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Removal of Nitrate from Groundwater by using Natural Zeolite as Adsorbent

Dr. Sachin Madhavrao Kanawade

Abstract

The present work was aimed at developing a cost effective, efficient and user friendly adsorption media for nitrate removal from water, surfactant modified clinoptilolite was evaluated as a potential adsorption media for this purpose. The effects of surfactant loading, adsorbent dosage and temperature on the adsorption process were investigated. Modification of the zeolite resulted in a significant increase in the adsorption capacity of the adsorbent. An increase in adsorbent dosage resulted in a corresponding increase in the percentage removal of nitrate from water. Column study and breakthrough analysis were carried out to get an understanding of the effects of inlet flow rate, adsorbent mass, initial concentration and column diameter on the adsorption of nitrates onto surfactant modified natural clinoptilolite in a fixed bed column. All the process variables save for changes in column diameter were found to have significant impact upon the adsorption of nitrates in a fixed bed column. Within the studied flow rate range, an optimum breakthrough and exhaustion points were found at a flow rate of 5ml/min. Results suggest that surfactant modified zeolite is a potential material for nitrate removal from water and hence further tests to explore its robustness are necessary.

Keywords: Nitrate, Surfactant modified natural clinoptilolite, fixed bed column, adsorption

1. Introduction

High levels of nitrates in groundwater are a cause for concern due to the possible human health risks associated with consuming nitrate contaminated water. Risks such as methemoglobinaemia [1, 2, 14] cannot be overemphasized as they are well documented. Thus, a maximum acceptable concentration of 50 mg/L NO_3^- is specified in guidelines for the World Health Organization [17]. The main causes of the elevated concentrations of nitrates in South African groundwater are not certain because of high levels in areas where there are indirect anthropogenic activities such as over application of nitrogen fertilizers during farming. Stadler *et al.* [13] tried to understand the origin of nitrate in groundwater of the Semi-Arid Kalahari of Botswana and he concluded that nitrate in groundwater of the study area appeared to be of natural origin. While there are conventional nitrate removal methods like reverse osmosis in use in South Africa, the methods are reported to be expensive and user unfriendly [3]. Therefore, it is not only necessary to provide a technology which answers these two challenges but a versatile treatment regime is compulsory. There are large reserves of natural resources like zeolites in India yet there is limited research on zeolite application in water and waste water treatment in India.

Based on batch equilibrium experiments conducted, zeolite technology is very promising for treating groundwater containing excess amounts of nitrates. The adsorptive capacity of natural zeolite on contaminants can be extensively increased by impregnation with suitable substances such as a surfactant. Treatment of natural zeolite with cationic surfactant dramatically alters their surface chemistry from a net negative to positive charge [12]**.** Surfactant modified zeolite with a positive charge will attract anionic contaminants like nitrates by electrostatic interactions. Li *et al.* [5] removed arsenic from water using surfactant modified zeolite. Perchlorate can also be removed by surfactant modified zeolite [11]. Majdan *et al.* [8] concluded that surfactant modified chabazite is an efficient adsorbent for the removal of chromates from aqeous solutions. In this study, surfactant modified zeolite (SMZ) was evaluated for nitrate removal in batch equilibrium and fixed bed column experiments. The project was aimed at exploring the application of surfactant modified natural zeolite in removing nitrates from South African groundwater.

2. Experimentation

2.1 Batch Equilibrium Experiments

The effects of three operational parameters namely surfactant loading, adsorbent mass, and temperature on the adsorption of nitrate in batch equilibrium were studied.

