Removal of nitrate ions from aqueous solution by modified sugarcane bagasse vermicompost

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Abstract: In this study, a series of experiments were conducted in batch condition to assess the performance of modified sugarcane bagasse vermicompost as adsorbent for removing nitrate ions from aqueous solution. The properties of modified vermicompost such as morphology, elemental contents, specific surface area, cation and anion exchange capacity were detected. The effect of different parameters such as pH, adsorbent dosage, contact time, temperature and common competing anions (phosphate, carbonate, sulfate and chloride) on nitrate removal was investigated. Result this study showed specific surface area, cation and anion exchange capacity of modified sugarcane bagasse vermicompost were 26.51 m2/g, 11.16 cmol/ kg and 7.76 cmol/kg, respectively. The optimum condition was observed at final solution pH of 3.78, after 120 min of contact time and with an adsorbent dose of 2 g/L. whit increasing temperature, nitrate removal increased. From between of competing anions the sulphate and chloride have maximum and minimum effect on decreasing nitrate removal by sugarcane bagasse vermicompost.
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1. Introduction

The main source of nitrate in the surface water and ground water is agricultural and urban runoff, septic tank systems, animal manure and industrial wastewater (Bhatnagar et al., 2010; Milmile, et al., 2011).

Increasing concentration of nitrate ions in drinking water cause health problems especially in infants, such as methemoglobinemia, also called blue baby syndrome (Wan et al., 2012; Bekhradinassab and Sabaghi, 2014).

Based on the US environmental protection agency (U.S. EPA) standard, the maximum allowable concentration of nitrate in drinking water is 10 mg/L NO3–N (Bhatnagar et al., 2010).

Numerous techniques exist to remove nitrate from waters and wastewaters such as ion-exchange (Milmile, et al., 2011), chemical precipitation (Yan et al., 2010), reverse osmosis (Richards et al., 2010), adsorption (Keränen et al., 2015) and electrodialysis (Liu et al., 2005).

Compared with the other methods for removal of nitrate, adsorption is one of the most effective methods due to its economic and efficient aspects and simplicity of design and operation (Bhatnagar et al., 2010; Wan et al., 2012). Numerous materials have been applied for the nitrate adsorption from aqueous solution such as sugarcane bagasse, rice hull, zeolite, chitosan, clays, slag and fly ash (Bhatnagar and Sillanpää, 2011).

The agricultural waste materials are cheap and non-toxic, therefore the use of them as adsorbent has been increased in recent years. Results of previous study showed that unmodified adsorbents have lower adsorption capacity compare whit modified (Orlando et al., 2002; Cengeloglu et al., 2006; Chintala et al., 2013).

In the present study, sugarcane bagasse vermicompost modified with epichlorohydrin, dimethylamine and N, N-dimethylformamide has been used as adsorbent for nitrate removal from aqueous solutions in batch condition.

The properties of modified vermicompost such as morphology, elemental contents, specific surface area, cation and anion exchange capacity were determined. The effect of parameters such as solution pH, adsorbent dosage, contact time, temperature and competing anions on the removal of nitrate was investigated.

2. Material and Methods

Materials

Stock solutions of 100 mg/L for the nitrate adsorption experiments were prepared by dissolving salt of KNO_3 in deionized water. All experiments were conducted at constant temperature of 22 ± 1 ºC.

Analysis of nitrate ions concentration was performed by using by spectrophotometer (model Hach, DR5000).

Preparation of chemically modified sugarcane bagasse vermicompost

For the experiment, vermicompost prepared from sugarcane bagasse using earthworm Eisenia fetida. The sugarcane bagasse was obtained from Amir Kabir sugar factory of Khuzestan in Iran and was washed with distilled water. For decrease of pollution, samples were dried at 105 ºC for 3 days.

The sugarcane bagasse was sieved in order to obtain particles smaller size. The material was put in plastic repository with small holes at the around. Initial moisture was adjusted about 65%.

Then earthworms added to repository. The moisture and temperature in the mixture of earthworms and organic matter in during vermicomposting process, was 60%-80% and 15 ºC-30 ºC, respectively.

The Vermicompost sugarcane bagasse was formed after 100 days period. The obtained Vermicompost has a dark color, a well-decomposed state and a fine texture.

In this study, for increasing adsorption efficiency, the Vermicompost was modified whit epichlorohydrin, dimethylamine and N, N-dimethylformamide.

Characterization of chemically modified sugarcane bagasse vermicompost

The surface morphology of the modified vermicompost was examined by scanning Electron Microscopy (SEM, Leo 1455 VP model, made in Germany). The specific surface area of the adsorbents was characterized by method of Methylene blue (Divband Hafshejani et al., 2015). Elemental (C, H, N, S, O) analyses were conducted using a CHNSO analyzer (vario ELIII- elementar- made in Germany). The cation exchange capacity (CEC) and anion exchange capacity (ACE) were measured by the method method of replacement $NaNO_3$ instead HCl and KCl (Chintala et al., 2013).

