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Efficiency of ultrasonic process in regeneration of graphene nanoparticles saturated with humic acid

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ABSTRACT

The presence of humic acid, as one of the precursors of trihalomethanes, in water resources causes many health problems for many communities. The purpose of the present study was to investigate the feasibility of ultrasonic process on regeneration of graphene nanoparticles saturated with humic acid. This experimental study was performed in batch condition, which the effects of main parameters such as regeneration time, pH, number of saturation cycles and frequency were investigated for the regeneration of the saturated adsorbent. In the regeneration of graphene nanoparticles saturated with humic acid, the maximum regeneration efficiency, at pH of 11 and regeneration time of 60 min, was 85.37% and 72.47% for frequencies of 60 and 37 kHz, respectively. Regeneration increased with increasing ultrasonic irradiation time. Moreover, the efficiency of regeneration was higher in frequency of 60 kHz compared with frequency of 37 kHz. Adsorption capacity of graphene nanoparticles after five cycles of saturation–regeneration at frequencies of 37 and 60 kHz decreased from 22.65 mg/g to 11.87 and 13.27 mg/g, respectively. The results of regeneration of graphene nanoparticles with ultrasonic waves at frequencies of 37 and 60 kHz showed that the process has a very high efficiency in the regeneration of graphene nanoparticles saturated with humic acid. The process can also be a promising alternative to chemical and thermal regeneration methods.

Keywords: Humic acid; Ultrasonic regeneration; Graphene nanoparticles

1. Introduction

The use of nanoparticles and nanocatalysts in the treatment of water and industrial wastewaters has been greatly increased in recent years. Given that nanoparticles have a high specific surface area and capacity, they can provide rapid adsorption kinetics [1,2]. The nanomaterials have been used for the removal of many organic components such as microbial pollutants and polyvalent ions. Among the adsorbent materials, graphene (G) nanoparticles are relatively new materials, which are used to remove organic pollutants from water, due to their high potential, adsorption capacity and specific surface area [3,4]. Methods for regeneration of graphene nanoparticles include biological regeneration, chemical regeneration, thermal regeneration and ultrasonic regeneration. Biological regeneration is performed using microbial activity that requires much time for regeneration and large reactors for microbial activity. The method has also been implemented on a laboratory scale, not on industrial scale [5,6]. Chemical regeneration requires separation and decomposition, which generally is not an appropriate regeneration method [7,8]. Thermal methods, that are widely used, have a number of disadvantages including loss of 5%–10% of carbon during oxidation and attrition, and high energy consumption to maintain a temperature range of 800°C–850°C [9,10]. Ultrasonic regeneration has attracted much attention

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due to its advantages such as removal of unwanted contaminants, decomposition of toxic organic pollutants (pesticides, solvents, dyes) and, most importantly, energy saving [5,11]. Feng and Aldrich [12] have reported that organic/inorganic materials adsorbed onto the adsorbent can significantly be released through sonication process. In a study by Lu et al. (2010) on the regeneration of granular activated carbon (GAC) using ultrasound in water treatment, various parameters such as different amounts of ultrasound power, frequency and contact time were studied in the regeneration of GAC. The results showed that GAC regeneration was effectively performed at a power of 120 W, frequency of 36 kHz and contact time of 15 min. It was also found that ultrasound regeneration can be a promising alternative to chemical and thermal regeneration of GAC [13]. The purpose of this study was to evaluate the efficiency of ultrasonic process in the regeneration of graphene nanoparticles saturated by humic acid.

2. Materials and methods

This study is an experimental research in a batch condition, which uses ultrasonic process for regeneration of graphene nanoparticles saturated with humic acid. Graphene nanoparticles were purchased from Iranian Research Institute of Petroleum Industry (Tehran, Iran) which prepared by chemical vapor deposition (CVD) method. All chemicals required in the study, including HCl, NaOH and humic acid with a purity of 55% were provided from Merck Company, Germany. Analysis of the samples containing humic acid was performed using a UV–visible spectrophotometer at a wavelength of 254 nm. pH-meter 765 was used to measure the pH of solutions, and a shaker (IKA-Werke-KS260C) was used for stirring the samples. Regeneration of adsorbent was performed using an ultrasonic device (Elmasonic E30H) at frequencies of 37 and 60 kHz with a feed power of 240 W.