2.1.1 Modification of clinoptilolite

Zeolites are naturally occurring hydrated alumino silicates characterised by a cage like structure, high surface area and high cationic exchange capacities. There are more than 40 distinct natural zeolites which occur throughout the world [12]. Clinoptilolite was chosen in this study, owing to its large availability in India. Hexadecyltrimethyl ammonium bromide (HDTMABr) from Sigma Aldrich, South Africa, was used (as the surfactant) for surface modification of Zeolite. A pre-weighed quantity of natural zeolite sample was mixed with HDTMABr solution in 1: 100 (solid: liquid) ratio. The concentrations of HDTMABR used for preparation of surfactant modified zeolite samples; SMZ-1, SMZ-2, SMZ-3 and SMZ-4 were 1 g/L, 2 g/L, 3 g/L and 4 g/L respectively. The solutions were agitated for 3 days at 200 rpm on a shaker. The solution was then vacuum filtered, and the solid residue was double washed with de-ionised water and air dried. The SMZs with different HDTMABr concentrations were subjected to treatment with nitrate contaminated synthetic water. To study the sorption behaviour of nitrate on various zeolites, uniform quantities of zeolite were added to plastic bottles containing 50 mL of 50 mg/L nitrate solution. The mixture was agitated at room temperature for 24 hours, followed by filtration and the filtrate was analysed by the Salicylate method. The salicylate method is based on the formation, under acid conditions and heat, of nitronium ions (NO_2^+), which react with salicylate under alkaline conditions to form mostly a nitrobenzoic compound of yellow colour. As nitrogen in NO_3^- has no electrophilic capacity, it must be activated to nitronium which is a strong electrophile.

The procedure involves heating of the sample until dry because water must be removed for NO_3^- to be converted to NO_2^+ The absorbance of the solutions was measured at 410 nm using a UV visible spectrophotometer (Hach DR/3000). The amount of nitrate adsorbed was calculated from the difference between the initial and the equilibrium solution concentrations. In order to critically evaluate the effect of SMZ, nitrate loading was also done on unmodified zeolite.

2.1.2 Effect of adsorbent mass

The effect of adsorbent mass on adsorption of nitrates onto functionalized zeolite was observed by using 50mL of nitrate solution of 50mg/L. No pH adjustment was made. The solutions were shaken in plastic containers containing 0.1g, 0.2g, 0.5g, 1g and 1.5g of the adsorbent.

2.1.3 Effect of temperature

To help understand the thermodynamic aspect and mechanism of adsorption of nitrates onto surfactant modified zeolite, the effect of temperature at 20 ºC, 45 ºC and 60 ºC was studied. 50 mL of nitrate solution was contacted with 0.5 g of the adsorbent and maintained at appropriate temperature for 24 hours. The resultant solution was filtered and analysed for residual nitrate. The pH of the solutions was not adjusted and all the experiments were done at their natural pH.

2.2 Column Experiments

Packed bed studies were conducted in a 30 cm long glass column of 20 mm internal diameter. Feed solutions were introduced at a constant volumetric flow rate, using peristaltic pump in up-flow mode in order to ensure complete wetting of the particles. The flow rate was checked periodically by noting the time taken to collect a given amount of effluent.

The capacity at the breakthrough point (QB) is defined as the amount of nitrates bound by the SMZ when the concentration of nitrates in the effluent reaches approximately 5% of the initial concentration [6]. Meanwhile, in this study the breakthrough point was considered to be the point when the maximum allowable concentration of 50 mg/L in drinking water [17] was reached. The effects of four operational parameters namely adsorbent mass, volumetric flow rate, initial nitrate concentration and the column aspect ratio on the adsorption of nitrates in a fixed bed column were studied.

2.2.1 Effect of adsorbent mass

Nitrate contaminated water (110 mg/L) was pumped through three columns of different mass of 30, 60 and 90g under a volumetric flow rate of 5 mL/minute.

2.2.2 Effect of volumetric flow rate

Three packed column of surfactant functionalized zeolite were used for this run of experiments. Field water of 160mg/L nitrate with initial pH of 6.93 was pumped through the columns under volumetric flow rate of 2.5, 5 and 10 mL/minute respectively. Adsorbent mass was 30 g in each case.

2.2.3 Effect of initial nitrate concentration

Four nitrate contaminated solutions of 110, 400 and 600mg/L were pumped through columns under a volumetric flow rate of 5 mL/minute. Adsorbent mass was 30 g in each case.

2.2.4 Influence of column aspect ratio

Three columns of three different diameters of 15, 20 and 30mm were used in this study. Adsorbent mass and initial nitrate concentration were kept constant at 40 g and 190mg/L respectively.

3. Results and Discussions

3.1. Nitrate Loading on Zeolite.

The sorption of Nitrates on unmodified zeolite and surfactant modified zeolites with different loadings of HDTMABr is shown in Fig. 1 and it can be seen that surface modification has greatly increased anion sorption on zeolite. The results clearly show that unmodified zeolite has very little adsorption capacity for nitrates. This observation concurred well with previous researchers like Mažeikienė *et al.* [1]. Yusof and Malek [7] also concluded that natural zeolite had little or no affinity to anion species of Cr (VI) and As (V).