Adsorption experiments

Effect of solution pH

The effect of solution pH on the removal nitrate was carried out by shaking 0.05 g adsorbent with 50 mL of nitrate solution with initial concentration of 50 mg/L at temperature of 22± 1 ºC and at speed of 120 rpm.

The pH values were adjusted by adding 0.1 M HCl or 0.1 M NaOH, and then were measured with a Mettler Toledo 320 pH meter. After 24 h, the solutions were centrifuged and a solid phase was separated. Residual nitrate concentration in the filtered solution was analyzed by spectrophotometer.

The nitrate removal percentage (R %) was calculated by equation (1) :

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

Where C_o and C_e are the initial and the equilibrium concentrations of nitrate ions (mg/L), respectivity.

Effect of adsorbent dosage

The effect of adsorbent dosage on nitrate removal by modified vermicompost was studied by adjusting the solution pH at optimum with an initial nitrate concentration of 50 mg/L, at temperature of 22± 1 ºC, with a speed of 120 rpm and by adding the varying adsorbent dosage ranging from 1-10 g/L to with 50 mL of nitrate solution. After 24 h the solutions were centrifuged (whit a speed of 4000 rpm for 20 min) and a solid phase was separated.

Residual nitrate concentration in the filtered solution was determined by spectrophotometer. The nitrate removal percentage (R %) was calculated by equation (1).

Effect of contact time

The effect of contact time on nitrate removal by modified vermicompost was investigated by a series of solutions with optimum pH, optimum adsorbent dosage 2 gr/L, the initial nitrate concentration of 50 mg/L, at temperature of 22± 1 ºC, with a speed of 120 rpm and contact time between 5 to 180 min. After completing predetermined time interval solutions were centrifuged and a solid phase was separated.

Residual nitrate concentration in the filtered solution was determined by spectrophotometer. The nitrate removal percentage (R %) was calculated by equation (1).

Effect of temperature

The effect of temperature on nitrate removal by modified vermicompost was conducted by taking a series of solutions with initial nitrate concentration of 50 mg/L, optimum pH, optimum adsorbent dosage 2 gr/L and temperature of 10, 22 and 30 ºC.

The mixtures were shaken with a speed of 120 rpm for constant time of 120 min (equilibrium time) and then solutions were centrifuged (whit a speed of 4000 rpm for 20 min) and a solid phase was separated.

Residual nitrate concentration in the filtered solution was determined by spectrophotometer. The nitrate removal percentage (R %) was calculated by equation (1).

Effect of competing anions

The presence of competing anions (phosphate, carbonate, sulfate and chloride) on nitrate removal by modified sugarcane bagasse vermicompost was investigated. Experiments were conducted by adding varying concentrations of competing anions (10, 50, 100 and 200 mg/L) in nitrate solution with a constant concentration of 50 mg/L, optimum pH, optimum adsorbent dosage of 2 g/L.

The mixtures were shaken with a speed of 120 rpm at 22± 1 ºC for constant time of 120 min (equilibrium time).

Then solid phase was separated from solution and residual nitrate concentration in the filtered solution was determined by spectrophotometer.

The nitrate removal percentage (R %) was calculated by equation (1).

3. Results

The SEM image of vermicompost shows that vermicompost has a string structure, which indicates existence of carbon in modified vermicompost. Also some fine pores are also visible in the SEM image of modified vermicompost (Figure. 1).

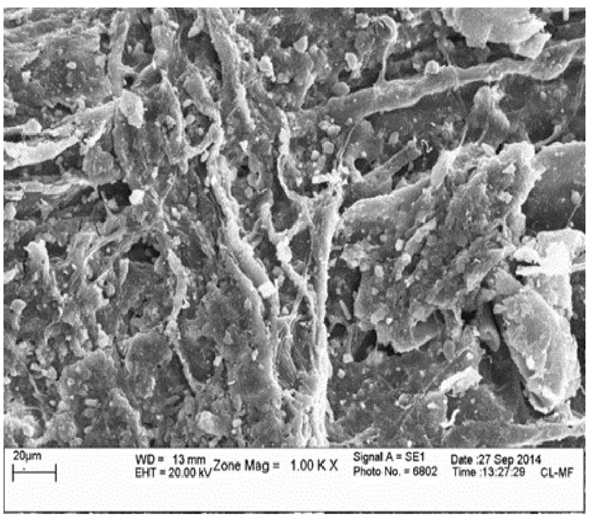

Figure 1. SEM photograph of modified sugarcane bagasse vermicompost

The surface area of modified vermicompost using methylene blue method was determined as 26.51 m^2/g. Also, cation exchange capacity (CEC) and anion exchange capacity (ACE) were obtained as 11.16 cmol/ kg and 7.76 cmol/kg, respectively.

