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PREPARATION OF RED MUD/GRAPHENE COMPOSITE AND ITS APPLICATION FOR ADSORPTION OF As(III) FROM AQUEOUS SOLUTION

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ABSTRACT

In this study, we produce a red mud/graphene composite (REEG) via electrochemical activation graphite in basic red mud slurry. The adsorption properties for As(III) on REEG were investigated by batch method. The influence of pH (2-12), contact time (0-300 min), and the amount of adsorbent (0.02-0.1 g) on As(III) removal efficiency by the REEG were also determined. Results showed that the equilibrium time, the optimal pH, and mass of adsorbent were 240 min, pH 3.0 and 0.05 g, respectively. The maximum adsorption capacity (q_{max}) calculated by Langmuir isotherm model was found to be 21.367 mg/g. The results showed that REEG promises to be a good absorbent for As(III) removal from aqueous solution.

Keywords: red mud; graphene; adsorption; arsenic; Langmuir.

1. INTRODUCTION

Water pollution by arsenic is a worldwide problem mainly related to its extensive presence in water resources [1]. Arsenic appears in water due to a combination of natural processes, mainly dissolution of arsenic-containing rocks and soil, and anthropogenic sources like miners, burning of fossil fuels, use of wood preservatives, or herbicides and pesticides production [2]. Because of their hypertoxicity and wide existence in the environment, arsenic concentration is required to be reduced to lower than 0.01 mg/L by World Health Organization [3]. Several treatment methods have been developed for the removal of arsenic from water. Among the most common methods, adsorption is a preferable choice since it does not require high-cost equipment and is easy to operate [4, 5]. Recently, Fe_3O_4-graphene composites [6] or Fe_3O_4 nanoparticles hybridized with carbonaceous materials [7] were effectively used for the removal of arsenate from aqueous solution [8]. However, most of these adsorbents require the preparation of graphite oxide via Hummer's method. Thus, they could cause additional environmental pollutions because of the potential release of residual toxic solution. To our best knowledge, a combination of graphene and red mud for removal of arsenite from aqueous solution has not been reported. In this study, we report the production of a red mud/graphene composite via electrochemical activation graphite in red mud slurry (REEG) and its application as an adsorbent for removal of As(III) from aqueous solution.

2. MATERIALS AND METHODS

2.1. Materials

Red mud (RM) slurry was taken at Tan Binh Chemical Factory, Ho Chi Minh City. The RM material without any pretreatment was mixed with 2.5 % $(NH_4)_2SO_4$ solution and further added with KOH solution to form an electrolytic solution at pH 14. Graphene was then prepared by electrochemical exfoliation process (EEP) using two high-purity graphite rods (HG) in above electrolytic solution with the bias voltage increased gradually to 10 V at temperature of 70–80 °C and mixing at 400 rpm using a magnetic stirrer for 120 min. After cooling to room temperature, the resulting composite of graphene and red mud was collected by vacuum filtration, washed with DI water, and dried at 150 °C under vacuum for 24 h. The obtained powder (denoted as REEG) was stored in a drying box at 50 °C.The structures of the REEG powders were examined by a D2 X-ray diffractometer equipped with a Cu K□ tube and a Ni filter (ʎ = 0.1542 nm). The morphology of materials was investigated using a Scanning Electron Microscope (SEM) and element composition was analyzed using Energy Dispersive X-ray (EDX, JEOL JSM-6500F). The concentration of As(III) was determine by inductively coupled plasma optical emission spectrometry (ICP-OES, OPTIMA DV7300).

2.2. Adsorption methods

The As(III) removal tests were conducted in batch adsorption experiments at room temperature. As(III) solutions were prepared from stock solution (1000 mg/L, Sigma Aldrich Dilutions). Factors affecting including contact time (0 to 300 min), initial As(III) concentration (1, 5, 10, 20, and 25 mg/L), adsorbent dosage (from 0.02 to 0.1 g), and initial solution pH (from 2.0 to 12) were investigated. Equilibrium isotherms were determined with different initial concentrations of As(III) (1, 5, 10, 20, and 25 mg/L) at room temperature and pH 3. In each adsorption experiment, 50 ml of As(III) of known concentration 1 ppm at pH 3 was added with 0.05 g of REEG in a 250 ml round bottom flask at 30 ± 1^oC. The mixture was stirred on a magnetic stirrer at speed of 200 rpm. After the test periods, the solutions were centrifuged at speed of 4000 rpm for 15 min and the supernatant was taken for determination of As(III) concentration using an ICP – OES analyzer. To evaluate the performance of REEG in As(III) removal on real water, water samples from Suoi Cat spring (near Nui Phao mine, Dai Tu District, Thai Nguyen Province) were taken and treated with REEG. The concentration of As(III) in water sample was found at 0.128 mg/L and its pH value was 6.5. During the As(III) removal experiment, the As(III) contained solution was magnetically stirred for well dispersion of REEG (0.05 g) in water sample (50 ml, pH 3, 25^oC). pH_{pzc} for the REEG was determined according to the methods of Faria P et al. [8]. The equilibrium adsorption capacity and removal efficiency were calculated as following equation:

