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SnO_2 quantum dots decorated reduced graphene oxide nanocomposites for efficient water remediation

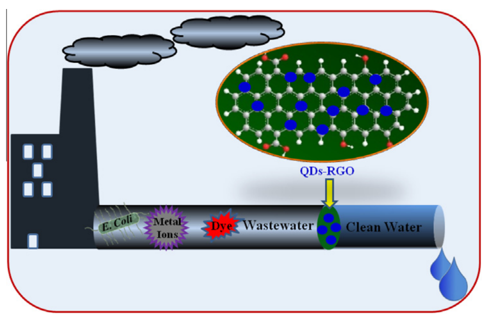
Dipa Dutta, Shankar Thiyagarajan, Dhirendra Bahadur *

Department of Metallurgical Engineering & Materials Science, Indian Institute of Technology Bombay, Mumbai, India

HIGHLIGHTS

- SnO_2 QDs decorated RGO is exploited for the first time for wastewater remediation.
- The composite not only removes organic dyes and toxic metal ions, but also *E. coli*.
- Excellent separation efficiency (94%) for MB/MO mixture, but 76% for MB/RhB.
- Registered maximum monolayer adsorption capacity (Q_m) of 40.81 mg/g for MB.

GRAPHICAL ABSTRACT



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ABSTRACT

An adsorbent, SnO_2 quantum dots (QDs) decorated reduced graphene oxide (RGO) nanocomposite, is used for removal of different organic dyes (methylene blue (MB), methyl orange (MO) and rhodamine B (RhB)), toxic metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+}, Hg^{2+} and As^{3+}), and pathogenic bacteria (*Escherichia coli*) from wastewater. It exhibits good removal capacity and fast adsorption rate for cationic dye MB. In binary solution the nanocomposite registered an excellent separation efficiency of 94% for MB/MO mixtures, whereas the same is 76% for MB/RhB mixture. The effect on removal process by different influencing parameters such as dosage of adsorbent (0.1–0.6 g/L), initial solution pH (3–11), initial dye concentration (10–50 ppm), contact time (0–60 min) and temperature (303–333 K) is investigated in order to find the optimum adsorption conditions. Adsorption isotherm data are extensively investigated using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms; it is found to fit well in Freundlich model. Adsorption kinetics is described by pseudo-second order kinetics. Thermodynamic study suggested that the MB adsorption on QDs-RGO is a spontaneous and exothermic process. QDs-RGO also shows good removal efficiency for lead (II) from individual as well as mixed solution. Adsorption kinetics and isotherm data are extensively investigated for adsorption of lead (II) and found to be better described by pseudo-second order kinetics and Freundlich model. Furthermore, QDs-RGO showed higher antibacterial activity towards *E. coli* than the individual constitute materials. It is essentially established from the results that QDs-RGO is an ideal aspirant for removal of positively charged organic dyes, toxic heavy metal ions and bacteria pathogen from wastewater.

1. Introduction

With steady expansion of industry, environment pollution has become a concern all across the world. Industrial wastewater containing heavy metals, organic dyes, and pathogenic bacteria

* Corresponding author. Tel.: +91 22 2576 7632; fax: +91 22 2572 3480.
E-mail address: dhirenb@iitb.ac.in (D. Bahadur).

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from different industries causes numerous undesirable consequences to the environment. Heavy metals and dyes are significant threat to the environment and public health due to their non-biodegradability and strong toxicity to plants, animals, and human beings even at trace levels [1–3]. Moreover, color effluents prevent penetration of sunlight to water bodies, affecting aquatic life by hindering photosynthesis [4]. Methylene blue (MB) causes permanent eye injury to the humans and animals [5]. Heavy metals have a tendency to accumulate in living organisms, causing serious diseases and health disorder [6]. Further, microbial threats on human health and safety have become a serious public concern [7]. In view of this, it is of immense importance to remove hazardous dyes, heavy metals and pathogenic bacteria from wastewater before discharging to water bodies. Various techniques are used for removal of different pollutants from industrial wastewater and among all conventional techniques; adsorption is extensively used due to its operational simplicity and low cost [8].

