Highly efficient removal of toxic organic dyes, chemical solvents and oils by mesoporous exfoliated graphite: Synthesis and mechanism

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ABSTRACT

Exfoliated graphite (EG) has been receiving much global attention in the last decade because of the growing number of potential applications. However, the production of EG has several disadvantages such as, requiring more than one chemical compound, consuming more chemical quantity, time and energy, etc. Here, we report a simple low cost one compound based rapid and efficient production of EG using microwave irradiation technique. As prepared EG material shows multifunctional outstanding performance including adsorption of various toxic organic dyes and absorption of various organic solvents, as well as, oils. The maximum adsorption capacity reaches 384.6 (± 10.2), 222.32 (± 8.6), 151.51 (± 9.2) and 196.08 (± 5.4) mg/g for malachite green (MG), methylene blue (MB), rhodamine 6 g (Rh6 g) and congo red (CR) dyes at equilibrium. It shows an efficient flow through filtration of dye contaminated water, showing potential as the best technique for industrial waste water treatment. It absorbs 40–120 g of various chemical solvents and oils per one gram of EG. To the best of our knowledge, this is the first report on single compound based rapid and efficient synthesis of EG in about one minute with multifunctional outstanding application performance.

1. Introduction

The exponential rise of human population coupled with industrialization causes severe environmental pollution, mainly water resources. Due to considerable depletion in useful water sources present on the earth, it is essential to protect them [1–3]. Organic dyes are one of the major pollutants, which are extensively used by many industries such as textile, paper, printing, leather, food, cosmetics, etc, and discharging waste water containing dyes directly into the surrounding atmosphere. Dyes in wastewater are very difficult to treat, because they are resistant to aerobic digestion, recalcitrant organic molecules, and are stable to light [1]. The presence of dyes even in very low concentration is highly visible and produces toxic products that can cause severe problems to environment, as well as, all forms of life [4,5]. Several methods have been developed for treatment of water contaminated with dyes [6–9]. Among all, adsorption is one of the most efficient process due to its ease of operation, cost-effectiveness, low residue formation, and the possibility of recycling the adsorbent materials [6]. Various adsorbent materials such as activated carbon (AC) [10,11], graphite oxide (GO) [12,13], reduced graphene oxide (rGO) [14–16], multiwalled carbon nanotubes [17], zeolites [18], metal oxides [19,20], metal-organic frameworks [21], nano membranes [22], and polymers [23], etc., have been used for water purification.

However, these materials exhibit several drawbacks such as high production cost, difficult process for large scale, separation of dyes from water after treatment, and are not suitable for removal of all dyes. Therefore, the problem is still challenging for purification of dye contaminated water. Moreover, the increase in the usage, as well as, transport of oils and chemical solvents, leakage of chemicals or oil spillage by accidents occur most commonly worldwide, and is considered as another type of major pollution. Such accidents can spoil our living environment, coastal area (e.g., the Gulf of Mexico oil spill accident in 2010), and can also cause a significant loss of valuable natural resources [24].

Exfoliated graphite (EG) refers to graphite upon expansion along c-axis up to several hundred times. It has excellent mechanical, electrical, thermal, dielectric, and other properties making it as promising candidate for potential applications [25–28]. The production of EG using H_2SO_4 [29–31] or HNO_3 [32] or $HClO_4$ [33–35] as the intercalation agent in combination with potassium permanganate or ammonium persulphate or nitric acid or hydrogen peroxide as the oxidation agent, followed by conventional or microwave heating or room temperature has been studied so far. However, the overall production of EG from these methods has several disadvantages. Firstly, synthesis process involving too many difficult steps, such as, requiring more quantity of chemicasl and time for intercalation of NGF with more than one

chemical compound at various conditions, water-washing, drying and thermal or microwave expansion, which will lead to large quantities of chemicals, time, water and energy consumption, etc. Secondly, the excessive usage of chemicals and washing will not only consume a lot of water resources, can also cause adverse effects to the environment. Thirdly, although, the direct preparation of EG by microwave irradiation technique or at room temperature is possible, the final product offers low quantity of exfoliated volume with certain amount of residue formation. Finally, in conclusion, the low exfoliated volume and formation of residue in the EG shows poor application performance especially in waste water purification. These drawbacks limit EG's usefulness to explore wide range of potential applications. Therefore, it is a great challenge to seek a more simpler, large scale, and less-polluting approach to produce EG for wide range of applications. In this study, we report a very inexpensive one compound based production of EG using microwave heating technique in about one minute (60–70 sec). The merits of present study over the previous are very simple process, inexpensive, low consumption of chemicals, time as well as energy; very light weight, high exfoliated volume and yet showing excellent performance over wide range of applications. The as prepared EG material shows an efficient adsorption of various dyes including malachite green (MG), methylene blue (MB), rhodamine 6 g (Rh6 g) and congo red (CR) in aqueous solutions and rapid absorption of various chemical solvents and oils. To the best of our knowledge, this is the first report on single compound based rapid and efficient synthesis of EG about one minute with multifunctional outstanding application performance.