The elemental content (CHNS) of vermicompost is presented in Table 1.

Table 1. Elemental analysis of modified sugarcane bagasse vermicompost

Elemental	C	H	N	S
Value (%)	28.89	3.97	1.21	0.73

Effect of solution pH on removal nitrate

To determine the optimum pH for the maximum removal of nitrate, the equilibrium adsorption of nitrate (with initial concentration of 50 mg/L) was investigated over a pH range of 2–11 by modified vermicompost (Figure. 2).

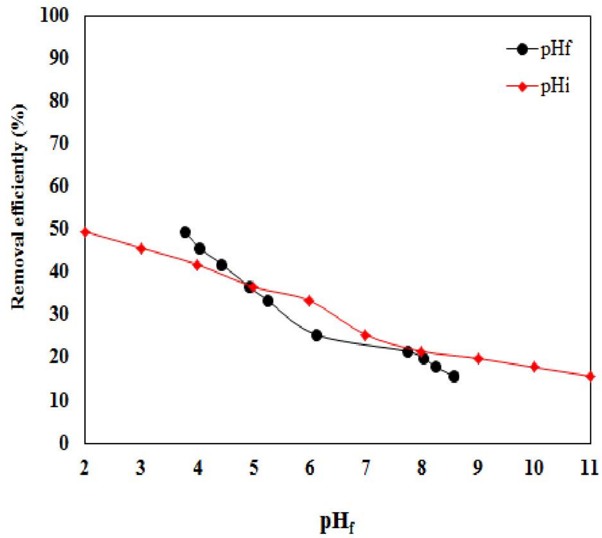

Figure 2. Effect of solution pH on nitrate removal

Effect of adsorbent dose on removal nitrate

The results effect of adsorbent dose on removal efficiency nitrate by modified vermicompost from solution with initial concentration of 50 mg/L, optimum pH (3.78) and contact time of 24 h was shown in Figure. 3.

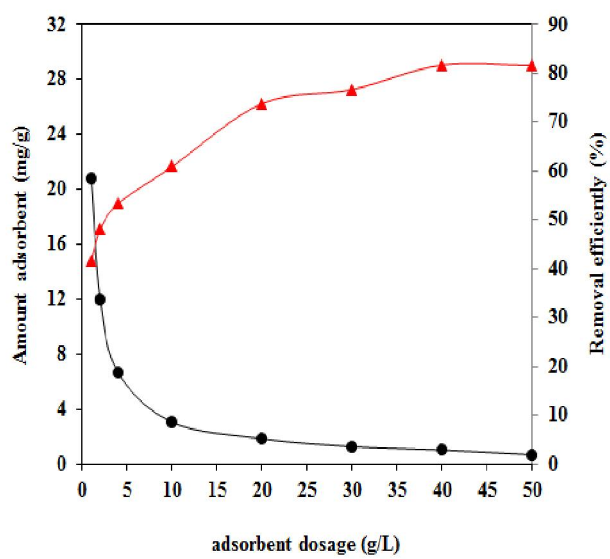

Figure 3. Effect of adsorbent dose on nitrate removal

Effect of contact time on removal nitrate

The results of contact time on removal nitrate in solutions with the initial nitrate concentration of 50 mg/L, adsorbent dosage 2 g/L, at optimum pH and temperature of 22± 1 ºC are shown in Figure. 4.

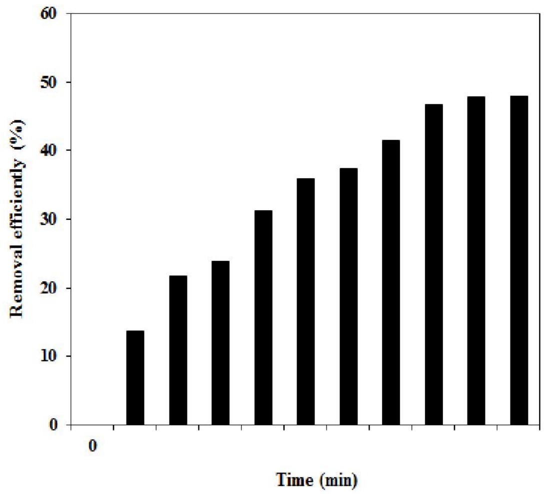

Figure 4. Effect of contact time on nitrate removal

Effect of temperature on removal nitrate

The effect of temperature on the nitrate removal by modified sugarcane bagasse vermicompost was also conducted at 10 ºC, 22 ºC (room temperature) and 30 ºC. The results of temperature effect were presented in Figure. 5.