Popularity of adsorption method encourages many researchers to find appropriate adsorption materials having high surface area and high adsorption capacity. High surface to volume ratio of nanomaterials make them likely choices for this purpose. Until recent time, low cost activated carbon was extensively used as an adsorbent material for removal of pollutants from wastewater. However, its use is restricted by low bio-degradability, occurrence of macropores and also because a large amount of adsorbent is required for swift removal of pollutants [2,8]. Inorganic materials such as zeolites, clay, and graphene are also being studied as possible adsorbents; among which graphene fascinates researchers because of its π–π interaction resulting from its π electron cloud. Considerable efforts are being made by many researchers to find appropriate materials with high adsorption capacity in order to effectively remove pollutants from wastewaters. Keeping these in mind, much attention is being paid by researchers to fabricate different carbonaceous nanomaterials as adsorbent [9–11]. In recent times, different composites of oxide nanomaterials and graphene have been studied as possible adsorbents for removal of water pollutants. Ai et al. [12] and Cui et al. [13] reported graphene/magnetite and Xanthate functionalized magnetic graphene oxide composites as effective adsorbent for methylene blue. Tiwari et al. [14] fabricated reduced graphene oxide hydrogels for efficient removal of dye pollutants. Yang et al. [15] reported lignosulfonate–graphene oxide–polyaniline ternary nanocomposite as an effective adsorbent for Pb^{+2} ions. Zhu and co-workers [16] efficiently captured heavy metal ions using magnetic graphene nanocomposites. Semiconducting SnO_2 quantum dots (QDs) decorated on different matrix are presently attracting consideration as adsorbent material for removing pollutants due to its high surface to volume ratio [8,17].

Here, we present a noble approach of decorating RGO with SnO_2 QDs. SnO_2 QDs loaded RGO may satisfy the necessary properties of a nano-adsorbent with its large surface area and excellent adsorption characteristics. To the best of our knowledge, SnO_2 QDs decorated RGO (QDs-RGO) is not exploited so far as a plausible adsorbent material for removing pollutants from wastewater. In this work we have explored its efficiency for the removal of different dyes (methylene blue, methyl orange and rhodamine B), toxic metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+}, Hg^{2+} and As^{3+}), and capturing of pathogenic bacteria (*Escherichia coli*). The condition for methylene blue removal is optimized in this study. QDs-RGO shows good removal efficiency for lead (II) from individual as well as mixed solution. Synergistic effect of RGO and SnO_2, improved the bactericidal nature of nanocomposites to a greater extent. Results indicate that QDs-RGO is an ideal aspirant for removal of positively charged organic dyes, toxic metal ions and bacterial pathogen from wastewater.

2. Experimental

2.1. Dye adsorption measurement

For single and binary dye adsorption; three model dyes, namely methylene blue (MB), rhodamine B (RHB) and methyl orange (MO) were selected. Their chemical structures are shown in Table S1. For single dye adsorption, a known amount of QDs-RGO was added to 10 ppm individual dye solution (80 mL). In case of binary dye solution two different dye solution of concentration 10 ppm was mixed in volume ratio 1:1. The adsorbent concentration remains same in both cases. Desorption of saturated QDs-RGO nanocomposites was easily carried out in acidic solution. Detail of these batch experiments are described in supporting information section.

2.2. Adsorption of heavy metal ions

Stock solutions of 100 ppm of individual heavy metal ions (namely Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Pb^{2+}, Cr^{3+}, As^{3+}) were prepared in MilliQ (18 MΩ) water. In order to investigate the simultaneous removal of toxic metal ions, wastewater containing 100 ppm of each heavy metal ions, was prepared. Adsorption experiments of heavy metal ions were carried out by adding 10 mg of QDs-RGO to 10 mL ion solutions of different concentrations at 30 ± 2 °C. The concentrations of heavy metal ions varied from 1 to 20 ppm while the pH was maintained at 6.5. Separation procedure of composite and analysis of different ions concentrations in the supernatant are given in supporting information.

2.3. Anti-bacterial activity

QDs-RGO nanocomposite was exploited for its potential as a bactericidal agent using *E. coli* (DH5α, Gram negative bacteria), as a model microorganism. From stock solution, 1 mL of solution containing 4.62×10^{17} CFU/mL was transferred to four sets of test tubes containing three different concentrations of QDs-RGO such as 50, 25, 12.5 μg/mL (treatment). A solution without composites was taken as a control. In another set of similar experiments, 1 mL of original stock solution (containing $\sim 10^{17}$ CFU/mL) was transferred to five sets of test tube containing 50 μg/mL of QDs-RGO, SnO_2, RGO, GO and control. The interaction between these nanocomposites and the bacterial cells is of prime importance in determining their bactericidal nature. This is investigated through SEM and TEM characterization techniques. Counting procedure and sample preparation for different microscopy are given in supporting information.

3. Result and discussions

In one of our earlier work, we reported a new strategy for fabrication of QDs-RGO from a hybrid complex $[(N_2H_4)m(SnCl_4)n]$, described elsewhere [9]. Different morphological characterization techniques were used to confirm the decoration of SnO_2 QDs onto RGO. Decrease in the restacking of graphene sheets results in a higher surface area for QDs-RGO, which is a favorable criterion for any good adsorbent. We attempt to explore the potential of QDs-RGO as adsorbent materials for removal of pollutants such as organic dyes, heavy metal ions, and pathogenic bacteria from wastewater.

3.1. Single dye adsorption

Due to its large surface area, QDs-RGO have outstanding adsorption ability for removing pollutants from water, the