 nm), but the Norit CGP mainly consists of mesoporous and a few micropores (Fig. S2). These data further manifested that the HPC both has high surface area and well developed pore structure.

3.2. Surface chemistry

The surface oxides on a carbon can have acidic as well as basic properties and determine the surface acidity/basicity and the adsorption characteristics of the materials. In this work, the surface functional groups of HPC and Norit CGP were characterized by using the FT-IR and Boehm Titration Method. The identification of various forms of different constituents in HPC and Norit CGP had been done with the help of IR spectra (Fig. S3). The broad band at around 3432 cm⁻¹ was observed in both samples, which was attributed to hydroxyl (O–H) stretching. The peak observed at 2980 cm⁻¹ and 2920 cm⁻¹ corresponded to the C–H group. The band at about 1595 cm⁻¹ corresponded to the carbonyl-stretching group (C=O) or carbon–carbon double bonds (C=C) generally found in activated carbons. The band at about 1121 cm⁻¹ was related with the C–O stretching vibration (Altun and Pehlivan, 2012). Since the absorption bands of various groups can overlap and shift which depend on their molecular structure and environment, it was hard to determine the specific functional groups on the surface of activated carbons (e.g., COOH) only by IR. In order to certify that the above result, the Boehm titration was used to evaluate the surface functional groups further. It can be seen that the mainly acid surface group of HPC is in the form of carboxyl group and the total number of acidic groups was more than that of Norit CGP (Table S1).

3.3. Effect of pH value

The pH value, associated with the adsorption mechanism, is one of important parameters in controlling the adsorption of Cr(VI). It causes the change of surface charge of the sorbent, conversion of the chromium species and other ions present in the solution, and extent of dissociation of functional groups on the active sites of the adsorbent. For chromium aqueous, the distribution of Cr(VI) species

<table>
<thead>
<tr>
<th>Textural property</th>
<th>HPC</th>
<th>Norit CGP</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m²/g)</td>
<td>2157</td>
<td>1281</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>2.26</td>
<td>1.33</td>
</tr>
<tr>
<td>Horvath–Kawazoe micropore volume (cm³/g)</td>
<td>0.77</td>
<td>0.21</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>4.18</td>
<td>3.14</td>
</tr>
</tbody>
</table>
is dependent on both the total concentration of Cr(VI) and pH value of the equilibrium solution. The Cr(VI) may exist in the aqueous phase in several anionic forms, such as chromate \( \text{CrO}_4^{2-} \) (pH > 6.0), dichromate \( \text{Cr}_2\text{O}_7^{2-} \) and \( \text{HCrO}_4^- \) (1.0–6.0) or \( \text{H}_2\text{CrO}_4 \) (pH < 1.0) (Kartthikeyan et al., 2005). In this work, Cr(VI) adsorption onto HPC and Norit CGP as a function of pH ranging from 2 to 10 was shown in Fig. 1. It can be seen from Fig. 1 that the adsorption abilities of Cr(VI) on both adsorbents were sharply decreased with the increase in pH from 2 to 10. One of the important reasons was that the pH influences the protonation or deprotonation of the sorbent. As the pH of the chromium aqueous was lowered, a large number of protons could easily coordinate with functional groups present on the activated carbon surface. Especially when the pH falls below each pHpzc of the reagent, the generated Cr(III) can also absorb as oxo anions in water. The lower pH, the better adsorption capacity for Cr(VI) was obtained. Particularly at pH 2, both HPC and Norit CGP had almost completely adsorbed the hexavalent chromium ion. Thence, the increase of Cr(VI) concentration from 100 to 1000 mg/L; HPC and Norit CGP = 1 g/L, respectively; Temp = 27 °C.

### 3.4. Adsorption isotherm

The Langmuir and Freundlich isotherm have been extensively used to describe the equilibrium established between adsorbed metal ions on the adsorbent \( q_e \) and metal ions remaining in solution \( C_e \) at a constant temperature (Gupta and Ali, 2004). In this research, adsorption isotherms of the type \( q_e \) vs \( C_e \) were used to verify the isotherm models (Fig. 2). And the equilibrium adsorption data were fitted with Langmuir and Freundlich models by the following equation, respectively:

\[
q_e = q_m b C_e / (1 + b C_e) 
\]  

\[
q_e = K C_e^{1/n} 
\]

where \( C_e \) (mg/L) is the equilibrium concentration of metal ions, \( q_e \) (mg/g) is the amount of metal ions adsorbed, \( q_m \) (mg/g) is the maximum adsorption capacity of metal ions, and \( b \) (L/mg) is the Langmuir isotherm coefficient, \( K \) (mg/g) and \( n \) are the Freundlich constants. The calculated Langmuir and Freundlich constants are summarized in Table 2. In comparison with the Freundlich model, both two kinds of adsorbents fit better to Langmuir model based on the correlation coefficient. The maximum Cr(VI) adsorption capacity on the HPC followed by the Langmuir isotherm was 398.40 mg/g at 27 °C, which was much higher than the commercial carbon Norit CGP under the same conditions. In addition, for both adsorbents, the maximum adsorption capacity of Cr(VI) increases with increasing temperature (from 27 to 47 °C). These results implied that the nature of process is endothermic.