Further increase in surfactant loading results in decrease in removal of nitrates. Therefore treatment with initial concentration of 3 g/L of surfactant appears to be the optimum loading for nitrate removal. This initial surfactant concentration exceeds its critical micelle concentration, thus these micelles attach to the external surface of the zeolite and rearrange to form a bilayer that tends to impart anionic characteristics [12]. Surfactant modification of clinoptilolite changes its surface charge from a net negative to a positive charge. Thus, electrostatic forces exist between the positively charged zeolite and the nitrates in solution.

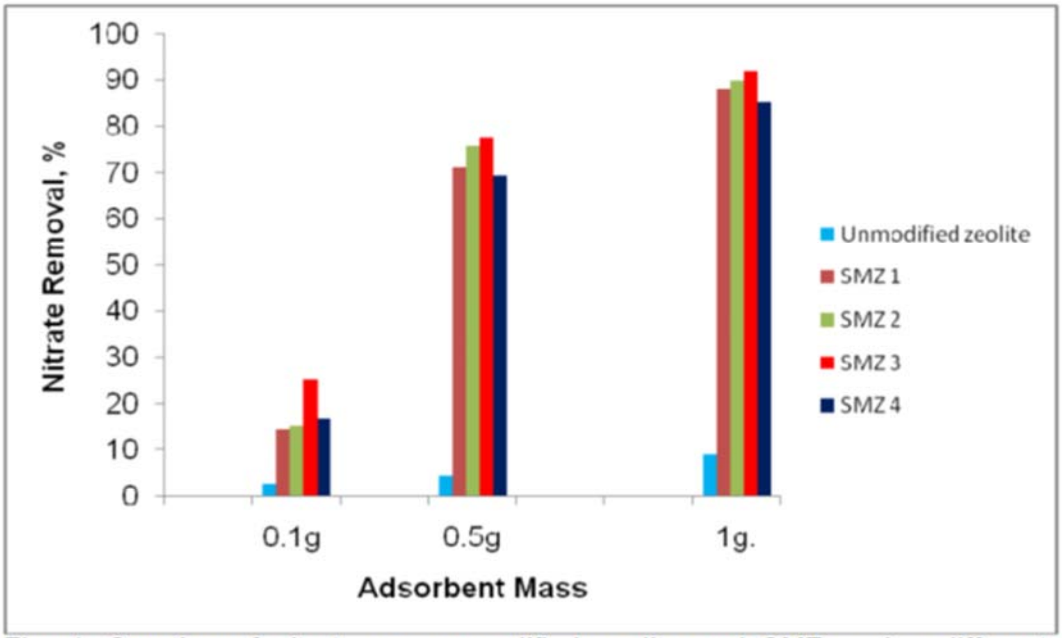


Fig. 1: Sorption of nitrates on unmodified zeolite and SMZs using different surfactant (HDTMABr) loading.

3.2 Batch Equilibria Experiments

3.2.1 Effect of adsorbent dose

The adsorbent dosage is another factor which influences the sorption equilibrium. The effect of variation of adsorbent dose on percentage removal of nitrate from water with SMZ is graphically shown in Figure 2. It is clear from the graph that the removal of nitrate increased with increase in adsorbent mass. This is to be expected because for a fixed initial solute concentration, increase in total dose present a greater surface area and increase adsorption potential [19]**.** However, it is observed that as the adsorbent mass increases, there was no change in percentage removal possibly due to overlapping of active sites at higher dosage.

