Nitrate removal from municipal effluent in the adsorption process on activated carbon of orange peel modified with chitosan and iron particles

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ABSTRACT: Nitrate removal from polluted waters is one of the most important environmental issues. The aim of this study was to remove nitrate from municipal effluent by activated carbon of orange peel modified with chitosan synthesized from shrimp peel and iron (III) chloride. Identification of activated carbon functional groups by FTIR, the morphology of carbon cavities by SEM, and porosity properties were investigated by BET analysis. The characterization results indicate a porous structure with different functional groups of modified activated carbon. Pseudo-first-order, pseudo-second-order, intra-particle, and Boyd kinetic models were used to describe the kinetic data, as well as Langmuir, Freundlich, and Dubinin-Radushkevitch isotherms to describe the adsorption equilibrium data. The effect of pH and the amount of adsorbent was investigated and the results showed that pH = 2 and the amount of adsorbent 0.2 g in 50 ml of solution are the optimal conditions to achieve maximum nitrate removal. The results showed that the adsorption followed the pseudo-second-order kinetics (R2 = 1). Also, among the studied isotherms, the Langmuir model described well the adsorption of nitrate onto synthesized activated carbon (R2 = 0.999) and the maximum adsorption capacity was 263.157 mg/g of activated carbon. This behavior means the adsorption of the monolayer and the predominance of the chemical adsorption mechanism. Nitrate uptake increased with decreasing temperature, indicating that the reaction was exothermic. Nitrate removal efficiency with modified activated carbon was estimated to be 99.58%. In general, it can be said that modified carbon can be a candidate for use on an industrial scale.

1- Introduction

Nitrates are important pollutants in wastewater that have harmful effects on human health. Therefore, its elimination and reduction in wastewater and water to less than the set standard has always been very important. The World Health Organization has set the maximum permissible level of nitrate in surface water at 50 mg/L [1]. The Iranian Institute of Standards and Industrial Research has set a limit of 45 mg/L nitrate in surface waters. The presence of nitrate in water up to the standard level (less than 45 mg/L) is not dangerous [2], but increasing the amount of nitrate above the standard level can be easily absorbed by the gastrointestinal tract and cause diseases such as methemoglobinemia, especially in children [3]. Nitrate water pollution can also lead to high blood pressure, increased neonatal mortality, goiter, cytogenic and premature birth [4, 5]. Studies in recent years have shown that the phenomenon of adsorption with the help of activated carbon is a convenient, easy, and low-cost way to remove various types of contaminants [4]. In this method, with the help of an adsorbent such as activated carbon, the entry of nitrate contaminants into water sources can be prevented.

Due to the high cost of commercial activated carbon, the production of activated carbon using agricultural wastes has attracted attention today. Also today, modification of activated carbon surface with various materials such as natural polymers and nanoparticles to improve its adsorption properties has received much attention [6]. In this study, activated carbon was prepared from orange peel waste, and chitosan (natural polymer) was prepared from shrimp shells, and then the surface of activated carbon was modified with chitosan and iron nanoparticles. Modified activated carbon was used to remove nitrate from drinking water by the adsorption process.

2- Methodology

Activated carbon was prepared from the orange peels by chemical activation with phosphoric acid [7, 8]. Chitosan was synthesized from the shrimp shells. Then the surface of activated carbon was modified using chitosan and iron nanoparticles according to the method presented by Sharififard et al. [6]. The porosity structure of activated carbon and its functional groups and the success of the surface modification

