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Effective and highly recyclable nanosilica produced from the rice husk for effective removal of organic dyes

Gehan M.K. Tolba [a,b], Nasser A.M. Barakat [a,c,*], A.M. Bastaweesy [b], E.A. Ashour [b], Wael Abdelmoez [b], Mohamed H. El-Newehy [d], Salem S. Al-Deyab [d], Hak Yong Kim [a]

[a] Organic Materials and Fiber Engineering Department, Chonbuk National University, Jeonju 561-756, South Korea
[b] Chemical Engineering Department, Faculty of Engineering, Minia University, El-Minia, Egypt
[c] BioNanosystem Department, Chonbuk National University, Jeonju 561-756, South Korea
[d] Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

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ABSTRACT

Amorphous nanosilica separated from rice-husk at yield of 81% by hydrothermal technique is introduced as effective and reusable adsorbent for the organic pollutants. The prepared nanosilica is spheroid with a particle size of 10–50 nm. As adsorbent, the results indicated that the nanosilica could remove 65% from the methylene blue dye (10 ppm) within the first minute. The calculated thermodynamic parameters indicated that the adsorption of MB is spontaneous and endothermic. Interestingly, regeneration of the introduced material by caclination at 450 °C enhanced the adsorption process as the removing percentage was linearly depending on the number of the successive cycles.

Introduction

Adsorption is a well-known equilibrium separation process, and an effective and economic process to remove dyes, pigments and other colorants and as well as to control the bio-chemical oxygen demand [1]. Activated carbon has been the most popular and widely used adsorbent in waste water treatment applications all over the world [2–5]. Despite its of productive use, activated carbon remains an expensive material and requires complexing agents to improve its removal performance for inorganic matters [6,7]. Moreover, its regeneration is complicated and non-economic process. In other words, up to now, activated carbon is considered one-time used material. Thus, research is interested in producing alternative inexpensive adsorbents to replace the costly activated carbon [8–10].

Recently, using nanostructured materials as adsorbents affords significant advantages in the environmental applications for water treatment [11–14] due to their high surface areas, large available surface adsorption site density, special functionality, and well-defined morphology. Compared to the traditional materials and their bulk counterparts, the nanosized materials usually exhibit much higher adsorption capacities and faster rates for pollutant removal. Complicated and expensive synthesis methodologies are the main constraints against wide applications for the nano adsorbents. Alternatively, extraction of functional nano materials from costless wastes can be considered industrial desirable strategy.

Rice husk is costless and a widely available agricultural waste which is produced from the processing and refining of rice [15]. The Food and Agriculture Organization of the United Nations (FAO) has been estimated that about 719.7 million tones of paddy (rice) were produced in 2012. On the average, 20% of the rice processed is husk meaning that around 144 million tones of rice husk were produced in 2012. In many countries such as Egypt, most of the rice husk produced is either burnt producing rice husk ash or dumped as waste [16]. It was estimated that about 89,000 tons of rice husk were burnt in 2012 (FAO). Moreover, about 75–90% of RH is organic matters such as cellulose, lignin, etc. and the rest (10–25%) are mineral components such as silica, alkalis and trace elements depending on rice variety, soil chemistry, climatic conditions, and even geographic location of growth [17]. Rice husk has been found suitable for using as a fuel [18], in building materials, as a raw materials for the production of high performance silicon and its

* Corresponding author at: Organic Materials and Fiber Engineering Department, Chonbuk National University, Jeonju 561-756, South Korea. Tel.: +82 632702363; fax: +82 632702348.
E-mail address: nasser@jbnu.ac.kr (Nasser A.M. Barakat).

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compounds such as silicon carbide [19], silicon nitride, silicon tetrachloride, zeolite and silica [20].

Rice husk is an excellent and the most efficient source of high-grade amorphous silica [21]. Therefore, finding an inexpensive way to produce nanosilica is of great significance. It not only avoids the environmental pollution produced from combustion, but also produces enormous economic benefits [17,22]. Amorphous silica has high porosity and surface area, and can be widely used in electronics, ceramic, pharmaceutics, and in dental materials. There are three main methods of nanosilica preparation from rice husk: chemical precipitation, thermal pyrolysis, and biotransformation method [23,24]. Production of silica by the precipitation method is of high purity, but the complexity, high cost of the process, and the massive reagent consumption limit the development of this method [24]. Additionally, production of silica by the pyrolysis method requires a large amount of energy. Moreover, the production of silica from fungus and worm needs long run time [25,26]. Therefore, it is interesting to develop an economic and a viable method to fabricate nanosilica from a silicon-containing biomass material.

Subcritical water, which is defined as liquid water in the temperature range of boiling point to critical point (373–647 K) or near critical point, is attracting attention as a medium for organic chemistry reactions. Furthermore, subcritical water exhibits properties that are very different from those of ambient liquid water [27,28]. It has low viscosity, low dielectric constant and high solubility of organic substances. Therefore, this medium can be used for various synthesis reactions and some degradation reactions, e.g. biomass liquefaction [29]. Since the reaction medium is water, wet biomass can be directly used as feedstock. These properties make subcritical water a very promising reaction medium for conversion of biomass such as lignocellulosic materials [30–32].