2. Experimental

2.1. Synthesis of exfoliated graphite (EG)

Natural graphite flakes (NGF of 500 mg, average particle size of 500micron) were added into diluted perchloric acid (1 g of 60%$HClO_4$) and mixed for 10s, it form graphite intercalation compound (GIC) due to quick absorption of acid by graphite flakes. GICs were directly placed into a domestic microwave oven (SAMSUNG CE103VD) operated at 800W for 50-60s. Microwave heating causes quick evaporation of intercalated species in the GICs, resulting in fuming and sparking of GIC which forms highly porous worm like structured material called exfoliated graphite (EG). Also, the same amount of GICs was placed under conventional tubular furnace at 1000 °C for 60 s (called conventional process) for comparison purpose (EG-C). Moreover, graphite oxide [36] and reduced graphene oxide [37] were also prepared using conventional methodsfor comparing the adsorption performance with EG.

2.2. Characterization

The surface morphology of NGF, GIC, and EG was recorded using field emission scanning electron microscopy (FESEM) (ULTRA 55 FESEM; Carl Zeiss). The structural analysis of NGF, GIC and EG was carried out with X-ray diffraction (XRD) using Rich Seifert Iso-Debyefle 202 diffractometer with CuK_α ($\lambda = 1.54184$) radiation. UV–VIS absorption spectra were recorded at room temperature in the wavelength range of 200–800 nm on a Shimadzu UV-3600 double beam spectrophotometer, with an appropriate baseline correction, and set to zero absorbance at 800 nm. The BET surface area of the EG samples was determined by nitrogen adsorption isotherms at 77 K using a surface area analyzer (Autosorb1Csystem, Quantachrome, USA). A Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectrometer was used to identify the functional groups of the EG material in the range of 4000–400 cm^{-1}.

The exfoliated volume of the EG was defined as: volume occupied to the weight of EG

In detail, known quantity of EG material was filled without any gaps in a volume measuring jar and measured the total volume occupied by

the EG. The observed values are the arithmetic mean of five experimentally measured values according to the above procedure.

2.3. Batch adsorption experiments

The batch adsorption experiments were performed on a magnetic stirrer with a constant stirring speed of 300r.p.m. In a typical experiment, 50 mL of dye solution was stirred with the addition of 5 mg for malachite green (MG) and 10 mg for methylene blue (MB), congo red (CR), and rhodamine (R6G) dyes of EG for 60 min. The initial concentration of all the dyes used for the adsorption study was 20 mg/L. The time-dependent adsorption studies of EG for all four dyes were carried out up to 60 min with an equal interval of 10 min. The adsorption of MG dye was studied by adding 5 mg of as prepared EG, conventional EG (EG-C), H_2SO_4 based EG (EG-SA), residue formed EG (EG-R), GO, rGO and commercial AC for comparison. The effect of solution pH on the adsorption was studied in a pH range of 2.0 − 10.0 at room temperature. The solution pH was adjusted with a 0.1 M HNO_3 or NaOH solution. The effect of ionic strength on the adsorption was studied with 0.1M-0.5 M NaCl concentration.

The Adsorption (%) of the dye by the adsorbent was described by the following:

$$Adsorption\,(\%) = \frac{C_0 - C_e}{C_0} X100$$

The adsorption capacity of dye by the adsorbent at equilibrium q_e (mg/g) was calculated according to the following:

$$q_e = (C_0 - C_e)\frac{V}{m}$$

Where Co and Ce, (mg/L) are the liquid-phase concentration of dye at initial and equilibrium, respectively; V is the volume of the solution in L; and m is the weight of the adsorbent in g.

2.4. Adsorption kinetics

To identify the mechanism of the adsorption process and rate constants, the conventional pseudo-first order and pseudo second-order kinetic models were used [4,5].

The pseudo-first order model is expressed by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

The slope and intercept of the linear plot of ln (q_e-q_t) against t yield the values of k_1 and q_e.

The pseudo-second-order model is expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where q_e and q_t are defined as adsorption capacity of dye by the adsorbent at equilibrium and time t (min) and k_2 is the rate constant of the pseudo-second-order model of adsorption (g/mg·min). The slope and intercept of the linear plot of t/q_t against t yield the values of q_e and k_2.

2.5. Adsorption Isotherm

The dye concentrations in the range of 10–40 mg/L were used to evaluate the maximum adsorption capacities of all dyes by EG at four different conditions such as normal (pH = 6), pH = 2, 0.5 M NaCl, and Both (pH = 2 + 0.5 M NaCl) conditions at room temperature.

The linear Langmuir adsorption isotherm equation can be expressed as follows [38]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$$

K_L is the Langmuir constant (L/mg), which is related to the affinity of