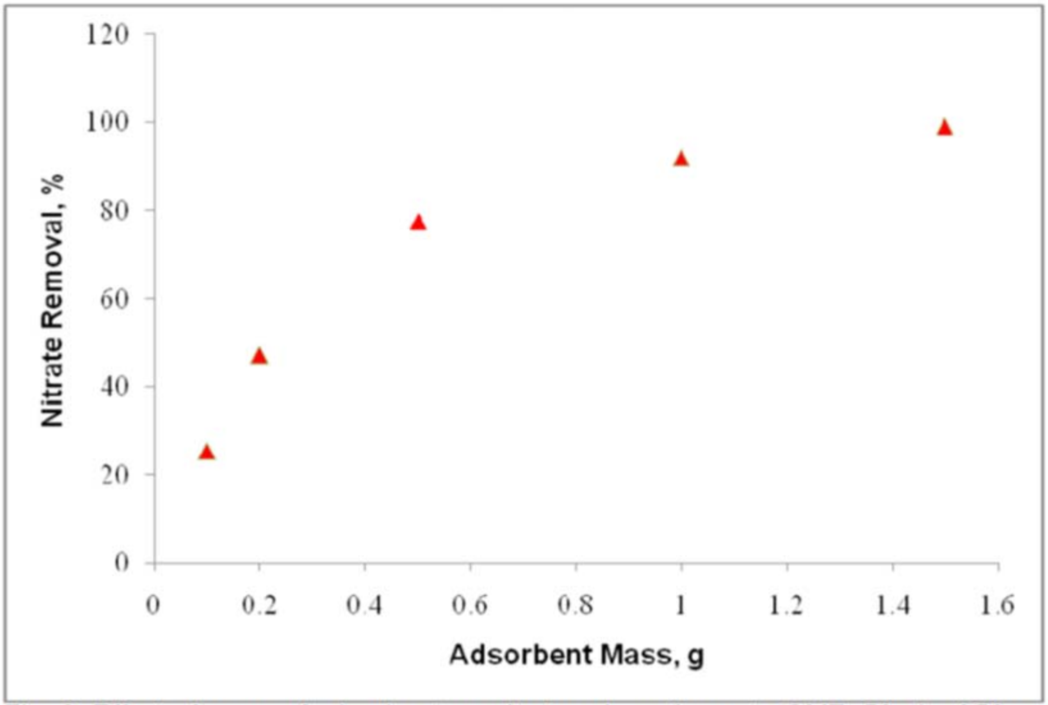


Fig. 2: Effect of mass of adsorbent on nitrate adsorption onto SMZ. 50mL of 50mg/L Nitrate solution was contacted with different adsorbent masses for 24hrs. Dose = 0.1g to 1.5g.

3.2.2 Effect of temperature

Temperature is known to have profound effect on various chemical processes. So, it was thought worthwhile to study the effect of temperature on the adsorption of nitrate onto modified zeolite. Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate [4]. Batch adsorption studies were carried out using adsorbent dose 0.5g and at varying temperature of 20, 45 and 60 °C. The effect of temperature on the adsorption of nitrate was studied and the results are presented as adsorption capacity versus temperature. From Figure 3, it can be concluded that the effect of temperature on the adsorption of nitrates onto modified zeolite is not pronounced. The maximum adsorption capacities for the zeolite under different temperatures are almost equal thus SMZ is very stable under a wide range of temperature

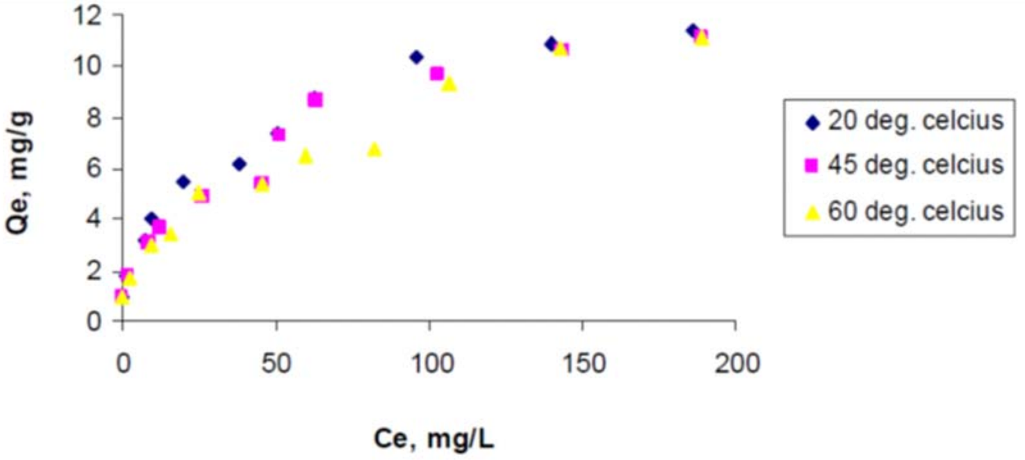


Fig. 3: Effect of Temperature on adsorption of nitrates onto functionalized zeolite. 50mL of 50mg/L nitrate solution was contacted with 0.5g modified zeolite at 20 °C, 45 °C and 60°C.

