In situ sludge magnetic impregnation (ISSMI) as an efficient technology for enhancement of sludge sedimentation: Removal of methylene blue using nitric acid treated graphene oxide as a test process

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A B S T R A C T

In this research, a novel technology called "In Situ Sludge Magnetic Impregnation" (ISSMI) was introduced, aimed at increasing the rate of sludge sedimentation and decreasing sludge volume index. Efficiency of the process was investigated through removal of methylene blue using nitric acid treated-graphene oxide (NAT-GO). In this technique, both magnetic nanoparticles and non-magnetic graphene oxide were added to wastewater, separately. During sludge formation, magnetic nanoparticles were trapped between sludge particles. As a consequence of sludge impregnation, magnetic sludge was achieved which settled quickly by a magnet. An enhancement sedimentation factor of 66.3 was obtained as the ratio of time at which 50% of sludge settled without and with magnetic impregnation. This can lead to a considerable decrease in hydraulic retention time which makes it possible to reduce the size of sedimentation tank. This method requires significantly lower amount of magnetic nanoparticles for sludge sedimentation compared to methods based on magnetic nanocomposite. Furthermore, sludge volume index decreases due to magnetic force. In order to increase the adsorption capacity of GO, it was treated with nitric acid. Langmuir isotherm was fitted to adsorption data, resulting in maximum adsorption capacity of 1242 mg g^{-1}.

1. Introduction

In the recent years, many treatment technologies have been developed for dye removal from industrial wastewaters, including biological treatment [1], coagulation and flocculation[2], ozonation [3], chemical oxidation [4], electrochemical [5], membrane filtration [6], ion exchange [7], photocatalytic degradation [8] and adsorption [9]. Adsorption process is one of the effective methods that have been successfully employed for dye removal from wastewaters due to simplicity, facile scale-up, ease of operation, high efficiency without releasing any byproduct to the environment, possibility of recovering the adsorbent, and availability of a wide range of the adsorbents [10–12].

Several adsorbent materials have been reported for dye removal from wastewaters, including activated carbon [13], zeolite [14], clay [15] and etc. However, these adsorbents usually suffer from the slow adsorption rate and low adsorption capacity which prevent them from large-scale application in the wastewater treatment. Therefore, novel adsorbents with high adsorption capacity and fast adsorption rate have been recently developed which have small particle size and subsequently high surface area. In this regard, the efficiency of graphene oxide (GO) and its derivatives towards the removal of synthetic dyes has been extensively investigated over a decade [16–19].

The unique structure, high surface area and functional groups (hydroxyl and carboxyl) of GO are the important characteristics that cause the GO to be considered as a suitable adsorbent for water and wastewater treatment [20]. However, the practical application of GO has been limited in wastewater treatment due to small particle size and high dispersibility in aqueous solutions, which make it difficult to separate it from wastewater after adsorption process.

In order to overcome this problem, several methods have been recently developed to immobilize the graphene oxide nanosheets in a 3D-structured nanocomposite. A 3D sponge-like graphene oxide gel was prepared by Zhou et al. and its performance was investigated in the fixed bed adsorption column. The major

drawback, which limits the application of the sponge like graphene oxide, is the high cost of production [22]. Calcium alginate immobilized graphene oxide composites has been reported by Li et al. for adsorption of methylene blue [23]. Zhang et al. introduced polyethersulfone as a porous and stable support to immobilize the GO for practical application in wastewater treatment [24].

Another solution to this problem is to use the magnetic adsorbents, which can ensure the convenient magnetic separation after adsorption process [25–27]. A variety of methods has been developed to prepare magnetic graphene oxide (mGO), including coprecipitation and covalent bonding [20,28]. These methods are generally multistep and hard to control. On the other hand, the adsorption capacity of GO decreases due to blockage of its active sites by magnetic nanoparticles and decrease of its surface area [29].

In this research, in order to overcome the mentioned disadvantages, an efficient technology, called "In Situ Sludge Magnetic Impregnation" (ISSMI), was introduced. This technique makes it possible to increase the rate of sludge sedimentation and to decrease the sludge volume index. In order to evaluate the performance of ISSMI technique, the removal of methylene blue using NAT-GO, was chosen as a test process. The non-magnetic graphene oxide and magnetic nanoparticles were added to the solution containing methylene blue (MB) as a test cationic dye. After adsorption of MB on the surface of GO, the charge density of GO decreased which led to aggregation of GO nanosheets. During aggregation, magnetic nanoparticles were trapped between aggregated GO nanosheets. As a consequence of magnetic impregnation, the magnetic sludge was achieved which was easily separated by a magnet.

