Journal of Environmental Management 230 (2019) 199–211

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Facile synthesis of graphene oxide–silver nanocomposite for decontamination of water from multiple pollutants by adsorption, catalysis and antibacterial activity

Hina Naeem[a], Muhammad Ajmal[b], Raheela Beenish Qureshi[c], Sedra Tul Muntha[a], Muhammad Farooq[a], Muhammad Siddiq[a,*]

[a] Department of Chemistry, Quaid-i-Azam University, Islamabad, 45320, Pakistan
[b] Department of Chemistry, University of Wah, Quaid Avenue, Wah Cantt, 47040, Pakistan
[c] Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, 60800, Pakistan

ARTICLE INFO

Keywords:
Graphene oxide
Silver nanoparticles
Wastewater treatment
Adsorption
Catalysis
Antibacterial activity

ABSTRACT

Here in, we presented a facile one-step method for the synthesis of Graphene oxide–silver (GO–Ag) nanocomposite and its applications as a sorbent for the elimination of some toxic pollutants from aqueous medium, as an efficient catalyst in the individual as well as simultaneous reduction reactions of multiple compounds, and as an antibacterial agent for the destruction of some harmful microorganisms existent in wastewater. GO was prepared using a modified Hummers method and Ag nanoparticles were integrated on GO sheets by chemical reduction of Ag^+ ions on the surfaces of GO sheets. The composition and morphology of the nanocomposite was extensively characterized with elemental dispersive X-ray analysis (EDX), Fourier transform infra-red (FT-IR) spectroscopy, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and thermal gravimetric analysis (TGA). The GO–Ag nanocomposite demonstrated remarkable adsorption capacities and recyclability for malachite green (MG) and ethyl violet (EV) dyes. Various experimental parameters affecting adsorptive behavior of nanocomposite like temperature, pH, time of contact between dye and adsorbent, and adsorbent dose were evaluated thoroughly. Experimental data was simulated with different adsorption isotherms and kinetic models to evaluate adsorption behavior of both dyes and results confirmed the adsorption of both the dyes to be followed by pseudo 2nd order kinetic model and Langmuir adsorption model. Moreover, adsorbent was regenerated in suitable media for both dyes without any loss in removal efficiency. The catalytic performance for the 2-nitroaniline (2-NA) reduction was investigated in detail. Most importantly, the prepared nanocomposite was found to have potential to adsorb multiple pollutants all together as well as to catalyze the simultaneous reduction of a mixture of dyes (MG, MO, and EV) and 2-NA. An additional advantage of the GO-Ag nanocomposite was its antibacterial activity acquired to the presence of Ag nanoparticles. Two bacterial strains (Gram-negative bacterium, *E. coli* and the Gram-positive bacterium, *S. aureus*) were used to test antibacterial activity of composite and the results confirmed the remarkable performance of the nanocomposite in destroying harmful pathogens.

1. Introduction

Waste water released from industrial effluents contains a variety of pollutants. These pollutants are becoming a serious threat to humans, aquatic life and environment. Among the various pollutants, organic dyes and aromatic compounds are considered to be the main water pollutants (Tiwari et al., 2013). They are commonly released from leather, textile, food processing, pulp and paper manufacturing industries and are easily transported within the aqueous environment due to their higher water solubility. These pollutants create some serious environmental and health problems even some of these dyes and aromatic pollutants have carcinogenic and mutagenic effects (Moussavi and Mahmoudi, 2009). So, the detoxification of wastewater from these pollutants is a matter of great concern. Various methods including physical, biological, membrane treatment and chemical treatment have been in practice previously for elimination of unwanted pollutants from the contaminated water (Gadd, 2009; Jang et al., 2008; Kennes et al., 2009). However, efficient adsorption is considered to be a preferred

* Corresponding author.
E-mail address: m_sidiq12@yahoo.com (M. Siddiq).

https://doi.org/10.1016/j.jenvman.2018.09.061
Received 10 June 2018; Received in revised form 16 September 2018; Accepted 19 September 2018
0301-4797/

way due to its simple procedure, easy operative method and extensive suitability for diverse dyes (Naushad and ALOthman, 2015; Naushad et al., 2015; Rafatullah et al., 2010). Also, in the case of adsorption there is no degradation of the pollutants as the degradation products of some dyes are also considered as harmful and after adsorption the adsorbent can be easily removed from water. An ideal adsorbent should express higher adsorption capacity along with higher adsorption rate (Kennes et al., 2009). Many different porous materials were previously used as an adsorbent like activated carbon, zeolite, mesoporous silica, metal organic frameworks but they showed lower adsorption capacities and poor selectivity (Ngah et al., 2011; Wang and Peng, 2010). Also, some of the advanced materials like nanostructured metal oxides, fullerenes, graphite and carbon nanotubes have been employed as adsorbents but these engineered carbonaceous materials also showed inadequate adsorption capacity and toxicity to the environment in addition to their complex synthetic procedures (Wang and Peng, 2010). Therefore, researchers tried to find some new adsorbent materials with improved efficiency.

