Synthesis of sludge@carbon nanocomposite for the recovery of As (V) from wastewater

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Abstract

A novel type of sludge@carbon nanocomposite was synthesized using municipal sewage sludge as raw material and ferrous iron sulphate as catalyst through hydrothermal carbonization (HTC) process. The prepared adsorbent was characterized by various analytical techniques as Scanning electron microscopy (SEM), transmission electron microscope (TEM) and X-ray diffraction patterns (XRD). The adsorption capacity of this nanocomposite for As(V) has been studied using a batch method. Various parameters affecting sorption such as pH, contact time and sorbate concentration were investigated and optimal experimental conditions were determined. It was found that 0.5 h was sufficient for complete removal of 0.5 mg/l As(V) from polluted water. The suitable adsorbent dosage and pH value were 3.6 g/l and 5.0, respectively. The arsenic desorbed could subsequently be separated by 0.5M NaOH solution. A modified linear driving force model conjugated with Langmuir isotherm was created to describe the adsorption kinetics. The resultant modified sewage sludge demonstrated a substantially high adsorption capacity of As(V) in comparison with dried sewage sludge and many other adsorbents reported in literature. The rates of adsorption were found to conform to the pseudo-second order kinetic model. The intra-particle diffusion was identified to be the rate-limiting step. The sludge@carbon nanocomposite could be reused after two adsorption-desorption cycles.

Keywords: Nanocomposite; sewage sludge; adsorption; arsenic removal

1. Introduction

Nowadays, removal of heavy metals from water is thus an important environmental issue. Which, the environment is globally polluted by toxic metals through industrial processes and waste disposal [1]. For
example, arsenic contaminate drinking water is a worldwide problem which it is hazardous for human use. It causes skin, lung, bladder and kidney cancer as well as pigmentation change, neurological disorders and muscular weakness [2]. The maximum allowable arsenic level in drinking water was set as 10μg/L by the World Health Organization (2008) [3]. Therefore, it is really necessary to remove arsenic from water to make sure that our environment as safe.

Many technologies have been developed to remove arsenic from drinking water resources, including enhanced coagulation, chemical precipitation, membrane separation (Vanghan and Reed, 2005) [4], ion exchange and adsorption onto activated alumina and other oxyhydroxides (Rau et al., 2003) [5]. However, most of these methods were not widely used in many situations because of high operational costs and the low feasibility for scale industries. But most commercial carbons have limited ability to remove the metals due to its high specific surface area and microporous nature. Besides this, the high cost of activated carbons restricts its wider application in wastewater treatment (Chen et al., 2007) [6], and this stimulates researchers to develop low cost adsorbents effective to removal metals.

In the last decade, due to the ever increasing amount of sewage sludge and the more stringent environmental quality standards, the treatment and disposal of sewage sludge has become an expensive and environmentally sensitive problem worldwide. The dried sludge collected in municipal wastewater treatment plants in China reaches 5.3x10^6 tons per year, and may increase by 10% each year [7]. Furthermore, with some traditional disposal routes coming under pressure and others being phased out. i.e. the manufacture of adsorbents. It is demonstrated that sludge can be converted into adsorbents (Seredyxch and Bandosz, 2006; Rio et al., 2006a; Bhatnagar et al., 2008 [8- 10]; Goldstone et al., 1990 [11] have found that only 34% was removed by activated sludge process in a full-scale treatment plant receiving wastewater containing 15μg/L as daily average; Watanabe et al., 2002 [12] have also reported that the removal of As by an oxidation ditch activated sludge process was very low (14%); Harinaivo Anderson Andrianisa et al., 2008 [13] have found that >95% of 200 μg/L of As(V) was removed by activated sludge with FeCl₃ and also when used autoclaved sludge to the As-containing solutions, no change in the form of As species was observed). Nevertheless, there are certain disadvantages in some adsorbents, such as the complicated preparation methods and the lower adsorption capacity [1]. Therefore, it is necessary to seek a cost-effective and innovative solution to the problem caused by sewage sludge disposal through the preparation of cheaper and more environmentally acceptable adsorbents for water purification.

