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Research Paper

Highly effective adsorption of crystal violet dye from contaminated water using graphene oxide intercalated montmorillonite nanocomposite

Chandni Puri, Gajjala Sumana*

CSIR-National Physical Laboratory, New Delhi, India

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ABSTRACT

Herein, graphene oxide intercalated montmorillonite nanocomposites were prepared by a facile chemical route and then used for the adsorption of crystal violet dye from contaminated water. Structural characterization of the nanocomposites were performed using Fourier transform infrared spectroscopy, Raman spectroscopy, transmission electron microscopy, scanning electron microscopy, zeta potential, X-ray diffraction, specific surface area and pore volume measurements. The isothermal data obtained using batch adsorption technique were fitted using Langmuir and Freundlich equations and it was found that the experimental data is well described by the Langmuir isotherm model with a very high adsorption capacity of 746.27 mg g^{-1}. The kinetics of the adsorption process showed rapid dynamics and conformed to pseudo-second-order model with a correlation coefficient of $R^2 > 0.99$. The influence of interaction time and initial dye concentration on the adsorption efficiency were also investigated. Additionally, thermodynamic studies revealed that the adsorption process was spontaneous and endothermic. Further, the results indicated that the synthesised nanocomposites adsorb crystal violet dye efficiently (~96%) with a small decrease in removal efficiency even after five cycles of adsorption and could be employed in wastewater treatment for the removal of cationic dyes.

1. Introduction

In the past few decades, providing clean water around the globe has emerged as a challenging problem. With exponential growth in population, irrigation practices and rapid industrialization, contamination of water resources by various chemical and biological agents is rising at an alarming rate. Among several water pollutants, dyes have attracted particular attention in wastewater management owing to their high toxicity and adverse effects on the environment (Ai et al., 2011). These hazardous organic compounds also affect the aquatic life by altering the photosynthetic activity of the biota due to reduced light penetration through water (Hu et al., 2013). Crystal violet is one such and common type of dye extensively used by the paper and textile industry. It is also used as a biological stain and dermatological agent in human and veterinary medicine (Zhang et al., 2014). In spite of its wide use, crystal violet has been found to have harmful effects on humans and has been suspected to be a potential carcinogen. Consumption of the dye even in small amount (< 1 ppm) may result in respiratory disorders, kidney failure and permanent blindness. Its exposure to large amounts irritates the skin and the digestive tract (Mohanty et al., 2006; Ahmad, 2009). Belonging to the class of triarylmethane dyes, it has a complex chemical structure and long half-life which results in their persistence in the environment for a very long time, aggravating the problem further (Haik et al., 2010). The dye has also been found to be teratogenic and mutagenic and is thus, categorized under biohazards (Au et al., 1978). Therefore, an increased interest has been focused on removing such dyes from the industrial wastewater prior to its reuse or discharge into the aquatic environment.

Various physical, chemical and biological processes including solvent extraction, chemical precipitation, photocatalysis, membrane filtration, ion exchange, adsorption, electrochemical treatment have been developed for the removal of dyes from wastewater (Jana et al., 2010; Muntean et al., 2013; Yi et al., 2015; Zhong et al., 2015). However, adsorption is considered to be one of the most effective methods due to its high efficiency, ease of operation, reusability and relatively low cost (Gupta and Ali, 2008). A wide range of organic and inorganic adsorbents including zeolites (Rida et al., 2013), fly-ash (Pengthamkeerati et al., 2008), activated carbon (Singh et al., 2003; Acharya et al., 2009), polymeric materials and mesoporous silica (Huang et al., 2011) are reported for the removal of dyes but they suffer with disadvantages of low adsorption capacities, poor selectivity and high cost (Rafatullah et al., 2010). Therefore, efforts are being made to obtain versatile and cost effective adsorbents with enhanced efficiency for water purification applications. Recently the use of adsorbents containing clay

* Corresponding author.
E-mail address: sumanagajjala@gmail.com (G. Sumana).

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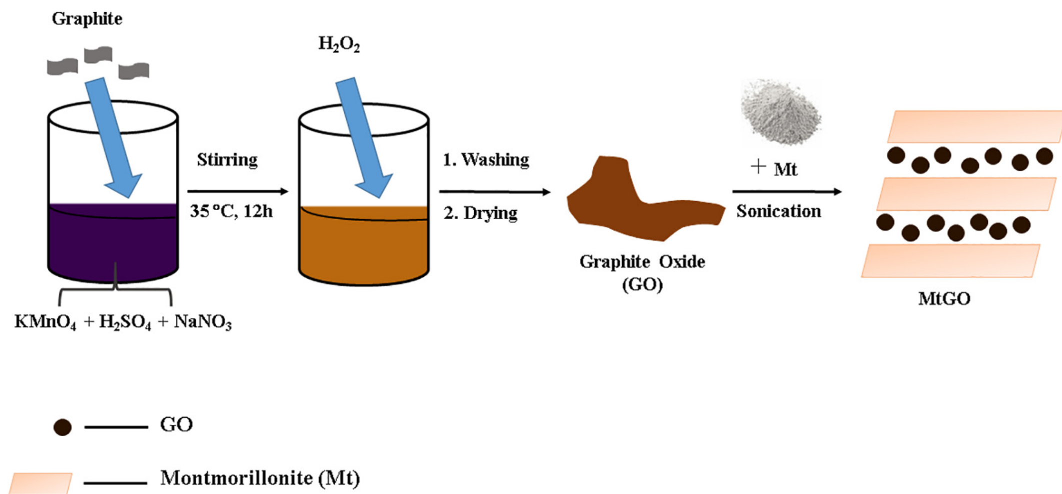

Fig. 1. Preparation of MtGO nanocomposite.

minerals has received great attention due to their abundant availability in nature. Their characteristic properties such as porosity, large specific surface area, non-toxicity, cost effectiveness, easy recyclability and strong complexation ability (Nandi et al., 2008; Rodríguez et al., 2012) make them widely used materials for the removal of dye effluents from wastewater.

