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Magnetite nanoparticles with surface modification for removal of methyl violet from aqueous solutions

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Abstract In this research, the potential of Fe₃O₄ magnetic nanoparticles (MNPs) for efficient removal of methyl violet as a cationic dye from aqueous solutions was investigated. For this purpose, Fe₃O₄ MNPs were synthesized via chemical precipitation method. The synthesized MNPs were characterized by XRD and SEM techniques. To remove methyl violet, the surface of the MNPs was modified with sodium dodecyl sulfate (SDS) as an anionic surfactant. Also, the various parameters affecting dye removal were investigated and optimized. The kinetic studies for methyl violet adsorption showed rapid sorption dynamics by a second-order kinetic model, suggesting chemisorption mechanism. Dye adsorption equilibrium data were fitted well to the Langmuir isotherm rather than Freundlich isotherm. The maximum monolayer capacity, (q_{\max}), was calculated from the Langmuir as 416.7 mg g⁻¹. The results show that, SDS-coated magnetic nanoparticles, can be used as a cheap and efficient adsorbent for removal of cationic dyes from aqueous solutions.

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1. Introduction

Dyes are used in large amount in many industries to color the products. Many dyes are toxic in nature with suspected carcinogenic and mutagenic effects that influence aquatic biota and also human beings (O'Mahony et al., 2002; Ozcan and Ozcan, 2004). Dyes usually have complex aromatic structures which make them stable and difficult to decompose (Kiran et al., 2006). Due to their good solubility, the discharge of dye-bearing wastewater into natural streams and rivers leads to a perilous problem, as dyes impart toxicity to aquatic life and, therefore, damage the esthetic nature of the environment (Mohan et al., 2002).

However, wastewater containing dyes is very difficult to treat, since the dyes are resistant to aerobic digestion and are

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stable to light, heat and oxidizing agents due to their structure and molecular size (Sun and Yang, 2003; Ravi Kumar et al., 1998). There are several methods for dyes removal, including membrane separation, flocculation, sonolysis, anaerobic biological treatments, oxidative destruction via UV/ozone treatment, photocatalytic degradation, which have certain efficiency, but their initial and operational costs are too high (Crini, 2006; Ramesh et al., 2007; Zaharia et al., 2006).

Adsorption has been discovered to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design and ease of operation (Garg et al., 2004; McKay, 1981; Jumariah et al., 2005). Most commercial systems currently use activated carbon as a sorbent to remove dyes in wastewater by reason of its excellent adsorption power. Activated carbon is structurally homogeneous material with high surface area, and has microporous structure and radiation stability, which are important in its use as adsorbent (Leyva-Ramos, 1989; Tsai et al., 2001; Pendleton and Wu, 2003), catalyst and catalyst support (Gerald and Russel, 1991), so it is extensively applied for industrial process, but activated carbon has not been able to reduce the concentration of contaminants at ppb levels (Pillay et al., 2009) and its use is usually limited due to its high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. Recently, many approaches have been studied for the development of cheaper and more effective adsorbents. Some of these adsorbents are perlite (Alkan and Dogan, 2001; Bereket et al., 1997; Gupta et al., 2000; Mohan et al., 2002), bentonite (Demirbas and Dogan, 2002), silica gels (Mohamed, 1996), fly ash (Dogan and Alkan, 2003), lignite (Allen et al., 1989), peat (Ho and McKay, 1998), silica (Masciaglioli and Zhang, 2003) etc. In most cases, these adsorbents are highly porous substances, providing sufficient surface area for adsorption.

In the last decade, comprehensive investigations and developments were observed in the field of nano-sized magnetic particles. These materials often possess unique electrical, chemical, structural, and magnetic properties allowing for use in the field of novel applications including information storage, drug delivery, biosensors, chemical and biochemical separation and environmental remediation (Leslie-Pelecky and Rieke, 1996; Elliott and Zhang, 2001).

Magnetic nanoparticles (MNPs) are a class of nanoparticles which can be manipulated using a magnetic field. MNPs have the advantages of large surface area, high number of surface active sites and high magnetic properties, which cause high

adsorption efficiency, high removal rate of contaminants, and easy and rapid separation of adsorbent from solution via magnetic field. After magnetic separation, the contaminants can be easily removed from nanoparticles by the desorbent agents, and the recovered MNPs can be reused (Oliveira et al., 2003).

The present work describes the chemical synthesis of Fe_3O_4 MNPs and the surface modification of synthesized MNPs with sodium dodecyl sulfate (SDS). After synthesis, the applicability of SDS-coated Fe_3O_4 MNPs as an efficient adsorbent for the removal of methyl violet as a cationic dye from aqueous samples was investigated.

2. Experimental

2.1. Reagents and materials

Methyl violet ($\text{C}_{23}\text{H}_{26}\text{N}_3\text{Cl}$) (Fig. 1) as a cationic dye, ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), sodium hydroxide, sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and hydrochloric acid were purchased with high purity from Merck (Darmstadt, Germany). A stock standard solution of methyl violet at a concentration of 1000 mg L^{-1} was prepared in double distilled water. This standard solution was diluted with doubly distilled water to prepare stock solutions with the concentration of 5, 10 and 50 mg L^{-1} of methyl violet.

2.2. Apparatus

All absorbance measurements were obtained using a Milton Roy (Spectronic 601) UV-Vis spectrophotometer. For absorbance measurements, 585 nm was chosen as the maximum absorbance wavelength (λ_{max}) of methyl violet. The pH of solutions was adjusted with a Jenway model 3320 pH meter (Staffordshire ST15 0SA, England) supplied with a combined glass electrode. A Stuart CB162 motor-stirrer (Staffordshire ST15 0SA, England) was applied to stir dye solutions by a magnet. Magnetic separation was done by a strong super magnet with 1.4 T magnetic field ($1 \times 3 \times 5 \text{ cm}$). A temperature controlled shaker was applied for shaking of the dye solutions in isotherm studies at constant temperature. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert company with mono chromatized $\text{Cu K}\alpha$ radiation. The morphology of synthesized samples was characterized with a scanning electron microscope (SEM) from Philips Company (XL30 ESEM).

2.3. Synthesis of Fe_3O_4 magnetic nanoparticles

Large scale synthesis of Fe_3O_4 MNPs with higher efficiency was carried out in a five-necked reactor that was designed in the laboratory as was written elsewhere (Faraji et al., 2010a,b,c,d). In the designed method, the synthesis of MNPs was done by introducing nitrogen gas through a sparger into the solution for oxygen removal. Sparger increases degassing efficiency of the solution by producing very small nitrogen bubbles. The bubbling of nitrogen gas through the solution protects MNPs against critical oxidation and reduces the particles size when compared to synthesis methods without oxygen removal (Kim et al., 2001).

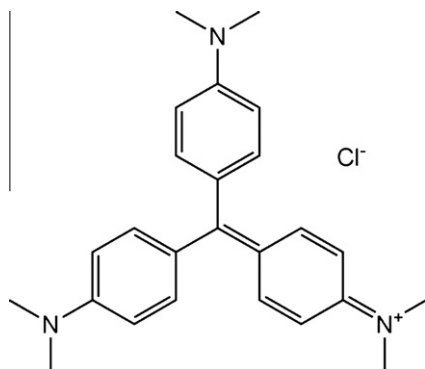


Figure 1 Chemical structure of methyl violet.

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