



Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Facile modification of graphite sheet by novel electrochemical exfoliation/oxidant method and its adsorption of caffeine from water

Yu-Ta Chung^a, Chih-Kai Wang^b, Kai-Sung Wang^a, Sin-Yi Huang^b, Shih-Hsien Chang^{a,c,*}

^a Department of Public Health, Chung Shan Medical University, Taichung 402, Taiwan, ROC

^b Institute of Environmental Engineering, National Chiao-Tung University, Hsinchu 300, Taiwan, ROC

^c Department of Family and Community Medicine, Chung Shan Medical University Hospital, Taichung 402, Taiwan, ROC

ARTICLE INFO

Article history:

Received 16 April 2017

Revised 18 August 2017

Accepted 11 September 2017

Available online xxx

Keywords:

Graphite sheet

Electrochemical exfoliation

Caffeine

Adsorption

Regeneration

ABSTRACT

Graphite is an abundant natural material, but its specific area and adsorptive ability are low. In this study, a graphite sheet modified by an electrochemical exfoliation/oxidant process ($GS_{EEO-modified}$) was used as an adsorbent to remove caffeine from solution. Experimental results indicate that $GS_{EEO-modified}$ effectively adsorbs caffeine and that the adsorptive ability of $GS_{EEO-modified}$ prepared with $KMnO_4$ is obviously higher than that of $GS_{EEO-modified}$ prepared with H_2O_2 or $S_2O_8^{2-}$. The optimal preparation conditions for $GS_{EEO-modified}$ were 1.2 M H_2SO_4 , 0.1 M $KMnO_4$, 80 °C, and an applied voltage of 4 V. $GS_{EEO-modified}$ of 4.0 g L^{-1} efficiently adsorbed 95% of the caffeine ($C_0 = 50$ mg L^{-1}) within 30 min. Langmuir isotherms describe the adsorption behavior well ($q_{max} = 1000$ mg L^{-1} , $b = 0.001$, $R^2 = 0.9912$). Additionally, 0.1 M acetone effectively regenerated exhausted $GS_{EEO-modified}$, which maintained a high adsorptive ability (81%) after seven cycles of adsorption-regeneration treatment.

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1. Introduction

Caffeine (1,3,7-trimethylxanthine) is a plant alkaloid often used as a central nervous system stimulant. It is the world's most widely consumed psychoactive drug and is legally used in foods, beverages, and commercial analgesic medicines [1]. Caffeine is likely to persist in water and is frequently detected in the influents and effluents of sewage treatment plants and raw water [2,3]. Caffeine may cause various adverse effects on human health, such as sleep deprivation, induced anxiety, and increased risk of miscarriage [4–6]. Caffeine has been listed as a hazardous pharmaceutical pollutant and is one of the emerging contaminants [4,7]. As such, its removal from wastewater has become a matter of importance. Even though advanced oxidation processes (AOPs) can effectively degrade caffeine wastewater [8,9], their high costs and formation of oxidation intermediates often limit their practical application [10].

Adsorption is a promising approach for removing caffeine from wastewater and graphite is a low-cost natural adsorbent. However, graphite's low specific area and low adsorptive ability often limit its use in pollutant removal [11]. Graphite has also been used in various applications as a source material for producing graphene

and graphene oxide [12]. For example, graphene applications include electrochemical devices, sensors, supercapacitors, and energy storage [13,14]. Graphene oxide can also be used to adsorb pollutants from wastewater [14,15]. However, because its small size and hydrophilic properties, graphene oxide tends to disperse in aqueous solution and is difficult to separate from water [16]. The electrochemical exfoliation approach can rapidly synthesize graphene sheets from graphite [17,18]. It utilizes electricity to exfoliate SO_4^{2-} and H_2O -intercalated graphite by the formation of gaseous SO_2 and O_2 within graphite sheets [18,19]. Different preparation parameters influence the quality of graphene sheets, including the acids used, voltage, temperature, and exfoliation time [17,18]. However, graphene sheets obtained by electrochemical exfoliation are also small and difficult to precipitate from solution.

In this study, the graphite sheets were modified by a facile electrochemical exfoliation/oxidant process to adsorb caffeine from solution. The effects of preparation conditions on the adsorptive abilities of $GS_{EEO-modified}$ were investigated. Additionally, the effectiveness of solvents for regenerating $GS_{EEO-modified}$ was also assessed.