The main objective of this study is to develop an efficient route to extract amorphous silica from rice husk in high purity and to investigate its effectiveness as an adsorbent. The adsorption performance of the nanosilica for the removal of organic dye from aqueous solution was evaluated by choosing methylene blue (MB) as a model dye. The results suggests that the produced silica could be explored as a new adsorbent with high efficiency and recyclability for removing organic dye pollutants from aqueous solution.

Experimental

Materials

The rice husk was collected from a rice mill in Egypt while nitric acid (HNO_3, 60% assay) was obtained from Sigma Aldrich, USA and distilled water was used to synthesize the nanosilica. For the adsorption test, methylene blue dihydrate ($C_{16}H_{18}ClN_3S{\cdot}2H_2O$, 95 assay) was obtained from Showa, Jaban and distilled water was used. All chemicals were of analytical grade.

Preparation of nanosilica

First, the rice husk was washed thoroughly with water to remove the soluble particles and dust or any other contaminants such as heavy impurities. Second, it was dried in an air oven at about 80 °C for 24 h. Then, 2 g of the dried rice husk were mixed with 10 ml of nitric acid and 10 ml of distilled water. The solution was well mixed and placed in a teflon crucible inside the reactor. The reactor was made of stainless steel with a height of 15 cm and a diameter of 7 cm. After that, the reactor was placed in the furnace at different temperature degrees and for different times. After the desired reaction time, the reactor was immediately cooled down by immersing it into a cold-water bath. The product obtained was filtered off, washed several times with distilled water, and dried at 60 °C for 48 h for further analyses and applications. The effect of reaction temperature and time on the recovery of the silica particles was studied.

Adsorption process steps

The adsorption of MB in aqueous solution on the as-prepared nanosilica was performed and duplicated in a batch experiment. At the beginning, specific amount of the nanosilica were added into 50 ml of an (10, 30, 50 and 100 ppm) MB aqueous solution. With shaking at speed of 140 strokes per minute, samples were taken out at regular time intervals. After shaking, the supernatant solution was separated from the adsorbent by centrifugation at 5000 rpm for 5 min. Then, the concentration of MB insupernatant was determined by aspectrophotometer. The amount of MB adsorbed per unit mass of the adsorbent was evaluated by using the mass balance equation (Eq. 1) and the percentage of the MB removal was evaluated as well (Eq. 2).

$$q = \frac{(C_0 - C)V}{W} \quad (1)$$

$$\text{Removal}\,\% = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

where q is the solid phase MB concentration (mg/g), C_0 is the initial MB concentration in the liquid phase (ppm), C is the liquid phase concentration (ppm), V is the volume of dye solution (l), and m is the mass of adsorbent used (g). Finally, the adsorption capacity and the percentage of the dye removal were plotted. Further, the effect of adsorbent dosage was invistigated with different adsorbent doses (20–200 mg) and 50 ml of 10, 30, 50, and100 ppm dye solutions at equilibrium time. In addition, the effect of pH was performed by dispersion of 20 mg of the silica sample in 50 ml of 10,30, 50, and 100 ppm MB solutions. The initial pH of MB solution was adjusted to pH 2.0–12.0 using 0.1 M HCl or 0.1 M KOH. The suspensions were agitated at room temperature for 60 min. The concentration of MB left in the supernatant solution was analyzed as above. Moreover, adsorption of 10, 30, 50 and 100 ppm of MB dye by 20 mg of adsorbent was carried out at 35, 40, 50 and 60 °C. Subsequently, the regeneration experiments were conducted in the 50 ml of 10, 30, 50 and 100 ppm MP solutions with 20 mg SiO_2 sample at room temperature for 60 min. The MB-adsorbed SiO_2 is collected through natural settlement for 10 min, calcined in air at 450 °C for 90 min, and then reused for the adsorption again. The supernatant solutions were analyzed by UV–vis spectroscopy.

Characterization

Thermal properties were analyzed by thermal gravimetric analyzer (TGA, Pyris1, Perkin Elmer Inc., USA). Surface morphology was studied by field-emission scanning electron microscope equipped with EDX analysis tool (FESEM, Hitachi S-7400, Japan). Moreover, information on the phase and crystallinity was obtained by using Rigaku X-ray diffractometer (XRD, Rigaku, Japan) with Cu Kα (λ = 1.540 Å) radiation over Bragg angle ranging from 10° to 80°. Normal and high resolution images were obtained with transmission electron microscope (TEM, JEOL JEM-2010, Japan) operated at 200 kV equipped with EDX analysis. The concentration of the dyes during the adsorption study was investigated by spectroscopic analysis using an HP8453 UV–vis spectroscopy system (Germany). Furthermore, the spectra obtained were analyzed by the HP Chemi Station software 5890 Series.