Montmorillonite (Mt), among the most studied clay minerals, chemically belongs to the family of hydrous layered aluminosilicates with structure composed of tetrahedral and octahedral sheets. This fine clay mineral possesses a good cation exchange capacity and a large specific surface area. Despite of it being a traditional adsorbent material, the adsorption capacity of Mt remains limited, when used individually (Zhang and Hou, 2008). The modification of Mt is therefore considered to be necessary for the enhancement of dye removal efficiency by modifying the structure through the introduction of more active sites on its surface (Ai and Li, 2013; Cottet et al., 2014; Peng et al., 2016; Bermúdez et al., 2017).

In recent years, with the advent of nanotechnology, carbon nano-adsorbents have emerged as suitable materials for the treatment of wastewater. Owing to a high surface to volume ratio, controlled pore size distribution and interesting surface chemistry, the use of carbon nano-adsorbents helps in attaining rapid equilibrium rates and high adsorption capacity with consistent adsorption isotherms. Since last decade, graphene oxide (GO) has emerged as an efficient adsorbent in the field of wastewater remediation. It is a carbonaceous material containing various functional groups on its surface and edges which can interact with dye molecules through hydrogen bonds and electrostatic interactions, making it a suitable candidate for dye adsorption (Bradder et al., 2011; Wang et al., 2013; Konicki et al., 2017). Considering the unique structures and high performances of GO and layered aluminosilicates compared to their conventional counterparts, clay-GO nanocomposites have recently attracted significant interest in scientific research and industrial applications (Darder et al., 2017; Yu et al., 2017).

The present study reports the successful incorporation of GO into Mt leading to a nanocomposite adsorbent (MtGO nanocomposite) and its use for the removal of crystal violet dye in order to evaluate its feasibility as a novel adsorbent in environmental remediation. The as-prepared nanocomposite exhibits enhanced adsorption capacity due to the resulting synergistic effect as compared to GO and Mt alone. The detailed adsorption properties of the novel material, including the contact time, temperature, isotherms, kinetics and thermodynamics on adsorption were investigated. In addition, the reusable property of the MtGO nanocomposite was also studied.

2. Materials and methods

2.1. Materials

Montmorillonite K10 and graphite powder were obtained from Sigma-Aldrich Chemicals (India), while Potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), concentrated sulphuric acid (H_2SO_4, 98% (*w*/w)), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2, 30% (w/w)) and crystal violet dye (C·I -42,555; MF: $C_{25}H_{30}ClN_3$, MW: 407.99 g mol^{-1}) were procured from Merck Chemicals (India). All the chemicals were of analytical grade and were used as received without further purification. All solutions were prepared using Mili-Q filtered deionized water. The working solutions with a desired concentration of dye were prepared by appropriate dilutions of the stock solution of the crystal violet dye.

2.2. Synthesis of montmorillonite-graphene oxide nanocomposite

Montmorillonite-graphene oxide nano composite (MtGO nanocomposite) was prepared by a solvent method with GO and Mt as precursors. GO was synthesised by oxidation of raw graphite powder using modified Hummer's method (Zhu et al., 2010). Briefly, graphite and sodium nitrate ($NaNO_3$) were mixed together in a ratio of 2:1, followed by the addition of conc. H_2SO_4 under constant stirring for 1 h. To this solution, $KMnO_4$ was added gradually, keeping the ratio of $KMnO_4$ and graphite to 3:1. The temperature of solution was maintained below 20 °C to prevent overheating and control explosive nature of the exothermic chemical reaction. The mixture was then stirred at 35 °C for 12 h and the resulting solution was diluted by adding water under vigorous stirring. To ensure the complete elimination of the residual metal ions, the dispersion was further treated with H_2O_2 solution (5 mL). The resulting product was washed with dilute HCl and H_2O respectively, followed by filtration and drying at 50 °C in a vacuum oven. Further, 7.5 g L^{-1} of synthesised GO was mixed with 25 g L^{-1} Mt in a flask and dispersed in distilled water (See Fig. 1). The mixture was then ultra-sonicated for 8 h using an ultrasonic cleanser (40 KHz, 200 W). Finally, the mixture was vacuum dried at 60 °C and was named as MtGO nanocomposite. The measured surface physical characteristics of the prepared MtGO nanocomposite are illustrated in Table 1. A high specific surface area and negatively charged surface in the Table 1 suggests the suitability of the nanocomposite to adsorb cationic dyes.

2.3. Instrumentation

The X-ray diffraction (XRD) patterns of the materials GO, Mt and