The thermodynamic parameters; changes in entropy (ΔS^o) and enthalpy (ΔH^o) for the adsorption of nitrates have been determined by using the following equation [14, 15]

$$Log\left(\frac{Q_e m}{C_e}\right)=\frac{\Delta S^o}{2.303R}+\frac{-\Delta H^o}{2.303RT}$$

Where m is the adsorbent dose (g/L), *Qe* is the amount of nitrate adsorbed per unit mass of adsorbent (mg/g), Ce is the equilibrium concentration (mg/L), T is the temperature in K and R is the gas constant (J/ g.K). Both the enthalpy (ΔH^o), and the entropy of adsorption (ΔS^o) are obtained from the plot of log (mQe/Ce) verses 1/T and the values for the three temperatures are as shown Table 1. The values of the Gibbs free energy were calculated, knowing the enthalpy of reaction and the entropy change, using the widely used equation:

$$\Delta G = \Delta H_{ads} - T\Delta S_{ads}$$

From the temperature range of 293 to 333 K, the negative value of the enthalpy showed that the adsorption of nitrate onto modified zeolite was exothermic in nature. Thus, adsorption of nitrate onto surfactant modified zeolite is more enhanced at lower temperatures [18]. The negative value of the Gibb's free energy change indicated that the adsorption process was spontaneous in nature [9].

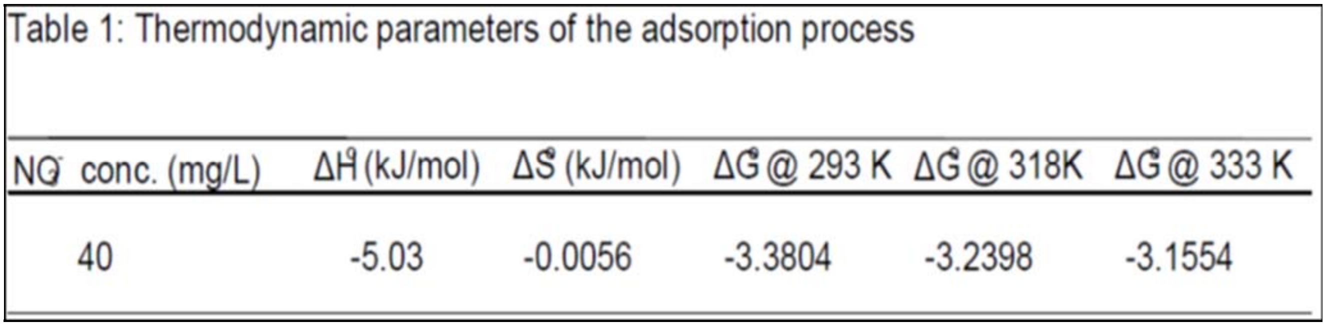


Table 1: Thermodynamic parameters of the adsorption process

NO_3^- conc. (mg/L)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol)	ΔG^o @ 293 K	ΔG^o @ 318K	ΔG^o @ 333 K
40	-5.03	-0.0056	-3.3804	-3.2398	-3.1554

3.3 Column Study and Breakthrough Analysis

The effects of different parameters which are relevant for designing a pilot plant for the adsorption of nitrates onto modified zeolite were studied. These include the effect of adsorbent mass, effect of initial nitrate concentration, effect of flow rate and the effect of column diameter among other parameters. Effect of pH was not considered under column experiments because batch experiments showed that pH has negligible effect on nitrate adsorption onto zeolite (results not shown).

3.3.1 Effect of adsorbent mass

The effect of the adsorbent mass on the effluent nitrate concentrations is presented for the flow rate of 5ml/min and inlet nitrate concentration of 110mg/L in Figure 4. An increase in mass of the adsorbent means more adsorption sites that will prolong the breakthrough time interval for a bulk solution [19]. It is clear from Figure 4 that as adsorbent mass increases from 30 g to 90 g, the breakthrough time increases from around 7.5 to 18 hours. The adsorbent becomes saturated faster for a smaller mass than for a bigger one. While the adsorbent used in this study is readily available in South Africa, regeneration of used adsorbent may be necessary to increase economical viability of the adsorption technology.