Recently, graphene has been emerged as a most stimulating advanced carbonaceous material with a two-dimensional (2D) carbon lattice resembling to honeycomb and has been considered as a functional material in numerous fields like sensors, photovoltaics, photocatalysis and wastewater treatment, owing to have some remarkable properties of good chemical stability, high transparency, large surface area, low cost and good π electrons mobility (Allen et al., 2009; Apul et al., 2013; Sharma et al., 2014). Graphene oxide (GO), a highly oxidized graphene layer, containing a large number of hydrophilic groups including epoxides, hydroxyl, carbonyl and carboxylic groups on its surface (Moussavi et al., 2016). These functionalities led to net negative charge and high dispersibility of GO in water. These remarkable characteristics make GO a strong candidate among adsorbents used in water purification based techniques (Chen et al., 2012; Geim and Novoselov, 2007). Many researchers have reported GO based materials as adsorbent for elimination of various toxic dyes. Removal of such toxic dyes like methyl green (MG) and methylene blue (MB) from water has been tested by using GO as an adsorbent (Chen et al., 2012). The electronic configuration of GO is involved in π-π and electrostatic interactions with the electronic structures of dyes in the adsorption process. However, it is hard to separate GO adsorbent from water upon the completion of adsorption process owing to its high dispersibility in aqueous medium. To meet this problem, GO is hybridized with other inorganic and organic materials. These GO based nanocomposites are the novel hybrid materials where inorganic particles especially the metal nanoparticles are synthesized onto the graphene sheets by first attachment of metal ions on the GO sheets through electrostatic interactions and then the reduction of metal ions into metal nanoparticles (Fan et al., 2012a). This type of hybridization not only prevents the agglomeration of nanoparticles and restacking of graphene layers but also imparts additional advantageous properties such as catalytic and antibacterial properties. Cheng et al. (2015) designed GO based magnetic composite gels by combining GO with poly (vinyl alcohol) and platinum (Pt) nanoparticles and studied their adsorptive and catalytic applications. The authors observed that these composite gels were not only having remarkable high adsorption capacity but also exhibit a simple and convenient separation capability by the applying external magnetic field. Also, Pt nanoparticles containing composite gels were found to possess excellent catalytic properties. GO has also been found as very suitable template for the fabrication of recyclable photocatalysts. For example, Wu et al. (2015)prepared palladium (Pd) nanoparticles by using reduced GO as a template and found that the resultant composite was having excellent photocatalytic activity. Similarly, a nanocomposite was prepared by Yuan et al. (2016) by decorating silver nanoparticles on reduced GO and it was observed that prepared material was stable to be used as photocatalyst with reasonable high catalytic activity. In addition to the above mentioned catalytic reactions, graphene oxide has been found as the most suitable substrate for the fabrication of highly stable catalysts applicable in water splitting, fuel cells and solar cells (Wang et al., 2015b). Except having high catalytic activity and stability, graphene oxide based nanocomposite also show high adsorption affinity for various pollutants. In this context, Wang et al. (2015b)prepared reduced graphene oxide based nanocomposite containing polypyrrole and iron oxide nanoparticles. The prepared composite was found to have high capacity for chromium (VI). Li et al. (2011) fabricated magnetic graphene nanosheets functionalized with $CoFe_2O_4$ for separation of methyl orange (MO) from aqueous environment. Similarly, Fan et al. (2012b) fabricated the carbon coated Fe_2O_3 NPs on GO sheets and studied the removal of toxic dyes and the recyclability of adsorbent. In another report, reduced-graphene oxide/titanate (rGO-Ti) nanohybrid was tested by Nguyen-Phan et al. (2012) to remove methylene blue from water and an adsorption capacity value of 83.3 mg/g was observed. Since the industrial effluents may contain variety of pollutants and microorganisms may also grow in polluted water. So there is a need to design materials which can eliminate these types of multiple pollutants from wastewater simultaneously. Unfortunately, less attention has been given to design such versatile materials. Here, we have designed a novel GO based nanocomposite integrated with Ag nanoparticles which can act as adsorbent for both the cationic and anionic dyes, as catalyst for the reduction of nitroaromatic pollutants and as antibacterial agent and hence have ability to decontaminate wastewater in short time from a variety of pollutants by performing multiple tasks simultaneously. To the very best of our study, this is the first time that a system having ability to clean water by performing triple actions simultaneously is being reported. The detailed adsorptive removal of MG and EV as well as catalytic reduction of 2-NA has not been studied using GO-Ag nanocomposite as an adsorbent. The details of various influential factors such as pH, temperature, dosage, and contact time were studied for both the dyes. Adsorption data was also simulated with adsorption kinetics as well as isotherms. The reusability of the adsorbent was also studied. Catalytic performance for the reduction of 2-NA was also studied in detail. Most importantly, the simultaneous adsorption of cationic and anionic dyes as well as degradation of mixture of MG, EV dyes and 2-NA was reported for the first time using GO-Ag nanostructure. Since the industrial wastes contain variety of pollutants, simultaneous removal of these pollutants from industrial water is highly beneficial. Also, the mechanism of interaction of dyes with the adsorbent has also been proposed in this article. Ag is known as an efficient antibacterial agent for centuries as it can inactivate numerous kinds of microorganisms by destroying their cell membrane and replicating ability of DNA, therefore, the synthesized nanocomposite was also assessed for antibacterial efficiency against Gram-negative bacteria (E.coli) and Gram-positive bacteria (*S. aureus*). So the reported nanocomposite provides a triplicate benefit in waste water treatment by simultaneously removing dyes, aromatic compounds and destroying harmful microorganisms.

2. Experimental

Graphite powder (99.9%), silver nitrate ($NaNO_3$, 99.5%), sodium borohydride ($NaBH_4$, 98%) were bought from sigma-aldrich. Malachite green (MG, 90%) and ethyl violet (EV, 90%) dye and the aromatic pollutant 2-nitroaniline (2-NA, 98%) were used without further purification and were bought from Aldrich chemicals. We used double distilled water (DDW) throughout the experiment.

2.1. Synthesis of GO-Ag nanocomposites

Initially, graphite powder was used to prepare highly exfoliated GO sheets following the previously reported modified hummers method (Tavakoli et al., 2015). For the preparation of GO-Ag nanocomposite, firstly GO sheets were exfoliated by dispersing 20 mg of GO in 50 ml of DDW in an ultra-sonication bath for 1 h. Then 10 ml of 0.025M $AgNO_3$