$$q = \frac{(C_0 - C_e)V}{M} \quad (1)$$

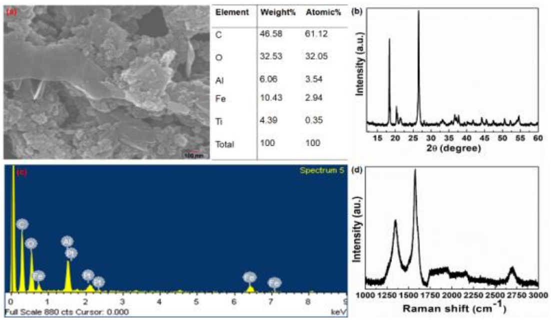
$$H\ \% = \frac{(C_0 - C_e)}{C_0} \times 100\ \% \quad (2)$$

wwhere V is the volume of the solution (L); M: the adsorbent amount (g); C_0: the initial concentration (mg/L); C_e: the equilibrium concentration (mg/L); q: the adsorption capacity at equilibrium time (mg/g); H: the removal efficiency of As(III).

3. RESULTS AND DISCUSSION

3.1. Characterization of REEG

The SEM micrograph of REEG is shown in Figure 1a. It can be observed that the surface of the REEG becomes coarser because of electrochemical treatment. Figure 1b displays X-ray diffraction (XRD) patterns of REEG. Besides characteristic bands of graphene (e.g. values of 2θ of 26.6°), REEG has peaks appear at values of 2θ of 17.8, 35.6, and 54.6°. These peaks are assigned to the phases of gibbsite (Gb = ɣ-$Al(OH)_3$), goethite (Gt = α-FeOOH), and hematile (Hm = Fe_2O_3) which could facilitate the adsorption of As(III) on the surface of REEG. To further examine the chemical composition of REEG, EDX analysis was conducted. It can be seen from Fig. 1c that C and O are the dominant components in red mud with 46.58 % in mass, and the other principal components are the oxides of Al, Fe, and Ti. Additionally, the Raman spectra revealed a shift in the position of 2D peak in REEG (Fig. 1d) to a lower frequency (from 2725 to 2708 cm^{-1}) with an symmetric 2D band, indicating the formation of few-layer graphene structures in the REEG [9].



Element	Weight%	Atomic%
C	46.58	61.12
O	32.53	32.05
Al	6.06	3.54
Fe	10.43	2.94
Ti	4.39	0.35
Total	100	100

Figure 1. (a) SEM image, (b) XRD pattern of REEG, (c): EDX spectrum of the in situ–recorded area and chemical composition of REEG, (d) Raman spectra of REEG.

3.2. As(III) adsorption

Adsorption experiments were conducted at pH 2–12. The pH_{pzc} of the REEG was about 8.0 as shown in Fig. 2a. Results from Fig. 2b shows that the removal efficiency of As(III) reaches 97.98 % at pH 3.0, and then gradually decreases when pH increased from 3 to pH 12. In the pH range of 2–7, H_3AsO_3 is the main specie while REEG is a positively charged adsorbent [10]. Hence, at lower pH, there is no electrostatic attraction taken place between the adsorbent and adsorbate. We suppose that red mud could form a high reactive iron specie (=FeOOH) in the aqueous and that bound to As(III) by ligand exchanges. The occurrence of ligand exchange between As(III) and adsorbent effective site (=FeOOH) suggests the completion of sorption process by forming inner-sphere surface complexes at the solid-water interface, as demonstrated in Eq. (3):

$$\text{FeOOH} + \text{As(III)} + \text{H}^+ \longrightarrow \text{FeO—As(III)} + \text{H}_2\text{O} \qquad (3)$$

Figure 2c presents the effect of contact time on the removal efficiency of As(III). The mandatory time to achieve equilibrium for As(III) adsorption onto REEG is found to be after 240 min. And there is no significant increase in adsorption with further increase in adsorption time. Figure 2d shows the effect of adsorbent dosage on the removal efficiency of As(III). Results clearly reveal that the removal efficiency of As(III) increases with an increase in adsorbent dosage from 0.02 to 0.08 g but was stable with further increase in adsorbent dosage.