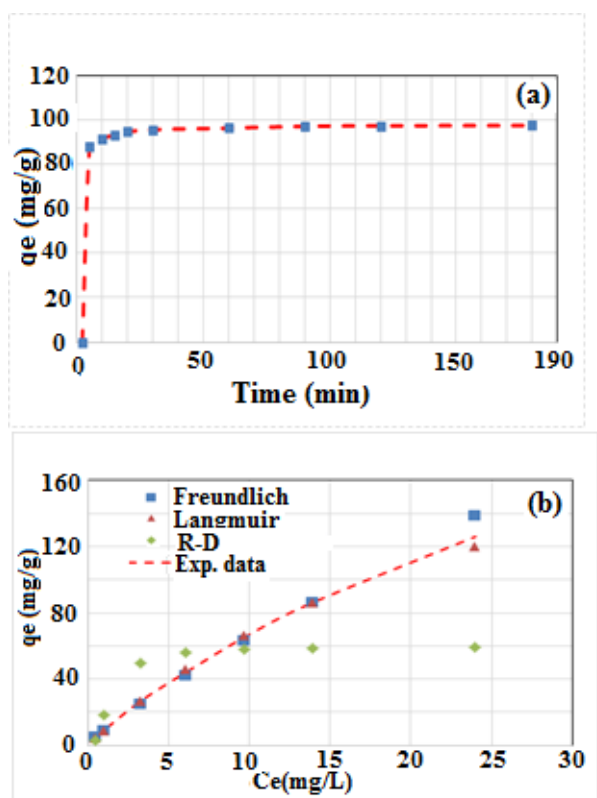*Corresponding author's email: hakimeh.sharifi@gmail.com

Fig. 1. (a): Kinetics result; (b): Equilibrium result

process were evaluated by BET, FTIR, and SEM techniques. Modified activated carbon was used to remove nitrate from municipal effluents via the batch adsorption process. The effect of pH and adsorbent amount on nitrate removal ability of modified activated carbon was investigated. Also kinetic and equilibrium experiments were performed and analyzed with different kinetic and isotherm models.

3- Results and Discussion

The results of BET and SEM analysis showed that the synthesized activated carbon has a porous structure with a specific surface area of 1526 m^2g^{-1}. The FTIR and EDX spectrums confirmed the successful synthesis and modification of activated carbon with amine groups of chitosan and iron functional groups. The FTIR peaks confirmed the main functional groups of activated carbon, including carboxylic acid, Lactonic, and phenolic groups. The value of pH_{ZPC} was 3.01. Results showed that the nitrate adsorption percentage decreased with increasing pH, and the highest amount of nitrate uptake occurs at pH equal to 2. At pH <3.01, the activated carbon surface has a positive charge and can attract the nitrate anions via electrostatic adsorption. The surface charge of the adsorbent is negative at pH> 3.01. Therefore, at pH>3.01 due to electrostatic repulsion, the nitrate adsorption is low. The results of the effect of the amount of adsorbent indicate an increase in nitrate removal efficiency with increasing the amount of adsorbent.

Figure 1a shows the results of kinetics experiments. These data were investigated with various kinetics models, including pseudo-first, pseudo-second-order, intra-particle, and Boyd models. According to the regression results, the pseudo-second model could describe well the kinetics of the removal process. The equilibrium data presented in Figure 1b were analyzed with Langmuir, Freundlich, and D-R isotherm models. The results show a good matching of experimental data with the Langmuir model. The maximum adsorption capacity of modified activated carbon for nitrate was 263.157 mg g^{-1} which is comparable with other adsorbents reported for nitrate removal via the adsorption process [9-12]. Thermodynamic studies show that the nitrate removal process using modified carbon is exothermic and spontaneous.

4- Conclusions

This study aimed to evaluate the effect of activated carbon of orange peel (modified with iron (Ⅲ) chloride and chitosan) as a low-cost adsorbent on nitrate removal from municipal wastewater. The study of the effect of pH showed that at pH equal to 2, the highest amount of nitrate uptake occurs. The kinetic results showed that the second-order kinetic model was very consistent with the experimental data. Therefore, it can be said that the mechanism of chemical adsorption is dominant. Higher regression for the Langmuir model was obtained by matching the data obtained from the nitrate adsorption equilibrium experiments by Langmuir, Freundlich, and Dubinin-Radushkovic models. Therefore, adsorption is considered a single layer. Using this model, the maximum nitrate adsorption capacity was 263.157 mg/g. Based on thermodynamic calculations, it can be said that the process of nitrate adsorption is exothermic, spontaneous, and possible.

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