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Optimization and modelling of synthetic azo dye wastewater treatment using Graphene oxide nanoplatelets: Characterization toxicity evaluation and optimization using Artificial Neural Network

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ABSTRACT

Azo dyes pose a major threat to current civilization by appearing in almost all streams of wastewater. The present investigation was carried out to examine the potential of Graphene oxide (GO) nanoplatelets as an efficient, cost-effective and non-toxic azo dye adsorbent for efficient wastewater treatment. The treatment process was optimized using Artificial Neural Network for maximum percentage dye removal and evaluated in terms of varying operational parameters, process kinetics and thermodynamics. A brief toxicity assay was also designed using fresh water snail *Bellamya benghalensis* to analyze the quality of the treated solution. 97.78% removal of safranin dye was obtained using GO as adsorbent. Characterization of GO nanoplatelets (using SEM, TEM, AFM and FTIR) reported the changes in its structure as well as surface morphology before and after use and explained its prospective as a good and environmentally benign adsorbent in very low quantities. The data recorded when subjected to different isotherms best fitted the Temkin isotherm. Further analysis revealed the process to be endothermic and chemisorption in nature. The verdict of the toxicity assay rendered the treated permeate as biologically safe for discharge or reuse in industrial and domestic purposes.

1. Introduction

Every year textile processing and manufacturing industries consume a massive volume of water and thereby generate an equally alarming quantity of dye-rich effluents. Such effluents contain dissolved and suspended compounds and colouring agents and may be highly acidic or alkaline in nature. Owing to its volume of discharge and composition, textile effluent has been rated as the most polluting amongst all other industrial effluents (Kumari and Emilia, 2007). Amidst all other contaminants, the coloured pigments are reckoned as pollutants of utmost concern due to their visibility to naked eye as well as their toxic nature (Gupta et al., 2006). Approximately, a global annual production of 7×10^5 t of 10,000 different commercial dyes and pigments have been previously reported (Gupta and Suhas, 2009). Several of these dyes have been found responsible for direct destruction of life in and around the natural water bodies when discharged through wastewater (Khan et al., 2013). Some dyes have been assessed to possess carcinogenic and mutagenic properties as well (Ponnusami et al., 2009; Khan et al., 2012a).

Safranin, one of the oldest known and most commonly used synthetic azine dye, (Gupta et al., 2006) has experienced wide application as food dye in candies and cookies besides being utilized in dyeing of leather, paper, wool, silk, cotton and jute fibres (Shah, 1998). Although safranin is not as toxic as other commercial dyes, acute exposure to it resulted in detrimental health effects like oral and throat irritation, stomach aches, vomiting and diarrhoea, eye and dermal irritation, etc. (Das and Mishra, 2012). Biodegradation products of such dyes have been reported as biorecalcitrant in nature due to their structural stability (Chowdhury et al., 2010).

In recent years, in comparison to its conventional precursors like coagulation, flocculation, biodegradation, membrane filtration and reverse osmosis, etc., the process of adsorption has received much significance as one of the most efficient, easy to operate and cost effective procedures implemented for treatment of effluents containing different types of dyes (Choy et al., 2000). Till date many low cost biosorbents such as waste pea shells (Khan et al., 2014a), chir pine sawdust (Khan et al., 2014b), water chestnut peel (Khan et al., 2013), bamboo sawdust (Khan et al., 2012a), mango leaf powder (Khan et al., 2011) and adsorbents like activated

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carbon with modifications (Ghaedi et al., 2015a; Ghaedi et al., 2015b, Ghaedi et al., 2013a; Roosta et al., 2014a; Roosta et al., 2014b), kaolinite (Khan et al., 2012b), fly ash (Khan et al., 2009), etc have been successfully implemented for selective removal of several dye pollutants from water. However, amongst all other adsorbents, carbon based materials have gained much significance because of their non-hazardous and cost effective preparation procedures, well-defined and uniform structures and high mechanical stability (Das et al., 2014). Graphene, a fascinating 2-D carbon-based material of atomic thickness has received substantial global attention since it was first reported (Novoselov et al., 2004). Graphene oxide (GO), used in this study, was an oxidized form of graphene (Dreyer et al., 2010) bearing an assortment of hydroxyl and epoxy groups arranged in the basal plane with carboxyl groups bordering the edges (Mkhoyan et al., 2009). Its hydrophilic nature coupled with very high (−)ve charge density (resulting from its oxygen-bearing functional groups) (Ramesha et al., 2011) rendered GO highly suitable for adsorption. In addition, GO was determined to exist as a single layer in solution and possesses the ability to intercalate water molecules (Ramesha et al., 2011). The layered nature of GO and assistance of its functional groups were effectively utilized for dye adsorption from aqueous solutions.