This method requires significantly lower amount of magnetic nanoparticles for sludge sedimentation compared to methods based on magnetic nanocomposites. On the other hand, the lower amount of GO is required, because the active sites and surface area of GO are higher than those of GO incorporated in the magnetic nanocomposites. In order to increase the capacity of GO, it was treated with nitric acid which led to decrease in layer thickness and 54% increase in adsorption capacity. Among the optimization methods available [30–32], Response Surface Methodology (RSM) was used to optimize the adsorption process. The relationship between dye removal efficiency and three main independent parameters, including initial pH, dye concentration and adsorbent dosage were evaluated by applying central composite design (CCD). The rate of sludge sedimentation was investigated with and without magnetic impregnation. Correlation coefficient (R^2), the residual root-mean-square error (RMSE) and the chi-square test (χ^2) were used to evaluate the fitting of the adsorption isotherm and kinetic models to the experimental results.

2. Experimental

2.1. Materials

Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), Iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), sodium nitrate, potassium permanganate, sodium hydroxide, methylene blue ($C_{16}H_{18}ClN_3S$), hydrochloric acid (37% wt), sulfuric acid (98% wt), nitric acid (65% wt), hydrogen peroxide (30% wt) and ammonium hydroxide (25% wt) were purchased from Merck Company (Darmstadt, Germany). Graphite fine powder was obtained from LOBA Chemie (India). All these reagents were of extra pure grade and used without further purification. Deionized water was used throughout the whole experiments.

2.2. Nitric acid treatment of GO

Fine powder of graphite (Extra pure) was used to prepare GO using Hummers method [33]. In order to increase the adsorption capacity of GO, it was treated with nitric acid. Briefly, 1 g of GO was added to 250 mL flask containing 100 mL of HNO_3 (65% wt) and then was refluxed at 130 °C with stirring for 5 h, followed by cooling at room temperature. After sedimentation and decantation of supernatant, the treated GO was washed several times with deionized water in the centrifuge tube until the pH value of washing solution reached about 5 and then was sonicated for 30 min, followed by drying at 40 °C for 12 h in a vacuum oven.

2.3. Preparation of the suspension of Fe_3O_4 nanoparticles

In order to prepare a suspension containing Fe_3O_4 nanoparticles with concentration of 2500 mg L^{-1}, 600 mL of deionized water was deoxygenated by bubbling with nitrogen for 30 min. Then 5.8 g of $FeCl_3 \cdot 6H_2O$ and 2.2 g of $FeCl_2 \cdot 4H_2O$ were dissolved in the deoxygenated water and the solution was poured into triple-neck glass flask. A mechanical mixer was placed into flask from central neck and N_2 atmosphere was purged into flask during synthesis. The synthesis process was performed at 80 °C. Under the mixing condition, 160 mL of NaOH 5 mol L^{-1} was added dropwise to the solution, followed by mixing for 30 min. Then the cooled suspension was transferred to a 1-L volumetric flask and brought to volume with the deoxygenated water and sealed [34]. The obtained suspension is stable at the alkaline liquor for about 30 days. Shortly before use, the required amount of nanoparticles was washed several times with the deionized water.

2.4. Characterization

The FT-IR spectrum of the GO was recorded on a Bruker FT-IR spectrophotometer with KBr pellets in the range of 4000–400 cm^{-1}. The size and morphological studies were conducted by field emission scanning electron microscope (FESEM, HITACHI S-4160) and transmission electron microscope (TEM, Zeiss EM900) with an accelerating voltage of 200 kV. The magnetization measurement for magnetite nanoparticles was carried out using a vibration sample magnetometer (VSM) with an applied magnetic field of 10 KOe. Thickness reduction of treated GO was confirmed by studying its Raman spectra recorded using Raman spectrometer (Bruker Senterra 2009). UV/visible spectrophotometer (Hatch model DR 5000) was used to determine the concentration of MB in the aqueous solutions. The particle size measurements were carried out using dynamic light scattering (DLS) method using a particle size analyzer (Malvern, Nano S). The X-ray diffraction (XRD) pattern of Fe_3O_4 nanoparticles was recorded on an X-ray diffractometer using Cu K α radiation. (X'Pert PRO MPD PANalytical Company)

2.5. Experimental design and data analysis

Batch experiments were performed according to the designed experiments. The optimization of effective parameters on the removal of MB was performed using CCD. A total of 20 experiments were carried out according to a full factorial design, consisting of 8 factorial points (coded as ± 1), 6 axial points (±α from the center) and 6 replicates (at the center points). The value of α was calculated by the following equation:

$$\alpha = 2^{\frac{k}{4}} \tag{1}$$

where k is the number of factors. Therefore, α is equal to $(2)^{3/4} = 1.68$ according to (Eq. (1)). For statistical calculations, the