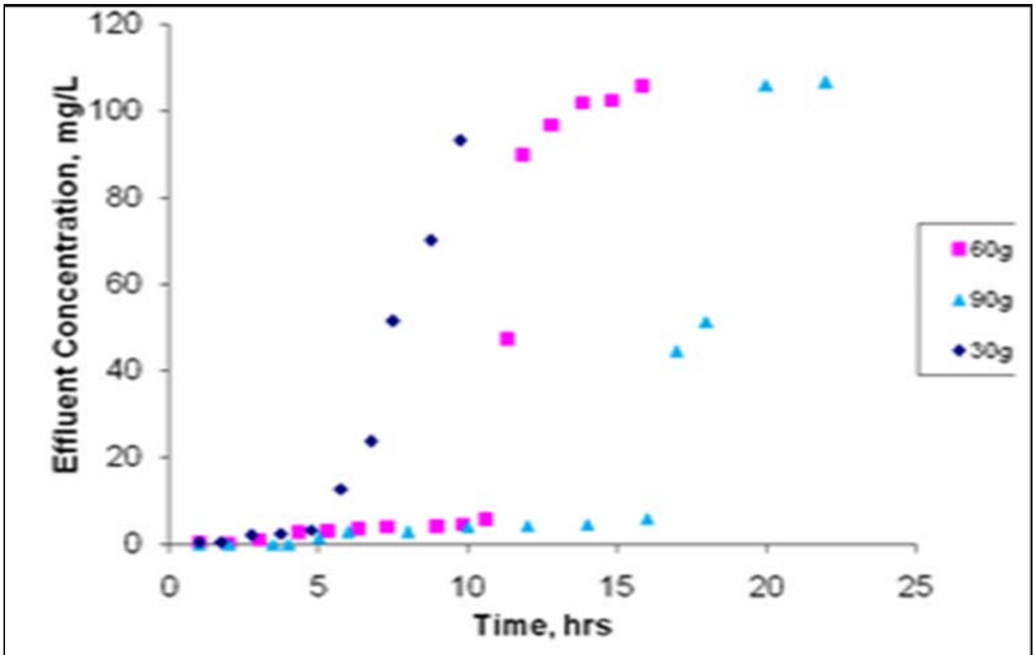


Fig. 4: Effect of adsorbent mass on breakthrough Curve.

3.3.2 Effect of initial concentration

Figure 5 shows the influence of inlet nitrate concentration on the breakthrough curve. Flow rate and adsorbent mass were kept constant at 5 mL/min and 30 g respectively in each case. An increase in initial nitrate concentration results in a significant decrease in breakthrough time. At low initial concentration, breakthrough occurred late and the treated volume was higher since the lower concentration gradient caused a slower transport due to decreased diffusion coefficient or mass transfer coefficient [16]. It is very clear from Figure 5 that inlet concentration has a major impact upon adsorption of nitrates onto surfactant modified zeolite. When concentration is high the adsorbent gets exhausted very fast thereby reducing nitrate removal efficiency of the adsorbent.