### 3.5. Adsorption kinetics

The effect of contact time on adsorption of Cr(VI) onto the Norit CGP and the HPC are shown in Fig. S4. The adsorption capacities of two adsorbents increased rapidly in the initial stages of contact time. Then the adsorption rate slowly decreased. In addition, to investigate the kinetic mechanism of Cr(VI) sorption onto the adsorbent, Two kinetic models were examined: pseudo-first-order (Eq. (3)) and pseudo-second-order (Eq. (4)).

\[ \log \left( q_e - q_t \right) = \log q_m - k_1 t / 2.303 \]  

\[ t / q_t = 1 / k_2 q_m^2 + t / q_m \]

Where \( q_t \) is the amounts of Cr(VI) adsorbed at time \( t \) (hour), And \( h = k_2 q_m^2 \) where \( h \) is the initial adsorption rate. The applicability of suitable kinetic model is evaluated by the magnitude of the correlation coefficients \( R \) listed in Table 3. It showed that values of correlation coefficients \( R^2 > 0.999 \) for pseudo-second-order model are greater than those of pseudo-first-order model. This result

![Fig. 1. Effect of pH on the adsorption of hexavalent chromium (Conditions: initial Cr(VI) concentration 100 mg/L; HPC and Norit CGP = 1 g/L, respectively; Temp = 27 °C).](image)

![Fig. 2. Adsorption isotherms of Cr(VI) onto HPC and Norit CGP. (Conditions: initial Cr(VI) concentration from 100 to 1000 mg/L; HPC and Norit CGP = 1 g/L, respectively; Temp = 27 °C).](image)
desorption cycles reveal that (Fig. S6) adsorption capacity addition, use of the regenerated adsorbent for five adsorption–

a chemical interaction between the adsorbents and adsorbate. In

on the HPC and negatively charged Cr(VI) ions), but also involves

uble Cr

existed in the solution after desorption due to the presence of sol-

seem to be high, about 80% for HPC. And the Cr(III) ion may also

this work, the desorption efficiency of the total chromium did not

igate desorption of the Cr(VI) adsorbed on the HPC. As indicated in

Financial support from the National Science Foundation of Chi-

and remains 92.70 mg/g even in the fifth cycle. Nevertheless, a

3.6. Desorption studies

Desorption studies help to determine the adsorption mechanism and to evaluate the feasibility of regenerating the spent adsorbent. Experiments were conducted with 1 M NaOH to investigate desorption of the Cr(VI) adsorbed on the HPC. As indicated in this work, the desorption efficiency of the total chromium did not seem to be high, about 80% for HPC. And the Cr(III) ion may also existed in the solution after desorption due to the presence of soluble Cr(OH)₄⁻ at very high pH. In addition, XPS analyses (Fig. S5) showed the presence of both Cr(VI) and Cr(III) species on the adsorbent surfaces. This proved that adsorbed Cr(VI) on the surface of the HPC was partially reduced to Cr(III) by electron–donor moieties. Hence, the adsorption process not only probably presents electrostatic attraction (the binding of positively charged groups on the HPC and negatively charged Cr(VI) ions), but also involves a chemical interaction between the adsorbents and adsorbate. In addition, use of the regenerated adsorbent for five adsorption–desorption cycles reveal that (Fig. S6) adsorption capacity (99.80 mg/g) of the HPC have almost same for first two cycles and remains 92.70 mg/g even in the fifth cycle. Nevertheless, a more in-depth research on the recovered chromium sorbent using OH⁻ treatment and regeneration performance still needs further study and improvement.

4. Conclusions

The hierarchical porous carbon obtained from pig bone was used for the adsorption of Cr(VI) from aqueous solution. Present work demonstrated that adsorption capacity of the HPC was strongly dependent on pH of the initial solution. The experimental data were fitted well to the Langmuir isotherm and pseudo-second-order kinetic model. Comparing with the Norit CGP, the adsorption capacity of the HPC was up to 398.40 mg/g, and the adsorption capacity increased with increasing temperature. These results confirm that the HPC can be considered as a promising and high-capacity adsorbent for the adsorption of Cr(VI) from aqueous solution.

Acknowledgement

Financial support from the National Science Foundation of Chi-

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.02.040.

References


Table 2

Langmuir isotherm parameters for adsorption of Cr(VI) onto HPC and Norit CGP at different temperatures.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temp. (°C)</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>qm (mg/g) b L/mg</td>
<td>Kf (mg/g) l/n</td>
</tr>
<tr>
<td>HPC</td>
<td>27</td>
<td>398.40 0.097</td>
<td>0.9960 156.36 0.152</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>471.69 0.113</td>
<td>0.9941 134.95 0.231</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>510.21 0.122</td>
<td>0.9979 142.73 0.221</td>
</tr>
<tr>
<td>Norit CGP</td>
<td>27</td>
<td>305.81 0.046</td>
<td>0.9794 169.09 0.101</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>326.79 0.049</td>
<td>0.9924 110.37 0.172</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>347.22 0.066</td>
<td>0.9943 110.89 0.169</td>
</tr>
</tbody>
</table>

Table 3

Comparison of parameters for pseudo first order and pseudo second order kinetic models for HPC and Norit CGP.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k1 (1/h) qe (mg/g) R²</td>
<td>k2 (g/mg/h) qe (mg/g) h (mg/g h) R²</td>
</tr>
<tr>
<td>HPC</td>
<td>0.134 14.73 0.8865</td>
<td>0.051 99.80 507.9 0.9998</td>
</tr>
<tr>
<td>Norit CGP</td>
<td>0.111 15.61 0.7808</td>
<td>0.049 98.55 475.8 0.9995</td>
</tr>
</tbody>
</table>