Recently, hydrothermal carbonization (HTC) process has become an important technique for the synthesis of carbon nanoparticles from carbohydrate sources such as glucose [14, 15]. The formation of these materials includes the process of dehydration, condensation, polymerization and aromatization [16, 17]. The advantages of HTC process are facile, using low temperature, the use of renewable resources and economy [17, 18]. These carbon nanoparticles have a unique structure, consisting of a carbon core and a stabilizing hydrophilic shell with a large number of reactive oxygen functional groups such as (hydroxyl, carbonyl and carboxylic) [16, 19]. The formation of these oxygen-containing groups on the surface of carbon nanomaterial in addition to the high carbon content leads to use as adsorbent for water decontamination [1, 20].

In the present study, a novel adsorbent sludge@ carbon nanocomposite was prepared by a simple hydrothermal carbonization (HTC) process using the cheap chemical glucose as carbon source. The prepared sludge@ carbon nanocomposite could be utilized as adsorbent and compared it together with the dried sewage sludge for arsenic removal from contaminated water.
2. Experimental

2.1. Materials

The sewage sludge sample used in this work was collected in the wastewater treatment plant from Weifang city, Shandong province, China and was dried at 105°C for 6h. and sieved to 0.3mm mesh size (this sample was labeled "dry sludge"). All chemicals used were analytical grade without further purification.

2.2. Synthesis of sludge@ carbon nanocomposite

In a typical synthesis, 2.5g of glucose and 1g of FeSO₄·7H₂O as catalyst were dissolved in 36ml distilled water. Then 0.5g of dry sludge was added under vigorous magnetic stirring for 2h. at room temperature to form a homogeneous dispersion. The final solution was transferred to a Teflon-lined stainless steel autoclave with 50ml volume capacity. Then, the container was closed and maintained at 200°C for 24h. After that, the autoclave was cooled naturally to the room temperature. The obtained nanocomposite was centrifuged, washed by double distilled water and ethanol for three times and then dried in an oven at 80°C for 6h.

Similar synthesis procedures were also carried out with different hydrothermal temperatures (160°C for 48h., 180°C for 48h. and 200°C for 24h.) but without adding the catalyst (FeSO₄·7H₂O). The signatures S@C¹⁶₀, S@C¹⁸₀, S@C²⁰₀ and S@C are used to designate the sorbents, sludge@carbon nanocomposite at 160°C, 180°C, 200°C and catalyzed sludge@ carbon nanocomposite, respectively.

2.3. Materials Characterization

Dry sludge and sludge@ carbon nanocomposites were characterized by scanning electron microscopy (SEM) (Hitachi S-300 N, Japan), transmission electron microscopy (TEM) was carried out by Hitachi-TEM (H-7500), Japan. The XRD patterns were obtained using a Rigaku X-ray diffractometer, the scanning was measured at values of 2θ in the range from 10 to 80°, using a CuKa radiation of incident beam (λ= 0.15406 nm) monochromator to determine the crystalline phase, the scanning speed was 8°/min and the applied voltage and current were 45kV and 250mA, respectively. As(V) concentration were measured by using inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin Elmer OPTIMA 2000, USA).

2.4. Adsorption studies

Initially, a stock solution of 1000 ml of strength 1000 mg/L As(V) was prepared by dissolving an appropriate amount of Na₃AsO₄·12H₂O in deionized water. The As adsorption experiments were performed in a batch system at a temperature of 25°C and a mixing rate of 170rpm. The effect of time, pH and initial arsenic concentrations were studied to obtain on the optimize conditions for arsenic removal.

In each experiments 3.6 g/L of sorbent was added into a 30ml of desired concentrations (0.2 - 20 mg/L) of As(V) taken in a 100 ml conical flask, shaken at 170rpm in a thermostatic mechanical shaker for an appropriate time (in the range from 5min. to 24h.) and the initial pH value of the solution was adjusted with a NaOH or HCl solution to reach a desirable value (pH = 1 – 12). Then filterated and the concentration of arsenic was measured using ICP-OES technique.