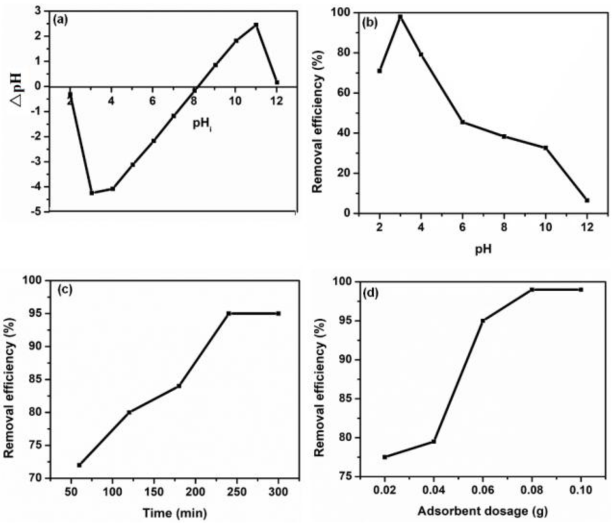


Figure 2. (a) Point of zero charge of REEG, (b) Effect of pH, (c) Effect of contact time and (d) Effect of adsorbent on the adsorption of As(III).

3.3. Effect of initial As(III) concentration and adsorption isotherms

Figure 3a shows the effect of the initial As(III) concentration on the removal efficiency, revealing a decrease from 99.21 to 90.65 % as As(III) concentration increased from 1 to 25 mg/L. At low As(III) concentration, the adsorption site was not completely occupied. Then, an increase in As(III) concentration with constant adsorbent amount lead to insufficient active sites on the surface of the adsorbent.

Adsorption isotherms analysis was also performed to describe the adsorption mechanism and also indicate how adsorbate molecules distribute between aqueous and solid phases. The expressions for the Langmuir isotherms are as follows:

$$q_e = \frac{q_0 b C_e}{1 + bC_e} \qquad (4)$$

where q_e is the equilibrium adsorption capacity at equilibrium condition (mg/L) and C_e is the equilibrium concentration of As(III) in solution. q_0 is the monolayer adsorption capacity and b

(L/mg) is the Langmuir constant related to the free energy of adsorption. The maximum monolayer adsorption capacity (q_{max}) calculated by Langmuir isotherm model was found to be 21.367 mg/g, and Langmuir constant is b = 1.529, which compares favorably with various adsorbents or composites (Table 1).

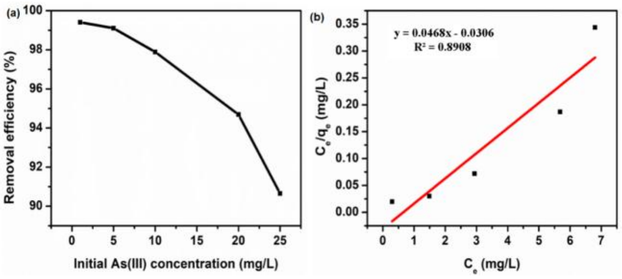


Figure 3. (a) Effect of initial concentration on removal efficiency and (b) The linear plot of Langmuir isotherm.

Table 1. Adsorption capacity for the adsorption of As(III) by various adsorbents.

Adsorbent	Adsorption capacity (mg/g)	References
Ce–Fe mixed oxide decorated multiwall carbon nanotubes	16.80	[11]
Iron mixed natural clay	19.06	[11, 12]
Green tea leaves	0.42	[13]
Zirconium polyacrylamide (ZrPACM-43)	41.48	[14]
CNTs functionalized by DESs (Deep eutectic solvent)	23.4	[15]
Red mud/graphene composites	21.36	This study

To evaluate the performance of REEG on As(III) removal in real water, water samples from Suoi Cat spring were taken and treated by REEGs. Due to recent industrial pollution by Nui Phao Mine Company (Dai Tu District, Thai Nguyen Province, Vietnam), this spring was seriously contaminated by metal ions, particularly As(III). The results show that As(III) is effectively removed after 60 min at near neutral pH environment (pH 6.5). The As(III) concentration reduced from 0.128 mg/L to about 0.003 mg/L after the treatment, with removal efficiency up to 97.6 %. Moreover, this process does not require any pre-treatment (e.g. oxidation and pH adjustment) and post-treatment (e.g. pH adjustment). The effluent quality in terms of As(III) concentration meet well standard for As(III) concentration in Vietnam National Technical Regulation on Surface Water Quality (Column A1, QCVN 08-MT:2015/BTNMT).

4. CONCLUSIONS

An effective adsorbent from red mud/graphene composite (REEG) was successfully prepared and applied for As(III) adsorption from aqueous solutions. A removal efficiency of 97.98 % at pH 3 was obtained after 240 min by using of 0.05 g of REEG for 50 ml of 1 mg/L As(III) solution. The maximum adsorption capacity (qmax) was calculated by applying the Langmuir equation for and found to be 21.367 mg/g. The REEG material has proven to be an effective but low-cost adsorbent for the removal of As(III), which could be a promising adsorbent for other wastewater treatment applications

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