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Comparative assessment on defluoridation of waste water using chemical and bio-reduced graphene oxide: Batch, thermodynamic, kinetics and optimization using response surface methodology and artificial neural network

*Swapnila Roy, Suvendu Manna, Shubhalakshmi Sengupta, Antara Ganguli, Sudipta Goswami, Papita Das**

Department of Chemical Engineering, Jadavpur University, Kolkata, India

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A B S T R A C T

In this study, reduced graphene oxide was synthesized from tea solution (TPGO) and by hydrazine hydrate and was used for the treatment of fluoride containing waste water. The batch study indicated that bio-reduced graphene oxide (TPGO) showed fluoride removal capacity of 94.22% whereas in case of chemically reduced graphene oxide, the removal was 87.4% at optimized condition. In both cases, the equilibrium data were fitted well with Langmuir adsorption isotherm and the adsorption kinetic data followed the pseudo second order model. The performance of TPGO was further optimized with response surface methodology and artificial neural network (ANN) analysis. The two-level, three-factorial (2^3) Central Composite Design (CCD) expert software was employed to find the optimum combination of process parameters for maximum fluoride adsorption capacity of TPGO. The exhausted TPGO was also regenerated using 1% sodium hydroxide solution and reused for the removal of fluoride present in solution.

1. Introduction

Fluoride is one of the most commonly found chemicals which pollute surface and ground water resources mainly through soil leaching, precipitation, weathering of fluoride bearing rocks and human activities like discharges from aluminum smelters, fly ash disposal. Though fluoride is essential for strengthening of dental enamel and normal bone mineralization, excessive intake could lead to molting of teeth and progressive crippling of skeleton leading to dental and skeletal fluorosis. Thus the WHO set a range between 0.5 mg/l and 1.5 mg/l of fluoride in drinking water. It is estimated that around 300 millions of people are suffering or in the risk of fluoride related health hazards. In India, the drinking water resources have fluoride concentration in range between 1.5 mg/l to 39 mg/l (Susheela and Andezhatih, 1998). Fluoride requirement in living being depends on the geographical conditions of the place. In USA, the fluoride content in drinking water should be between 0.6 and 0.9 mg/l (US Department of Health and Human Services, 2015). The concentration and duration of continuous fluoride uptake determine whether the impact will be beneficial or detrimental. In addition to fluorosis the fluoride gets deposited in joints of pelvic, knee, neck and shoulder bones and makes it difficult to move or walk. It also related to a rare bone cancer, spondylitis or arthritis even osteo-sarcoma (Chae et al., 2007). Therefore it is necessary to reduce the fluoride content to the safe limit before its consumption.

Till date various chemical as well as physical methods have been used to reduce the fluorine content in water. The methods include electro-coagulation and precipitation, membrane filtration, electrochemical process, ion-exchange, and adsorption (El-Gohary et al., 2010; Ghosh et al., 2013; Tezcan Un et al., 2013; Guo and Tian, 2013; Goswami and Purkait, 2014; Dey et al., 2014; Goswami and Purkait, 2013). Among all these processes adsorption based process is known to be simple, easy to handle, inexpensive and less sludge producing. The study

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* *Corresponding author.*
E-mail address: papitasaha@gmail.com (P. Das).

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undertaken in this paper also used adsorbent for fluoride removal from water. Materials which have high adsorption capacity, wide selectivity for pollutants, reusability and high specific surface are suitable to be used as adsorbents. Moreover removal efficiency of an adsorbent mostly depends on raw water quality such as sorbate concentration, pH, temperature, contact time, adsorbent dosage and competitive ions (Bhatnagar et al., 2011; Rao, 2003; Tomar and Kumar, 2013; Mohapatra et al., 2009; Fan et al., 2003; Mohammad and Majumder, 2014).

Reports indicated that large numbers of different types of adsorbents have been used for the removal of fluoride from water. The removal efficacy of those adsorbents was improved by modifying them. The adsorbents used for defluoridation include activated carbons (Mohan et al., 2008), activated alumina (Malay and Salim, 2011), bauxite (Sajidu et al., 2012), hematite (Teutli-Sequeira et al., 2013), polymeric resins (Viswanathan et al., 2013), activated rice husk (Ganvir and Das, 2011), brick powder (Yadav et al., 2006), red soil, charcoal, brick, fly ash and serpentine (Nath and Dutta, 2010), granular ceramics (Chen et al., 2011), hydroxyapatite (Mourabet et al., 2015), zirconium and cerium modified materials (Wang et al., 2013), titanium-derived adsorbent (Wajima et al., 2009), zeolite (Gómez-Hortigüela et al., 2013), and magnesium-modified sorbent (Zhang et al., 2013). It has been reported that titanium hydroxide-derived adsorbents also exhibited high adsorption capacity for fluoride ions even in the presence of different competitive ions. Fluoride adsorption onto granular ferric hydroxide was also studied with different experimental conditions. Granular ferric hydroxide found to be effective and environmentally friendly adsorbent for removal of fluoride (Tang et al., 2009). In addition, biochars prepared from different biomasses have also been used for water defluoridation (Ahmad et al., 2014). Now a day's nanomaterials are being used very often for fluoride removal. Graphene is one of the most promising nanomaterials have been tried for defluoridation of water (Botas et al., 2012). In most of the previous study graphene was synthesized following Hummers methods.