2. Materials and methods

2.1. Chemicals

Caffeine ($C_8H_{10}N_4O_4$, M.W. = 194.19 g mol^{-1} , purity 98.5%) was purchased from Merck (Germany) Graphite sheet (GS, GH-50) was

* Corresponding author at: Department of Public Health, ChungShan Medical University, Taichung 402, Taiwan, ROC.

E-mail address: shchang@csmu.edu.tw (S.-H. Chang).

<https://doi.org/10.1016/j.jtice.2017.09.012>

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obtained from I. M Technology Co. Ltd. (Taiwan). KMnO_4 (KMnO₄ 99.3% Osaka, Japan), H_2O_2 (30% purity, Hayashi Pure chemical, Japan), and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, min. 99.0%, Merck) were used as oxidants. Union Chemical Works (Taiwan) provided sulfuric acid (H_2SO_4 , purity 97%). Acetone (purity 99.87%, Shimakyu's pure chemicals) and methanol (purity 95%, Shimada's chemical works) was used as regeneration solutions for exhausted adsorbents.

2.2. Adsorbents prepared by EE and EEO

To prepare the $\text{GS}_{\text{EE-modified}}$ and $\text{GS}_{\text{EEO-modified}}$, an electrochemical exfoliation (EE) process and an electrochemical exfoliation/oxidant (EEO) process were used, respectively. The exfoliation processes were conducted in a 500-mL beaker containing 400 mL of electrolyte solution. Graphite sheets were used as electrodes with an immersed area of 4 cm × 7 cm and an electrode gap of 5 cm. A regulated DC power supply (GPC-3030D, Taiwan) was to provide different voltages in the preparations and a hot-plate magnetic stirrer to continually mix the solutions. The effects of the preparation parameters on the adsorptive ability of the $\text{GS}_{\text{EEO-modified}}$ were evaluated, including the use of different oxidants (H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, and KMnO_4), applied voltages [2–5 V], solution temperatures (25–100 °C), and exfoliation times (5–45 min.).

2.3. Adsorption experiments

The adsorption experiment was performed to determine the adsorptive ability of $\text{GS}_{\text{EEO-modified}}$. In the experiment, a known amount of $\text{GS}_{\text{EEO-modified}}$ to a 300-mL flask containing 100 mL of caffeine solution (50 mg L⁻¹) was added. The initial solution pH was adjusted by adding either 0.1 M NaOH or HCl. The flask was covered with parafilm and shook it in a water bath (25 °C, 50 rpm). At pre-set time intervals, 3-mL samples, were taken and analyzed with a UV–vis spectrophotometer (Shimadzu, UV-mini 1240, Japan), and the amount of caffeine adsorbed was calculated. The concentration of the caffeine solution was analyzed with reference to constructed calibration curves at an absorption wavelength of 274 nm.

2.4. Characteristics of GS and $\text{GS}_{\text{EEO-modified}}$

The Brunauer–Emmett–Teller (BET) surface area of the GS and $\text{GS}_{\text{EEO-modified}}$ was analyzed at 77 K on a BET Specific Surface Area Analyzer (Micromeritics Gemini 2370C). The N_2 adsorption-desorption technique was employed on the surfaces to analyze their textural properties. The Fourier-transform infrared (FTIR) spectra of the adsorbents measured with an FTIR-8400S Shimadzu (Japan). The powder samples with spectroscopic-grade KBr and pressed them into disks 10 mm in diameter and 1-mm thick. The samples were scanned in the spectral range of 450–4500 cm⁻¹. The adsorbent powder was dried, passed through a No. 70–80 sieve, and stored in a plastic bag.

3. Results and discussion

3.1. Adsorptive abilities of different adsorbents

Two exfoliation processes—electrochemical exfoliation (EE) and electrochemical exfoliation with oxidant (EEO)—were used to prepare the $\text{GS}_{\text{EE-modified}}$ and $\text{GS}_{\text{EEO-modified}}$, respectively. The exfoliation conditions were as follows: 0.4 M H_2SO_4 , 0.1 M KMnO_4 , 4 V of applied voltage, a solution temperature of 80 °C, and a preparation time of 30 min.

Fig. 1a shows that during the EE process the GS dissociated into fine particles ($\text{GS}_{\text{EE-modified}}$), dispersed in the solution, and then proved difficult to precipitate and separate from the solution

(Fig. 1a). In contrast, when using EEO, the GS surface became crumpled and rough (Fig. 1b and c) and only 11.5% of the graphite sheets dissociated into the solution. BET analysis result shows that the specific surface area of $\text{GS}_{\text{EEO-modified}}$ (28.46 m² g⁻¹) was much greater than that of original GS (6.2 m² g⁻¹).