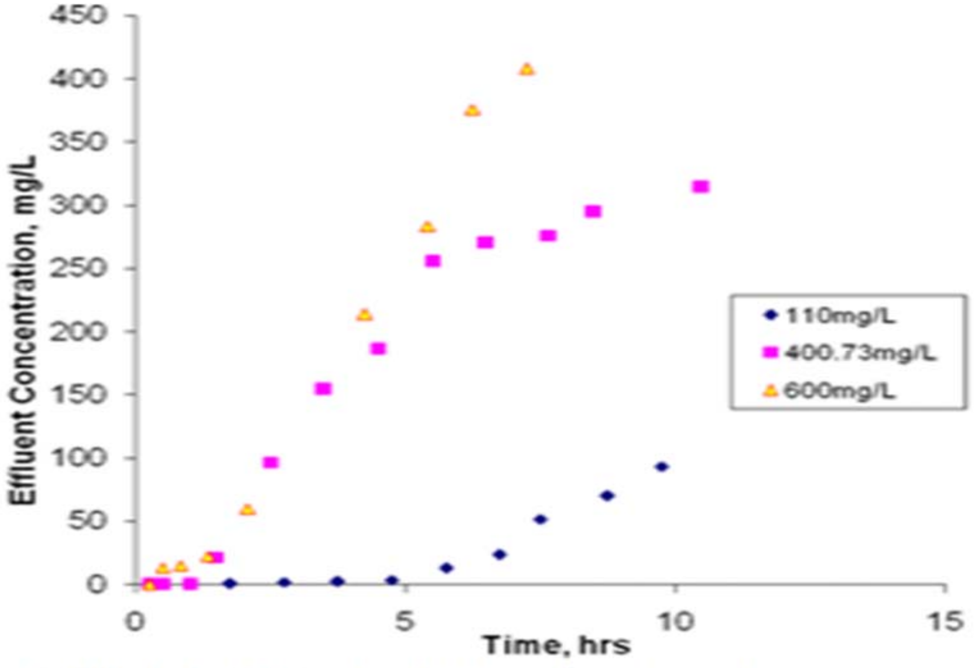


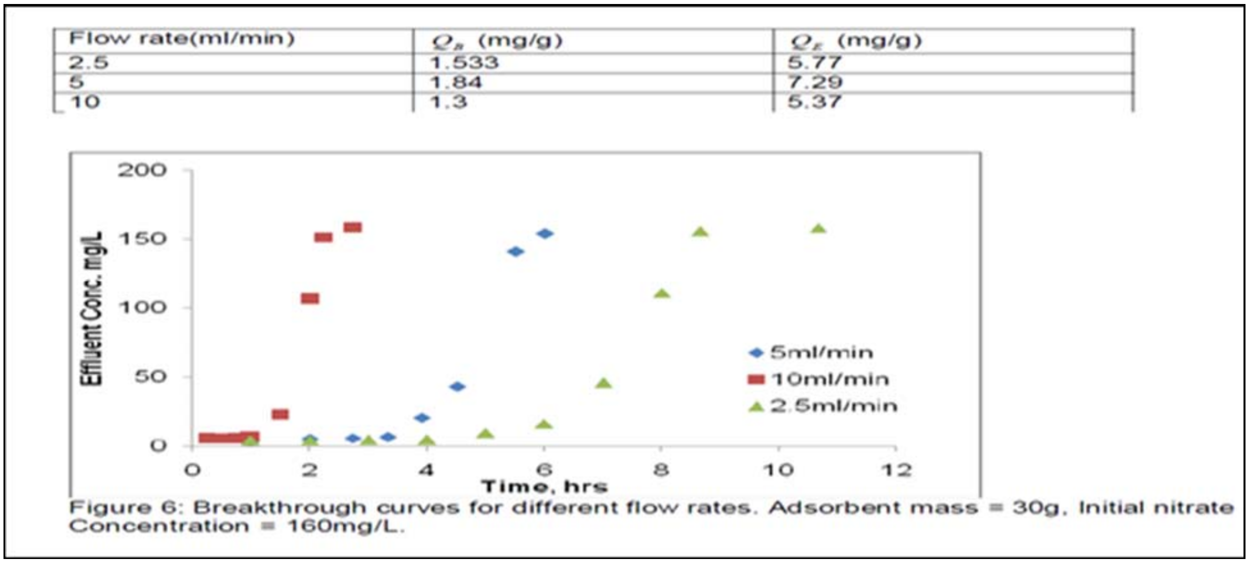
Fig. 5: Effect of initial Concentration on Breakthrough curve

3.3.3 Effect of flow rate

Figure 6 shows the effect of flow rate on the adsorption of nitrates onto surfactant modified zeolite. The results show that flow rate has a major effect on the breakthrough behaviour. It is clear from Figure 6 that high flow rate results in a drastic decrease in breakthrough time. This is because of residence time of the solute in the column, which is not long enough for adsorption equilibrium to be reached at a high flow rate. While, lower flow rates result in high residence times in the column. According to Burn *et al*., (quoted by 16) zeolites have a relatively slow loading kinetics hence the need for long residence times. This leads to earlier saturation of active sites.