The adsorption capacity and the removal percentage of As(V) were calculated as follows:
\[ q_e = \frac{V}{m} x (C_i - C_f) \] (1)

\[ \text{Removal\%} = \frac{(C_i - C_f)}{C_i} \times 100 \] (2)

Where, \( q_e \) is an adsorption capacity (mg/g), \( C_i \) and \( C_f \) are initial and final arsenic concentration (mg/L), respectively, \( V \) is volume of solution (L) and \( m \) is the mass of adsorbent (g) (Ghanizadeh Gh. et al., 2012) [21].

3. Results and discussion

3.1. Characterization

The crystalline phases present in the dry sewage sludge and in the sludge@C- nanocomposite were identified by X-ray diffractometry (XRD), Fig. 1. The dry sewage sludge presents mainly quartz SiO\(_2\) (peaks at \( 2\theta = 21^\circ, 26.6^\circ, 36.4^\circ, 36.9^\circ, 50.1^\circ, 60.01^\circ \) and \( 68.4^\circ \)) and calcite CaCO\(_3\) (\( 2\theta = 29.8^\circ \)) with other small unidentified peaks [22]. But for sludge@C, peak of calcite is disappeared. While, the peaks of iron oxalate C\(_6\)Fe\(_2\)O\(_{12}\) (\( 2\theta = 25.49^\circ \)), and iron formate hydrate C\(_3\)H\(_3\)FeO\(_6\).H\(_2\)O (at \( 2\theta = 31.35^\circ \)) arises from using ferrous sulfate as catalyst, also the peak of chaoite (C) at \( 2\theta \) around \( 20^\circ \) was appeared due to glucose derived carbon in the formation of Sludge@C nanocomposite. Accordingly to previous studies (Cui et al., 2006, Hu et al., 2008 and Shi et al., 2009) [23-25], the carbonization process of glucose occurred and formed carbon materials which, the glucose molecules have polymerized and successively carbonized as carbon. The absence of peaks of carbon may be due to the cover of strong peaks of sludge [26].

![Fig. 1. XRD of sludge and sludge@ carbon nanocomposite.](image)

The morphological changes of the dry sludge and nanocomposites were examined by scanning and transmission electron microscopies. The SEM image of the dry sludge, Fig. 2a. is characterized by aggregates of flat plates with boundaries and variable sizes. Fig. 2b. of S@C at 160°C indicated the aggregated of carbon microspheres on sludge surface and this agree with the results reported in literature (Cui et al., 2006 and Hu et al., 2008) [23, 24]. Then, by increasing the hydrothermal temperature to 180°C, 200°C and 200°C with catalyst, resulting in a decrease of carbon microspheres and an increase coating of
carbon nanoparticles onto the surface of sludge, Figs. 2c, d, e. So, the carbon content of the nanocomposite increased when the hydrothermal temperature increased to 200°C.

The TEM image reveal that after hydrothermal carbonization at 200°C for catalyzed S@C, the presence of dense nanoparticles dispersed along the surface of sludge, Fig. 2f. Because of the catalytic role of Fe²⁺ (Cui et al., 2006) [23], the deposition rate of carbon onto sludge apparently increased.

Fig. 2. SEM image of (a) dry sludge; (b) S@C160; (c) S@C180; (d) S@C200; (e) S@C and TEM image of (f) S@C.
3.2. Batch mode adsorption studies

3.2.1. Adsorbent selection

The main tasks of this section were to investigate and to select the best adsorbent for the removal of arsenic from wastewater. The results are shown in Fig. 3. It indicated that all the sludge@ carbon nanocomposites heated at 160°C, 180°C and 200°C and with FeSO₄ at 200°C and dry sludge have complete adsorption of As(V) at initial concentration 0.2mg/L of As(V). Whereas, sludge@ carbon nanocomposite with FeSO₄ (S@C) have the highest removal of As(V) and the removal percent was 74% at initial concentration 5mg/L of As(V) but for dry sludge, the removal percent was 54.4% at same the initial concentration of As(V). So, S@C was used as adsorbent in all the adsorption experiments for As(V) removal and compared with the dry sludge.