In the present study reduced graphene-oxide has been used for fluoride removal. The reduced graphene oxide has been synthesized using an innovative and sustainable bio-reduction method. For this type of reduction very less amount of chemical has been utilized than the chemical based reduction methods. Simple tea solution has been utilized for reduced graphene oxide preparation. This would make the process more economic and sustainable. Thus the main novelty of this study is synthesis of reduced graphene oxide through a bio-based and more economic technique. Also a comparative analysis of the efficiency of the bio-reduced graphene oxide was compared with chemical reduced graphene oxide. The entire experiment has been carried out using the process variables such as adsorbent dose, contact time, temperature. The nature of the adsorption process was described by isotherm, kinetic and thermodynamic study for both chemically reduced (CRGO) and bio-reduced graphene oxide (TPGO). To study the mechanism of adsorption, the most common adsorption isotherm viz., Langmuir and Freundlich isotherm models were used. The process was optimized by Response surface Methodology using Design Expert Software (10.1.6, Stat Ease, USA) and artificial neural network analysis (ANN) using Matlab programming. A regeneration technique was also proposed to reuse the spent adsorbents, to make the process cost effective. The novelty of this study is to synthesis of reduced graphene-oxide using green technology (tea waste solution) and its efficiency for fluoride capture.

2. Material and methods

2.1. *Chemicals*

Graphene oxide (GO) was prepared from graphite powder following modified Hummers' method. This GO was used to prepare reduced graphene oxide. Fluoride stock solution of 1000 mgL^{-1} was prepared by dissolving 2.21 g of NaF (Merck, Germany) in 1000 mL of distilled water in a volumetric flask. Using this stock solution different concentration of sodium fluoride solution was prepared. Analytical grade flake graphite powder, 98 wt.% sulphuric acid, potassium per manganite, sodium nitrate, deionized water, hydrochloric acid, 30% hydrogen per-oxide and 80% hydrazine hydrate solution (all chemicals from Merck, India) were used.

2.2. *Preparation of adsorbents*

2.2.1. *Chemical synthesis of graphene oxide (modified hummer's method)*

Mixture of graphite powder and $NaNO_3$ in 2:1(w/w) ratio was mixed into a beaker with 98 wt% H_2SO_4 at room temperature. Then, $KMnO_4$ powder (3 times of mixture) was slowly added to the mixture with continuous stirring. The suspension was stirred continuously for 2 h at room temperature. Temperature of the mixture was kept at 308 K for 30 min after dissolution of $KMnO_4$. Thereafter deionized water was added into the mixture drop wise. This was done within ice bath. Then hot water and 30% H_2O_2 were added into the mixture with continuously stirring to stop the reaction. The yellowish brown colored paste was then washed with dilute HCl and distilled water and dried in vacuum oven at 373 K for 24 h. Graphene oxide(GO) prepared in this way was used for further modifications and studies (Hummers and Offeman, 1958; Ban et al., 2012; Chen and Feng, 2012).

2.2.2. *Reduction of graphene oxide*

2.2.2.1. Chemical synthesis of reduced graphene oxide (CRGO). For chemical reduction 400 mg of GO was dispersed in 400 mL deionized water by means of 30 min ultrasonication. The pH of the brown GO suspension obtained after the sonication was made alkaline by adding ammonium hydroxide drop wise. Then hydrazine hydrate was added into suspension and heated at 363 K for 24 h (weight ratio of hydrazine hydrate and GO = 10:7). The black flocculent substance precipitated out of the solution was then collected by filtration. The solid materials was washed with methanol and water and oven dried at 353 K for 24 h (Balaprasad, 2012; Viet et al., 2012; Zhu et al., 2010) and termed as Chemical Synthesis of Reduced Graphene Oxide (CRGO) hereafter.

2.2.2.2. Biochemical synthesis of graphene oxide (TPGO) by tea polyphenol. The GO was also reduced by using tea solution. The tea solution was prepared by mixing 2 g of green tea powder (contains about 10–15% polyphenolic compounds) (Zhu et al., 2010) in 100 mL of deionized water and boiling at 373 K for 20 min followed by filtration. Then 50 mg GO powder was added in the tea solution and sonicated for 30 min and then it was refluxed at 363 K in a nitrogen atmosphere. After that, the resultant Tea Polyphenol Reduced Graphene Oxide (TPGO) was collected by filtration and washed with deionized water several times to remove the excess polyphenols.

3. Characterization of reduced graphene oxide

3.1. *X-ray diffraction (XRD) analysis*

X-ray diffraction analysis of the adsorbent was carried out using X-ray diffractometer (Bruker, D8 Advance, Germany) with a Cu Kα radiation.