2.1. Experiments on saturation–regeneration of graphene nanoparticles

At this stage, in order to saturate the adsorbent, 1 g of graphene nanoparticles was added to 500 mg/L humic acid in a 250-mL Erlenmeyer flask. The solution was then placed on a shaker at an agitation speed of 240 rpm for 120 min. The saturated adsorbent was filtered using a 0.2-μm filter paper and then was left at room temperature to be dried completely.

Adsorption capacity of humic acid was calculated using Eq. (1):

$$q = \frac{(c_o - c_e)V}{M} \quad (1)$$

where C_0 is the initial concentration of humic acid in the solution (mg/L); C_e is the equilibrium concentration of humic acid (mg/L); q is the adsorption capacity (mg/g); V is the volume of the solution (mL) and M is the mass of the adsorbent (mg).

Regeneration of graphene nanoparticles saturated with humic acid using ultrasonic process was calculated by Eq. (2):

$$RE = \left(\frac{HA_{Total} - HA_{Residual}}{HA_{Total}} \right) \times 100 \quad (2)$$

where RE is the regeneration efficiency (%); HA_{Total} is the total amount of humic acid adsorbed by graphene nanoparticles before ultrasonic regeneration (mg) and $HA_{Residual}$ is the residual amount of humic acid after ultrasonic regeneration (mg).

2.2. Experiments to determine the optimum pH for the regeneration of graphene nanoparticles saturated with humic acid

0.01 g of saturated graphene nanoparticles was weighted and poured into three 250-mL Erlenmeyer flasks. Then, 100 mL of distilled water with pH of 7, 9 and 11 was added to each flask. 0.1 normal solutions of NaOH and HCl were used to adjust the solution pH. The solutions were put in an ultrasonic device at frequencies of 37 and 60 kHz, a power of 240 W and different times up to 60 min, and after passing through a 0.2-μm filter paper, residual amounts of humic acid were measured using a spectrophotometer at a wavelength of 254 nm.

2.3. Experiments to determine the optimal time for the regeneration of graphene nanoparticles saturated with humic acid

At this stage, 1 g of graphene nanoparticles saturated with humic acid and also a determined amount of distilled water with an optimum pH (previous stage) were poured into a 250-mL Erlenmeyer flask. The Erlenmeyer flask was then placed in an ultrasonic device at frequencies of 37 and 60 kHz. Regeneration efficiency of saturated graphene nanoparticles in different contact times of 5, 10, 15, 30 and 60 min was evaluated for both frequencies and, after passing through 0.2-μm filters, the residual concentration of humic acid was measured using a spectrophotometer at a wavelength of 254 nm.

2.4. Experiments to determine the number of saturation/ regeneration of graphene nanoparticles saturated with humic acid

At this stage, after each saturation–regeneration cycle, graphene nanoparticles saturated with humic acid were separated and dried. Moreover, to determine the adsorption capacity at each saturation cycle, it is necessary to use all optimal parameters (pH of 3, initial concentration of 10 mg/L, contact time of 15 min and adsorbent dosage of 0.01 g/L). Saturation–regeneration of the adsorbent was repeated in five cycles, adsorption capacity was calculated at each cycle, and the obtained values were compared.

3. Results and discussion

3.1. Characterization of the adsorbents

Fig. 1 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images for graphene nanoparticles. For determination of the accurate diameter of graphene nanoparticles bundles, the SEM method was used. This technique gives information mainly regarding surface morphology of the graphene samples. The TEM was used for the measurement of graphene nanoparticles diameter in the bundle [14]. From the TEM image, it is possible to determine directly the diameter of one nanoparticle and bundle diameter. Using this information, the number of graphene

in the bundle can be found. According to Fig. 1, diameter of graphene nanoparticles used in this study was in range of 2–18 nm. Moreover, the number of layers of these nanoparticles was 32 layers.