Fig.3. Adsorbent selection.

3.2.2. Effect of pH

The pH of solution is an important variable affecting metal ion adsorption. The pH value affects the surface charge of adsorbents, the metal ionization degree and the metal speciation, all of which can affect the adsorption mechanism and the uptake capacity [27]. Fig. 4. shows the effect of pH on adsorption of As(V) on S@C. The results indicated that nearly complete adsorption of As(V) at pH=5-7, which, the adsorption of As(V) maintains nearly constant (100%, 99.8% and 99.9%) at pH= 5, 6 and 7, respectively. The adsorption increases with increasing pH values from 1 to 5, then decreases gradually at pH >7.
It can be pointed out that the sludge carbon nanocomposite was catalyzed by ferrous sulfate which, Fe is converted into Fe(OH)$_4^{-}$ or Fe(OH)$_2^{+}$ depending on the pH of the solution. Fe(OH)$_4^{-}$ exists at high pH values, and Fe(OH)$_2^{+}$ exists in acidic solutions [28]. It is known that the arsenate species, according to the successive acid dissociation constants (pK$_a$) could be presented by following chemical equilibrium [29] for H$_3$AsO$_4$,

\[
pK_a = 2.3 \quad \quad \quad pK_a = 7.0 \quad \quad \quad pK_a = 11.5
\]

\[
H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^- \rightleftharpoons 2H^+ + HAsO_4^{2-} \rightleftharpoons 3H^+ + AsO_4^{3-}
\]  

(3)

Therefore, it can be inferred that As(V) exists in the anionic form over pH range used in the experimental study [28]. Two factors determine the complete adsorption of As(V) at pH = 5. The first factor, could be due to increased the Coulombic attraction between adsorbent positive surface (Fe(OH)$_2^{+}$) and monovalent anion H$_2$AsO$_4^{-}$ [29]. At iron loading adsorbent surface potential becomes less negative [30], and thus more attractive towards negatively charged arsenic species. This is one of the factors explaining higher capacity of S@C. The second factor, the carbon content of the nanocomposite increased when the hydrothermal temperature increased from 160°C to 200°C [26] and this lead to increase the adsorption of As(V). So, pH 5 was selected to be the optimum pH for further studies.

3.2.3. Time dependence

The influence of contact time on the removal of As(V) by S@C and dry sludge at pH 5 is presented in Fig. 5. The results showed that the adsorption of arsenic reached to 100% and 50.75% on S@C and dry sludge, respectively after contact time 0.5h. and adsorption equilibrium was attained in 6h. for dry sludge.

The presence of divalent cation (Fe$^{2+}$) could contribute to the increased positive charges on the surface of nanocomposite and hence provide conditions more favorable for As(V) sorption compared to the system without divalent cation [31]. Gräfe et al., 2004 [32] observed that Zn$^{2+}$ increased the sorption of As(V) on goethite at pH 4 and 7. Masue et al., 2007 [33] demonstrated that Ca$^{2+}$ enhanced As(V) retention on iron hydroxides only at pH >5.
Fig. 5. Effect of contact time on adsorption of As(V) on S@ C and dry sludge

To describe the mechanism of adsorption of As(V) with time, several kinetic models were examined and evaluated. The kinetics of As(V) adsorption on S@ C was analyzed using pseudo first-order, pseudo second-order and intraparticle diffusion kinetic models. Based on the correlation coefficient between the different kinetic models and the obtained results, only the pseudo second-order kinetic model is suitable to fit the results, Table 1.