The objective of the present investigation was to evaluate the efficiency of safranin removal using Graphene oxide (GO) as adsorbent. The effect of operational parameters such as pH, temperature and adsorbate concentration on dye removal efficiency was determined after specific time intervals. Langmuir, Freundlich and Temkin adsorption isotherms were used to fit the adsorption data obtained experimentally. Adsorption kinetics and process thermodynamics were also evaluated. Artificial Neural Network modelling was also carried out to predict the % dye removal under optimized conditions. Additionally, a toxicity analysis was performed for assessing whether the treated water was biologically safe and fit for discharge or reuse.

2. Materials and methods

2.1. Preparation of Graphene oxide nanoplatelets (GONPs)

GONPs were prepared by oxidation of exfoliated graphite powder (Merck,Germany) by modified Hummers method (Hummers and Offeman, 1958) using H_2SO_4 and HNO_3 in a 3:1 ratio for 24 h. After 24 h, potassium permanganate was added to this mixture whereby a bright yellow coloured end product was formed (Raoet al., 2009). This compound was vigorously washed thrice with 30% HCl followed by a wash with distilled water forneutralizing the solution. The *GONPs* obtained was isolated by centrifugation, dried in avacuum desiccator and stored for further analysis and adsorption experiments. All thechemicals used in this experiment were of analytical grade (Merck, Germany).

2.2. Preparation of adsorbate solution

Safranin powder [λ_{max}=516 nm] (Merck, Germany) was dissolved in distilled water for preparing a stock solution (100 mg L^{-1}). Safranin solutions of different concentrations wereprepared in volumetric flasks by diluting the stock solution with required amount of distilled water.

2.3. Determination of effect of pH, temperature and adsorbent dose

For all experiments, 100 mL safranin solutions (50 mg L^{-1}) were taken in Erlenmeyerflasks. The influence of varying experimental parameters like pH of the solution (2, 4, 6, 8 and 10), contact time (15, 30, 45, 60 and 90 min), adsorbent dose (0.25, 0.5, 0.75 and 1 g L^{-1}) and temperature (293, 298, 303 and 308 K) were determined during the present study. The pH of the solutions was adjusted with 1.0 MNaOH and/or 0.1 N HCl prior to each experiment as and when required. Samples were collected from the flasks at predetermined time intervals for analyzing the residual concentration of safranin in the solution, which was measured at a wavelength of 516.0 nm using an UV/VIS spectrophotometer (Model Hitachi-2800, Japan). All experiments were repeated thrice to minimize handling error.

2.4. Determination of point of zero charge (pH_{zpc}) of GONPs

The pH at the pH_{pzc} for the *GONPs* was determined by the batch equilibration technique (Kongsri et al., 2013). 0.1 M NaCl was selected as an inert electrolyte. Initial pH ($pH_{initial}$) values (2–10) of the NaCl solutions were adjusted with 0.1 M HCl or NaOH as required. 0.1 g of GONP was added to 25 mL of 0.1 M NaCl solution and allowed to equilibrate for 24 h with constant agitation at 25°C. After 24 h, the solution was filtered and the final pH values (pH_{final}) were recorded. The pH_{zpc} of the adsorbent was calculated from the point of intersections of the curves obtained in the plot of pH_{final} vs. $pH_{initial}$(Khan et al., 2013, Ghaedi et al., 2013b).

2.5. Optimization using Artificial Neural Network (ANN)

ANN is a simple mathematical and computational model developed following the structure of biological neural networks analysis. This model is generally utilized for interpretation of complex input–output relationships or determination of patterns in data. Neural networks have been previously used to execute complex functions in different fields of application for the purpose of time series forecasting, recognition of patterns, for identification and classification and in case of speech, vision as well as control systems. The main advantage of ANN model over traditional methods of optimization is that it disentails the complexities underlying the process of biosorption (Dutta et al., 2010; Khataee et al., 2011). In the present study, a 3-layer network with linear transfer function and back-propagation neural network (3:10:1) was considered. In this study, different algorithms of 'poslin', 'purelin' and 'traincgp' were selected to guide the model. The input variables selected for the feed forward network were pH of the adsorbate solution, contact time (min), adsorbent dose (g L^{-1}) and temperature (K). The experimental responses or output variables was denoted by % removal of dye recorded in the adsorption process. The ANN model was designed using MATLAB 7, USA.

2.6. Characterization of the adsorbent

The GO (prior and post adsorption) was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM).

FTIR analysis of GO was obtained throughthe potassium bromide (FTIR grade) pellet method and was recorded at a resolution of 4 cm^{-1} with JascoFTIR-6300 Fourier Transform Infrared Spectrometer in transmittance model (JASCO, Japan).

Scanning electron microscopy (SEM) was performed to determine the alterations in the surface morphology of GO that had occurred due to adsorption. The samples were gold coated with a sputter coater for making them conductive and visualized using a scanning electron microscope (ZEISS EVO-MA 10, Germany).

Changes that had taken place in the structure and roughness of GO as a result of adsorption were observed using a *transmission electron microscope* (TEM) (JEOL, Japan; Model No. JEM 2100 h with EELS) and an *atomic force microscope* (AFM) (Innova,Veeco, Bruker AXS Pte Ltd.) respectively. TEM grids were prepared by placing