3.2. Effect of solution pH on the ultrasonic regeneration of graphene nanoparticles saturated with humic acid

The effect of solution pH on the ultrasonic regeneration of graphene nanoparticles saturated with humic acid is shown in Fig. 2. The results showed that with the increase of pH, regeneration of graphene nanoparticles saturated with humic acid increases during ultrasonic process, so that at a pH of 11, regeneration was 72.47% and 85.37% for frequencies of 37 and 60 kHz, respectively. Regeneration of graphene nanoparticles saturated with humic acid is directly related to pH values.

The effect of pH on the ultrasonic regeneration of graphene nanoparticles saturated with humic acid at frequencies of 37 and 60 kHz is shown in Fig. 2. The results showed that regeneration of graphene nanoparticles saturated with humic acid during ultrasonic process increases with the increase of pH. With the increase of pH, repulsive forces between molecules of humic acid and graphene nanoparticles increase, which leads to reduced adsorption capacity of humic acid by graphene nanoparticles [15], so that at a pH of 11, regeneration was 72.47% and 85.37% for frequencies of 37 and 60 kHz, respectively. Regeneration of graphene nanoparticles saturated with humic acid is directly related to pH.

As pH increases, the humic acid molecules will become less coiled and less compact due to greater charge repulsion, and the weakly acidic humic with carboxylic and phenolic moieties becomes more negatively charged. Thus, at higher pH values, repulsion between humic acid and graphene surface increases.

Similar results were obtained in a study by Rege et al. [16] who investigated the regeneration of graphene nanoparticles and polymeric resin saturated with phenol using ultrasonic process. Another study was performed by Clifford et al. [17] who investigated the efficiency of chemical and electrochemical regeneration of active carbon. These results is consistent with the results of this study.

3.3. Effect of ultrasonic irradiation time on the regeneration of graphene nanoparticles saturated with humic acid

Effect of ultrasonic irradiation time on the regeneration of graphene nanoparticles saturated with humic acid is shown in Fig. 3. The results show that regeneration of adsorbent saturated with humic acid increases with increasing ultrasound irradiation time for both frequencies. At a frequency of 60 kHz, regeneration was approximately 89.95% during 60 min, while at a frequency of 37 kHz, regeneration was 68% during the same time. Hamdaoui et al. [18] investigated the effects of ultrasound on adsorption–desorption of GAC and concluded that regeneration of GAC increases with the increase of ultrasonic irradiation time. The results of this study are also consistent with a study by Derakhshani and Naghizadeh [11] on ultrasound regeneration of multiwall carbon nanotubes saturated with humic acid.

In fact, with increasing ultrasound irradiation time the amount of humic acid desorbed increased, because with increasing of times more cavitation events occurred and more molecules were desorbed.

3.4. Effect of the number of saturation/regeneration cycles of graphene nanoparticles

The results of this stage are shown in Fig. 4. Adsorption capacity of original graphene nanoparticles was 22.62 mg/g and reached to 11.87 and 21.54 mg/g, respectively, after five cycles of saturation–regeneration at frequencies of 37

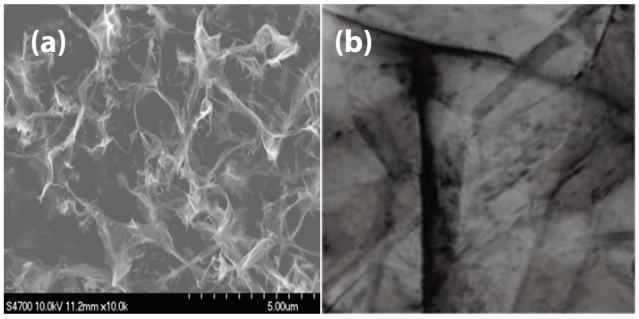

Fig. 1. (a) SEM and (b) TEM images of graphene nanoparticles.

