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Graphene oxide for the treatment of ranitidine containing solution: Optimum sorption kinetics by linear and non linear methods and simulation using artificial neural network

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ABSTRACT

In this present study, Graphene oxide nanoplateletes were synthesized and used as nano-adsorbent for the treatment of ranitidine present in synthetic wastewater. 99% ranitidine was removed using synthesized Graphene oxide. Comparative analysis was performed between linear and non-linear kinetic model for estimating the kinetic parameters. Four linear pseudo-second-order kinetic models were analyzed with non-linear kinetic model. Error analysis between non-linear and linear model were studied for determining the best-fitting model. It was observed that non-linear method proved to be a better alternative than the linear kinetic model for obtaining the important kinetic parameters which can be used further to determine the mechanism of the adsorption study. In addition, the treatment procedure was simulated using artificial neural network analysis to estimate the maximum percentage of ranitidine removal from wastewater in terms of various operational parameters.

1. Introduction

Control of pollution of water due to presence of drugs in domestic sewage and industrial wastewater pose a challenge in environmental science and technology (Shrain et al., in press). Review of literature till date has shown that cost effective natural polymeric sorbents have been widely used for adsorption (Bezerra et al., 2014). However, we have not come across use of graphene oxide as adsorbent in removal of pharmaceuticals from industrial effluents. Treatment of pharmaceutical wastewater can be possible using some other techniques such as coagulation, flocculation, chemical process, membrane process, advanced oxidation, ion exchange and other techniques (Sokol et al., 2011; Basavaiah and Nagegowda, 2004) but most of these techniques are so costly that these techniques cannot be applied on a large scale in some industries especially in developing Country. Among all these methods, adsorption is the low initial cost process, ease of operation compared to other techniques. More important is that the process can be used in situ with proper design and can be integrated with different systems easily.

Ranitidine hydrochloride, a non-imidazole compound acts as selective hydrogen receptor blockers in therapeutic doses. It is used widely to reduce hydrochloric acid secretion from stomach disorders such as peptic ulcer and Zollinger–Ellison syndrome (Shrain et al., in press; Bezerra et al., 2014; Sokol et al., 2011; Basavaiah and Nagegowda, 2004; Addamo et al., 2005; Rivas et al., 2010).

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Ranitidine has been found widely in effluents of water treatment plants and is obtained in aquatic environment. It undergoes incomplete biodegradation (about 71% in 28 days) (Bezerra et al., 2014) and accumulates on surface of water bodies. Photolysis of the non-degraded component can alter its chemical structure. This may lead to production of potentially toxic products which last longer in the environment.

Since ranitidine can have similar effects on biologically different organisms possessing some cellular regions, it can produce effects in non-human microorganisms, residing in aquatic sources. Therefore, removal of ranitidine and its photolytically generated toxic products is important to conserve the aquatic micro-flora.

Different low cost materials like clays, polymer and carbon-based materials have been used to treat different several organic and inorganic pollutants present in waste water. In this present study, Graphene oxide (GO) has been used for adsorption of Rantidine present in wastewater due to its cost effectiveness, large surface area, ease of synthesis and requirement in low quantities (Banerjee et al., 2015; Rathour et al., 2016; Das et al., 2014).

GO has been synthesized using graphite by chemical oxidation routes. The strong oxidation of the graphite results in formation of oxygen-containing functional groups on different layers of GO. Due to its structure and electronic properties, GO has potent adsorbent properties. Due to its nano-sized structure and electronic properties, it can interact strongly with different organic molecules, The interaction may be in the form of hydrogen bonding, electrostatic forces, π–π stacking, Van der Waals forces and as a result GO has different advantages like rapid equilibrium rates, high adsorption capacity and effectiveness over a wide range of pH values (Chowdhury and Balasubranmanian, 2014a,b)

Adsorption kinetics is a very important factor to predict the mechanism involved in sorption process. Several kinetics models such as pseudo-first order model, pseudo-second order model, Wesber and Moris sorption kinetics model, Elovich's model can be applied for the kinetic analysis but from study of literature it was observed that pseudo first and pseudo second order kinetic models are the most important models which can be used in most adsorption kinetic studies. Linear regression analysis is used to determine the kinetic parameters by converting the non-linear kinetic model equation to linear kinetic model equation. But transformation of non linear equation to linear form may alter the error structure. On contrary non linear method provides a complex mathematical method to determine the kinetic parameters and thus drawbacks of linearization may be reduced (Ho, 2006; Chowdhury et al., 2011; Chowdhury and Das, 2011).

The aim of the present study is to investigate the adsorption capacity of graphene oxide for the treatment of a drug-ranitidine and a comparison of linear and non-linear kinetic models was conducted to predict the best adsorption kinetics and kinetics parameter using GO as nano-adsorbent.

Artificial neural network is a new mathematical computing technique to solve the complex problem. In this regards, another aim of the work is to develop a multilayered neural network computing model to predict the removal efficiency of graphene oxide using ranitidine present in solution and the ANN model may predict the performance of the removal technique.

2. Materials and methods

2.1. Synthesis of graphene oxide nano platelets

Graphene Oxide was synthesized by modified Hummers' method and reported in our previous work (Banerjee et al., 2015). In this study, GO was synthesized by exfoliating graphite powder (Merck, India) in the presence of potassium permanganate ($KMnO_4$; Merck, Germany) and concentrated sulphuric acid (H_2SO_4; Merck, India) as oxidizing agent using Ultrasonication technology.

2.2. Batch Studies for the removal of ranitidine using synthesized GO

Experiments were performed in Erlenmeyer flasks under continuous stirring and at constant optimum temperature. In each set of experiment four different dose of adsorbent 1.0, 1.5, 2.0, 2.5 g/L of adsorbent were added to 10 mg/L of ranitidine concentration in solution. The flasks were agitated at a constant speed of 150 rpm and incubated at 35 °C in an incubator shaker (Model: CIS - 24PLus LCD, REMI, India) for 1 h. Solution at regular time intervals were collected, centrifuged any analyzed. The initial and final concentration of ranitidine in the solution was analyzed using UV/VIS spectrophotometer (Model: Lambda 25, PerkinElmer, USA) and High performance liquid chromatography (Model: Series 200, PerkinElmer, USA). The amount of ranitidine adsorbed at equilibrium q_e (mg g^{-1}) was calculated by:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i is the initial ranitidine concentration (mg L^{-1}), C_e is the equilibrium ranitidine concentration in solution (mg L^{-1}), V is the volume of the solution (L), and m is the mass of the nano-sorbent used (g).

All experiments were performed in triplicate and the mean values were considered.

2.3. Characterization of synthesized GO

The Fourier Transform Infrared Spectroscopy (FT-IR) (Model: PerkinElmer), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-Ray Diffraction(XRD) were performed to characterize the structure of GO. SEM analysis was used to study the structure and smoothness/roughness of the GO, FTIR was used to study the functional groups present in the nanosheet, TEM was used to know the surface and particle size of the GO and XRD was used to study the interlayer spacing of the synthesized GO.

2.4. Modeling using Artificial Neural Network (ANN)

ANN model is developed using the structure of biological neural networks analysis. Matlab 7 was chosen to develop the ANN model in this study (Chakraborty et al., 2013; Sinha et al., 2013; Chowdhury and Das Saha, 2013; Sinha et al., 2012; Das Saha and Dutta, 2012; Kumar and Porkodi, 2009; Lee et al., 1998). 4-layer network with linear transfer function and back-propagation neural network was considered. The input variables selected for the feed forward network were adsorbent dose (mg/L) treatment time (min), temperature (K) and concentration (mg/L) since all are dependent variables. The