Table 1. The adsorption kinetic model rate constants

<table>
<thead>
<tr>
<th></th>
<th>Pseudo first-order</th>
<th>Pseudo second-order</th>
<th>Intraparticle diffusion</th>
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<tbody>
<tr>
<td></td>
<td>Log(qe-qt)=log(qe)-(kt)/2.303</td>
<td>t/qt=1/(kqe²)+t/qe</td>
<td>qe = kid t¹/²</td>
</tr>
<tr>
<td>qe(0)</td>
<td>kᵢ</td>
<td>rᵢ</td>
<td>qe(0)</td>
</tr>
<tr>
<td>0.091</td>
<td>0.03279</td>
<td>0.99575</td>
<td>0.1148</td>
</tr>
<tr>
<td>kᵢ</td>
<td>rᵢ</td>
<td></td>
<td>1.62479</td>
</tr>
<tr>
<td>0.9987</td>
<td>0.01386</td>
<td>0.99724</td>
<td></td>
</tr>
</tbody>
</table>

The intraparticle diffusion model was applied to describe the sorption process from which the rate determining step can be ascertained. In this concern, the amount of adsorbed arsenic (qₜ) Vs. t¹/² is plotted in Fig. 6. according to the following equation [34].

\[ qₜ = k_{id} t^{1/2} + C \]  \hspace{1cm} (4)

Where, k_{id} (mg g⁻¹ min⁻⁰.⁵) is the intraparticle diffusion rate constant and C is the intercept of the line (mg g⁻¹) which is proportional to the boundary layer thickness.
The plot in Fig. 6 depicted three distinguishable adsorption stages. The first one may be related to boundary layer diffusion effect [35]. The linear portion is due to intraparticle diffusion effect. The final stage may be due to the active sites of adsorbent surface are completely occupied by arsenic and the adsorption reaches equilibrium state. The $r^2$-value led to the conclusion that the intraparticle diffusion process is the rate-limiting step in the adsorption process. Large value of $k_{id}$ illustrate a better adsorption mechanism, which is related to an improved bonding between As(V) and the adsorbent particles.

3.2.4. Concentration dependence

The metal adsorption is particularly dependent on initial heavy metal ion concentration. At low concentration values, metals are absorbed by specific sites, while with increasing metal concentration, the specific sites are saturated and exchange sites are filled [36]. The results of concentration dependence of As(V) adsorption on nanocomposite and dry sludge are depicted in Fig. 7. It is indicated that the adsorption percentage of As(V) reach to the maximum value 100% and 69.8% on S@ C and dry sludge, respectively at initial concentration 0.5 mg/L of As(V).
The adsorption capacity increases while As(V) removal percentage decreases with increasing the initial concentration of As(V). It is difficult to identify the existence of point of saturation. The adsorption percentage, however, demonstrates that adsorption finally reaches a saturation point. With the increase of the concentration of As(V) in solution, the availability of arsenate ions also increases at the solid-solution interface, resulting in the increase of adsorption performance. However, the saturated point of adsorption is reached when the limited active surface sites on the adsorbents are covered fully by the adsorbate [37].

In this study, sorption isotherms were determined to compare the sorption capabilities. The experimental data in Fig. 7. were fitted with Langmuir and Freundlich isotherm models. Isotherms show the relationship between metal concentration in solution and the amount of metal adsorbed on the sorbent at a constant temperature. Langmuir model demonstrates a monolayer sorption mechanism with homogeneous sorption energies, while Freundlich model demonstrate multilayer sorption sites and heterogeneous sorption energies. The equations of Langmuir (Eq. (5)) and Freundlich (Eq. (6)) are given as below:

\[
q_e = \frac{(b q^0 C_e)}{(1+b C_e)} \quad (5)
\]

\[
q_e = k C_e^{1/n} \quad \text{or} \quad \log q_e = \log k + \frac{1}{n} \log C_e \quad (6)
\]

Where, \(q_e\) is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), \(C_e\) is the equilibrium concentration (mg/L), \(q^0\) is the amount of sorbate at complete monolayer coverage (mg/g) and \(b\) is a constant that relates to the heat of sorption (L/mg). The constants of \(k\) and \(n\) in the Freundlich model are related to the strength of the adsorptive bond and the bond distribution.