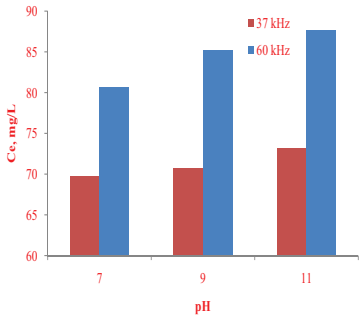

Fig. 2. Effect of pH on the regeneration of graphene nanoparticles saturated with humic acid at frequencies of 37 and 60 kHz (ultrasonication time of 60 min, 1 g of saturated graphene nanoparticles and humic acid concentration of 500 mg/L).

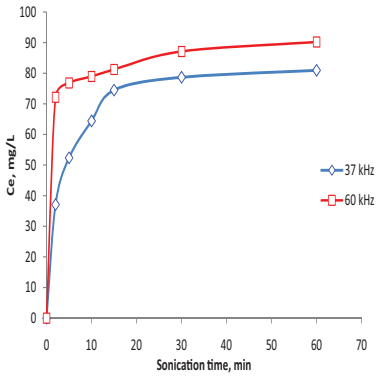

Fig. 3. Effect of ultrasonic irradiation time on the regeneration of graphene nanoparticles saturated with humic acid at frequencies of 37 and 60 kHz (pH of 11, 1 g of graphene nanoparticles saturated with humic acid).

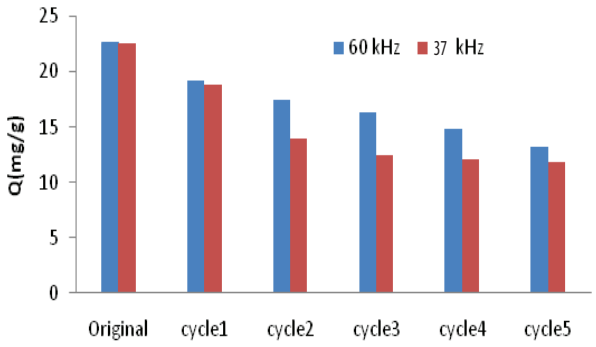

Fig. 4. Effect of the number of saturation–regeneration cycles of graphene nanoparticles saturated with humic acid at frequencies of 37 and 60 kHz.

and 60 kHz. The results indicated that adsorption capacity decreases after each cycle of saturation–regeneration.

The results indicated that regeneration efficiency at 60 kHz frequency was higher than that in 37 kHz frequency. Moreover, adsorption capacity of humic acid decreases after each cycle of saturation–regeneration, so that, for 60 kHz frequency, the adsorption capacity reached from 22.62 to 13.27 mg/g after five cycles of saturation–regeneration. However, at 37 kHz frequency, adsorption capacity decreased from 22.62 to 11.87 mg/g after five cycles of saturation–regeneration. Therefore, it was found that higher frequencies (frequency of 60 kHz compared with frequency of 37 kHz) have higher efficiency for graphene nanoparticles regeneration, because cavitation phenomenon occurs at high frequencies and thus more molecules are desorbed. In addition, high frequencies lead to breaking of bonds formed between the adsorbent and humic acid [19,20]. The results of this study are consistent with the results reported by Naghizadeh et al. [21] that studied Fenton regeneration of carbon nanotubes. At higher frequencies, the bubbles collapse producing higher-speed jet of liquid which produce severe effects on the adsorbent surface, and are responsible for pitting and erosion of the solid surface.

4. Conclusions

In this study, ultrasonic process was applied for the regeneration of graphene nanoparticles saturated with humic acid. The results showed that regeneration of graphene nanoparticles saturated with humic acid was more effectively performed at 60 kHz frequency. In addition, regeneration efficiency increased with increasing ultrasonic irradiation time. In general, the results of this study suggest that ultrasonic process has a high capability to regenerate graphene nanoparticles saturated with humic acid.

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