Next, the adsorptive abilities of pristine GS, $\text{GS}_{\text{EE-modified}}$, and $\text{GS}_{\text{EEO-modified}}$ were also compared. The adsorption conditions were as follows: 4.0 g L⁻¹ of adsorbent, 50 mg L⁻¹ of caffeine, a pH₀ of 7, and an adsorption time of 30 min. Fig. 1d shows the adsorption ability of $\text{GS}_{\text{EEO-modified}}$ (80%) to be much higher than both $\text{GS}_{\text{EE-modified}}$ (1%) and GS (< 1%).

While EE is often used to exfoliate graphite into graphene sheets, the graphene sheets are difficult to recover [17,18]. In contrast, in this study, $\text{GS}_{\text{EEO-modified}}$ prepared by EEO, which maintained the integrity of the $\text{GS}_{\text{EEO-modified}}$ (Fig. 1c). This can be attributed to the addition of KMnO_4 during the EE process, which may form oxygen functional groups on the graphite sheet and retard its dissociation during the electrochemical exfoliation process. Several oxidative treatments, including the Brodie, Hummers, and Staudenmeier methods, have been used to exfoliate graphite into graphene oxide [20,21]. In the Hummers method, the strong oxidant KMnO_4 has been used to prepare graphene oxide [20]. In this study, KMnO_4 effectively oxidized H_2SO_4 -intercalated graphite and introduced oxygen atoms into the graphite layers, thereby leading to the formation of C=O, C–H, COOH, and C–O–C chemical bonds with the graphite layers [22–24]. GO with a high proportion of carboxyl and carbonyl groups exhibit low conductive properties [23]. GO is an electrical insulator, because graphene oxides contain saturated sp³ bonds, a high density of electronegative oxygen atoms that are bonded to carbon, and some defects [21,25,26]. Oxygen groups are known to inhibit the further dissociation of $\text{GS}_{\text{EEO-modified}}$ and maintain its integrity [27]. Two factors were responsible for the increase in the specific area of the $\text{GS}_{\text{EEO-modified}}$ when EEO was used to modify the graphite sheet. (1) As mentioned above, electrochemical exfoliation utilizes electricity to exfoliate SO_4^{2-} and H_2O -intercalated graphite through formation of gaseous SO_2 and O_2 within the graphite sheets [18,19]. (2) KMnO_4 oxidizes the graphite sheet to form oxygen groups in $\text{GS}_{\text{EEO-modified}}$, leading to crumple via bending or buckling of the graphite sheets [18,19].

Since the $\text{GS}_{\text{EEO-modified}}$ exhibited a higher adsorptive ability than both GS and $\text{GS}_{\text{EE-modified}}$, the influences of the $\text{GS}_{\text{EEO-modified}}$ preparation conditions on its adsorptive ability and its characteristics were experimentally investigated, as discussed below.

3.2. Effects of preparation parameters on $\text{GS}_{\text{EEO-modified}}$ adsorption ability

First, the effects of different oxidants (H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, and KMnO_4) on the adsorptive ability of $\text{GS}_{\text{EEO-modified}}$ were investigated. The modification conditions were as follows: 0.1 M oxidant, 1.0 M H_2SO_4 , 6 V, 100 °C, and an exfoliation time of 45 min. Fig. 2a shows that when $\text{GS}_{\text{EEO-modified}}$ was prepared with KMnO_4 (82%), it exhibited considerably higher adsorptive ability than when it had been prepared with either H_2O_2 (41.6%) or $\text{S}_2\text{O}_8^{2-}$ (< 1%). The effect of KMnO_4 concentration on $\text{GS}_{\text{EEO-modified}}$ adsorption was also assessed. Fig. 2b shows that increasing the KMnO_4 concentrations from 0.02 M to 0.2 M improved the adsorptive ability of $\text{GS}_{\text{EEO-modified}}$. Other preparation factors with respect to the $\text{GS}_{\text{EEO-modified}}$ adsorption ability were also investigated. Fig. 2c–f show that increasing the H_2SO_4 dose, applied voltage, solution temperature, and exfoliation time all enhanced the $\text{GS}_{\text{EEO-modified}}$ adsorptive ability. The optimal preparation conditions were 98% H_2SO_4 , a 0.1 M KMnO_4 concentration, an applied voltage of 4 V, a solution temperature of 80 °C, and an exfoliation time of 30 min.

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