From Figure 6 it can be deduced that an increase of the flow rate of an influent concentration from 2.5 to 10 mL/min decreases the breakthrough time from around 7 to 2 hours. Onyango *et al* [10] also indicated that the residence times of fluid inside the bed decreases with increase in flow rate thereby depriving the solute of adequate time to penetrate and diffuse to the internal matrix of the sorbent. Table 2 shows the parameters calculated from the column experimental data. From Table 2 it is observed that the flow rate of 5 mL/min gave the maximum adsorption capacity. Thus the flow rate of 5 mL/min was considered the optimal operating condition for this system and all the other data were obtained at this flow rate.

Table 2: Parameters calculated from the column experimental data.



Flow rate(ml/min)	Q_s (mg/g)	Q_E (mg/g)
2.5	1.533	5.77
5	1.84	7.29
10	1.3	5.37

Figure 6: Breakthrough curves for different flow rates. Adsorbent mass = 30g, Initial nitrate Concentration = 160mg/L.

3.3.4 Effect of column diameter

The effect of column diameter on the effluent concentration is shown in Figure 7. Three columns of diameters 15, 20 and 30 mm were used in this study while the adsorbent mass and initial nitrate concentration were kept constant at 40 g and 190 mg/L respectively. Figure 7 shows that column diameter has negligible effect on the adsorption of nitrates on modified zeolite in a fixed bed column.

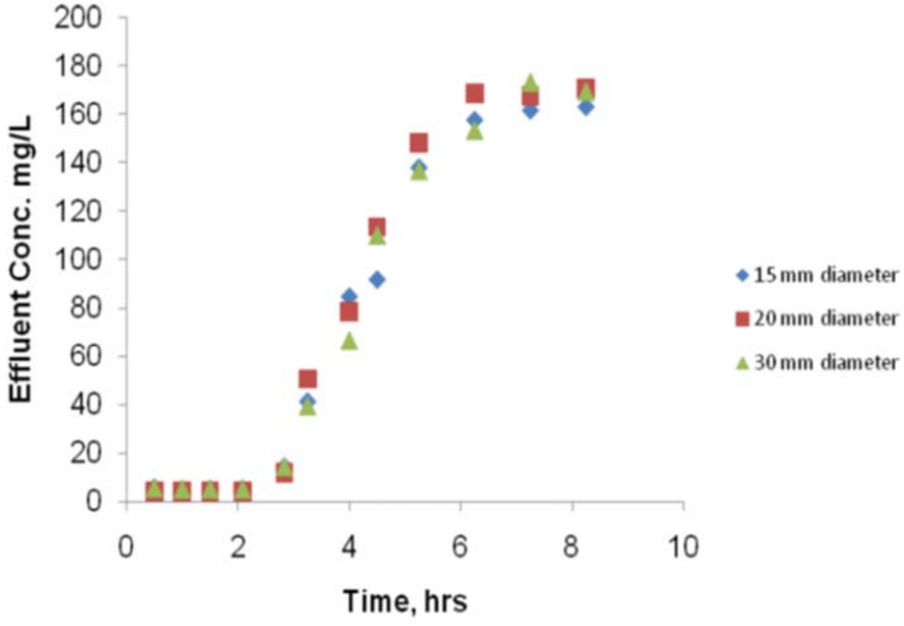


Figure 7: Effect of column diameter on nitrate adsorption.

4. Conclusions

Nitrate removal from ground water through adsorption by surfactant modified zeolite was done in both batch and column experiements. The results showed that surfactant modification of zeolite using Hexadecyltrimethyl ammonium bromide resulted in a significant increase in the adsorption capacity of the adsorbent. Experimental data showed that adsorption of nitrate onto SMZ is exothermic in nature as shown by a negative enthalpy change. In the column study, a high breakthrough point, which indicate good performance of the adsorption media, was observed on the zeolite column at higher adsorbent mass and at a flow rate of 5ml/minute. Considering the experimental results gathered to date and the low cost of clinoptilolite, SMZ is a promising technology for nitrate removal from water.

Recommendations

Based on the results of the present exploration, the following recommendations may be
made for future work:

- Extensive characterization of the adsorbent may be necessary to understand the nanoporous nature of the zeolite.
- There may be a need to regenerate used adsorbent to know if it can be reused.

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His research topic includes & interested in Chemical Engineering, Environmental Engineering, Wastewater Treatment by Adsorption, Advanced Separation Process, Chemical Engineering Design, Mass Transfer, Chemical Process Synthesis, Chemical Engineering Thermodynamics etc.