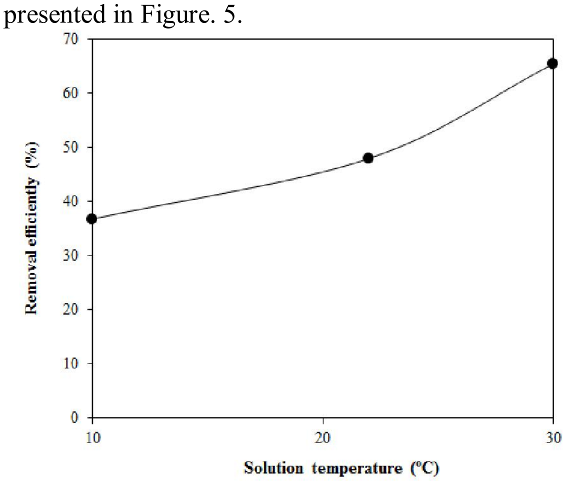

Figure 5. Effect of temperature on nitrate removal

Effect of competing anions on removal nitrate

The results of competing anions on nitrate removal are presented in Figure. 6.

The effect of competing anions on nitrate removal by modified vermicompost was studied by varying initial concentrations of competing anions (10, 20, 50 and 100 mg/L) in a nitrate solution with a constant nitrate concentration of 50 mg/L, at optimum pH, an optimum adsorbent dosage of 2 g/L, contact time of 120 min at room temperature (22ºC). The result showed due to the presence of competing anions (phosphate, carbonate, sulfate and chloride) in the water, the nitrate removal decreased. The sulfate and chloride have maximum and minimum effect on decreasing removing of nitrate, respectively.

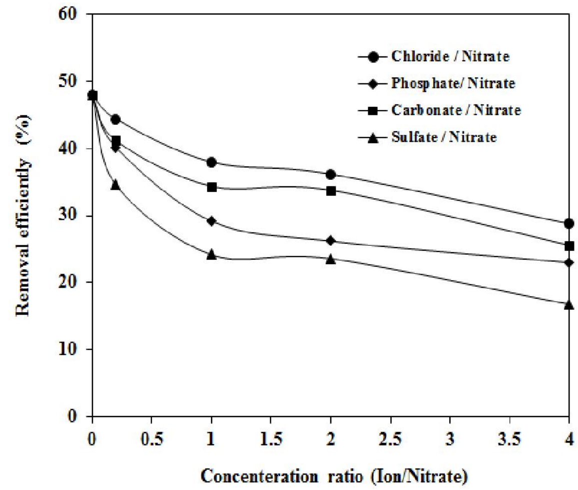

Figure 6. Effect of competing anions on nitrate removal

4. Discussions

The pH is an important parameter influencing on the nitrate adsorption (Bekhradinassab and Sabaghi, 2014). It was found that by changing the initial pH of the solution from 2 to 11, final pH changes from 3.78 to 8.58 and the maximum removal efficiency of nitrate (49.58%) by modified vermicompost was observed at initial and final pH of 2 and 3.78, respectively. also, the minimum removal efficiency (15.76%) of nitrate occurred at final pH 8.58. At low pH values, the surface of modified vermicompost is positively charged and it can attract the negatively charged nitrate ions. At high pH values, the relatively high concentration of OH^- ions will compete strongly with nitrate ions for available adsorbent sites. Similar behavior has been reported for the nitrate ions adsorption by other materials (Demiral and Gündüzoğlu, 2010; Bekhradinassab and Sabaghi).

It was evident that by increasing in adsorbent dosage from 1 to 40 g/L, nitrate removal efficiency was increased from 41.58% to 81.7% and further increase the amount of adsorbent does not effect on nitrate removal. It can be explained by the fact that the increase in the adsorbent dose, adsorption active sites and surface area of adsorbent increased. Similar results were reported by other researchers where increase in adsorbent dose, was increased nitrate removal efficiency and after reach to optimum dosage, further adsorbent dose have not effect on removal efficiency (Xu et al., 2010).

Figure 4 shows that in the beginning stages of contact time, the rate of nitrate removal is rapid. With the time nitrate removal process decreased and it reached to equilibrium after 120 min.

This phenomenon could be due to the presence of greater number of active sites on modified sugarcane bagasse vermicompost for the removal of nitrate during the initial stages. Other researchers were also reported the similar results, where the nitrate removal increase with increase in contact time and after reaching to equilibrium time, removal remained constant. The nitrate removal efficiency in equilibrium time was 41.58%.

It is clear (Figure. 5) that with increase in temperature from 10 ºC to 30 ºC, the nitrate removal efficiency increases from 36.8% to 65.5%. This result (increasing nitrate removal with increasing temperature) shows the adsorption process in this study is endothermic in nature (Ganesan et al., 2013).

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