The plot of Langmuir isotherm model is shown in Fig. 8. and the values of isotherm constants are presented in Table 2. The results indicated that the Langmuir isotherm fits the experimental data very well with the \(R^2\) value 0.9982 and 0.98411 for S@C and dry sludge, respectively and it is better than the Freundlich isotherm which indicates that As(V) ions are adsorbed on S@C and sludge as a monolayer adsorption. But the adsorption capacity obtained from the Langmuir isotherm model of S@C (\(q^0 = 2.233\) mg/g) show higher value than dry sludge (\(q^0 = 1.095\) mg/g) and also higher than other adsorbents as activated sludge (0.266 mg/g) (So-Young Kang et al., 2007) [38].

Fig. 8. Langmuir plot of As(V) removal using S@C and dry sludge.
3.2.5. Desorption studies

After saturation, desorption behaviour was studied using 0.5M NaOH as eluent to regenerate the adsorbent, and then can be reused to adsorb As(V). The results showed in Fig. 9.

![Fig. 9. Desorption of As(V) from S@C using 0.5M NaOH and shaking time for 4h.](image)

Fig. 9. Desorption of As(V) from S@C using 0.5M NaOH and shaking time for 4h.

From this figure, it indicated that, only 79.92% of As(V) is released from the adsorbent (S@C) after 4h. of contact between the loaded matrix and NaOH (first cycle). In the second cycle after another 4h., complete leaching of As(V) from S@C was appeared. As a consequence, 0.5M NaOH was used to investigate the reusability of S@C adsorbent for As(V) removal.

3.2.6. Comparison with other adsorbents

The adsorption of As(V) on S@C and dry sludge from aqueous solution was compared with those of other adsorbents reported in the literature (So-Young Kang et al., 2007; Ghanizadeh Gh. et al., 2010; Ansanay-Alex S et al., 2012; Muhammad Aslam Malana et al., 2011) [38, 21, 40, 2], Table 3. As can be seen in table 3, the S@C has high adsorption capacity which is the highest capacity in this series.

### Table 3. Comparison between (a) As (V) sorption capacity; (b) As(V) removal % with published data

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q^0 ) (mg/g)</th>
<th>Reference</th>
<th>Adsorbent</th>
<th>dosage (g/L)</th>
<th>( C_i ) (μg/L)</th>
<th>Removal%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>S@C</td>
<td>2.119</td>
<td>this work</td>
<td>S@C</td>
<td>3.6</td>
<td>500</td>
<td>100 %</td>
<td>this work</td>
</tr>
<tr>
<td>Dry sludge</td>
<td>1.095</td>
<td>this work</td>
<td>S@C</td>
<td>3.6</td>
<td>1000</td>
<td>89.72 %</td>
<td>this work</td>
</tr>
</tbody>
</table>
4. Conclusions

A novel method using a hydrothermal carbonization process was developed for the synthesis of new sludge@ carbon nanocomposite (S@ C) under the optimized conditions of mild temperature (200°C) using FeSO₄.7H₂O as a catalyst and the reaction time was 24h. S@ C show good adsorption affinity for As(V) in a wide range of initial pH values. The second-order equation fits the kinetic data. The adsorption equilibrium data can be well described with the Langmuir model. This new nanocomposite is qualified for wastewater treatment as a low-cost, sustainable, and effective adsorbent. Finally, desorption studies was undertaken using NaOH as leaching agent and the results indicated that the basic solution have superior leaching behavior which showed complete desorption of As(V) from S@ C nanocomposite after two cycles.

Acknowledgments

This work was supported by the Chinese Academy of Sciences (CAS) and TWAS, the academy of sciences for the developing world under Grant No. 3240240217. The National Water Pollution Control Project (2009ZX07212-002) of China.

References