

Adsorption of Nitrate from Ground Water using Indian Bentonite: Fixed Bed Column Study

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Abstract— With the ultimate objective of developing an inorganic, naturally occurring, low-cost, alternative, sustainable and eco-friendly sorptive media for nitrate removal from drinking water, in the present work treated bentonite has been studied as adsorbent medium. The characterization of the adsorbent was done using FTIR, SEM+EDS, BET and XRF. It was observed that Acid Activated bentonite clay shows the potential of an effective adsorbent for the nitrate from aqueous solution. During column operations it was observed that time of breakthrough increases with the increase in bed height or EBCT. Also it was observed that the breakthrough time of the filter depends on the type of sand used for preparation of the sorption bed in column operation.

Keywords— Nitrate Removal, Column, Fixed bed column, Bentonite clay, Drinking water, Acid activation

I. INTRODUCTION

Water is one of the most significant and basic natural resource available. It is not only one of the most essential commodities of our day-to-day life, but it also plays a crucial role in economic and social development processes [1]. About 70.9% of surface of Earth is covered with water and is important for all known life forms. On Earth, 96.5% of the planet's water is found in oceans, 0.9% is available in other saline sources and only 2.5% of the water available is fresh water. Out of this available fresh water 30.1% is available as ground water, 1.2% as surface or other freshwater and the rest 68.7% is as glaciers and ice caps.

Ground water serves as the source of drinking water for a large population in India. More than 95% of the rural population and about 30 to 40% of urban population in India depend on ground water for their domestic requirements. However, ground water is getting contaminated due to various reasons including inorganic or organic chemicals, radionuclide, and microorganisms rendering it unfit for use. The contaminants that are commonly observed in water are arsenic, fluoride and iron, which are geogenic, whereas contaminants such as nitrates, phosphates, heavy metals etc. have their origin due to various human activities including domestic sewerage, agricultural practices and industrial effluents. The urbanization, modern civilization, industrial development, and increase in population have led to fast degradation of quality of ground water [2].

Presence of trace levels of toxic inorganic anions doesn't usually cause any organoleptic changes in water; it is therefore possible that some of them may remain undetected. Thus, increasing the possible risks they pose on human and animal health. A number of inorganic anions have been found

in potentially harmful concentrations in numerous drinking water sources. Inorganic anions are of greater importance as even at very low concentrations these are toxic and harmful to both humans and animals, such as on parts per billion (ppb) levels.

Due to very high solubility, nitrate is possibly the most widespread groundwater contaminant in the world [3]. Nitrate is highly susceptible to leaching as it does not readily bind to the soil. Point and non-point sources of NO_3^- contamination include the intensive use of fertilizers in agricultural, urban runoff, disposal of untreated sanitary and industrial wastes in unsafe manner, leakage from septic systems, landfill leachate, animal manure, NO_x stripping waste from air pollution control devices.

In humans, increasing NO_3^- concentrations in drinking water causes two adverse health effects: induction of "blue-baby syndrome" (methemoglobinemia), especially in infants, and the potential formation of nitrosamines which are regarded carcinogenic in nature. Studies have shown that excess NO_3^- in drinking water may also be responsible for causing diverse kinds of cancers in humans [4].

In India A total of 381 districts in 22 states are affected by nitrate contamination (>45 mg/L) in ground water [5]. Maximum permissible limit of nitrate is 102 mg/L in Netherland [6], and a minimum is of 20 in South Africa [7]. In India the permissible limit for nitrate is 45 mg/L in drinking water [8].

Nitrate is very stable form of nitrogen present in water and is highly soluble, with little or very low potential for co-precipitation or adsorption. These properties of nitrate make it very difficult to remove using conventional water treatment technologies like lime softening and filtration [9]. There are many other sophisticated technologies that have been developed for denitrification or removal of nitrates from drinking water, such as chemical denitrification [3][10], ion exchange [11][10], reverse osmosis [12], electro dialysis [13], adsorption[3] and biological denitrification [14][15].

Of all the processes known, adsorption is generally considered to be the most attractive due to its convenience, ease of operation, simplicity of design, and economic considerations if low-cost adsorbents that can be easy regenerated are used [3][16]. Several adsorbents are used for nitrate removal such as carbon based adsorbents, various types of clays, various inorganic materials.

Of all the adsorbents that are generally used inorganic adsorbents are gaining importance in the recent years, many researchers [17] [18] have shown inorganic materials to be better than their organic counterpart.

Clays are hydrous aluminosilicates and are defined as those minerals that make up the colloid fraction ($<2\mu\text{m}$) of soils, sediments, rocks and water [19] and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. In the environment Clay plays an important role by acting as a natural scavenger of pollutants by taking up cations and anions either through sorption or ion exchange or both [20]. Of all the inorganic adsorbent researched, many of the researchers have studied naturally occurring adsorbents like clay, because of its low cost, sustainable and eco-friendly nature and local occurrence. Also clay acts as a natural scavenger for pollutants in the natural system. Therefore, in the present work the suitability of bentonite clay has been studied for its effectiveness in nitrate removal from aqueous solution in column operation.

II. MATERIALS AND METHODS

Literature has witnessed that bentonite activated using 2N HCL showed better results than that activated using 2N H_2SO_4 [21]. Also, it was shown that activation of bentonite clay with HCl using acid concentrations 0.5 to 4 M was found to increase specific surface area [22]. It was reported that maximum surface area and optimum porosity was achieved when 2M HCl was used for activation, which decreased when the acid concentration was further increased. Cation exchange at lower concentration is ascribed to the increase in surface area of the clay (i.e. replacement of exchangeable cation by H^+ ion) and removal of impurities (eg. Calcite). However, the decrease in surface area of clay when the concentration of the acid was further increased beyond 2M HCl is due to structural reformation and decomposition of samples.

For bentonite activation 10 g of sample was taken in 50 mL of 2M HCL and was kept in a water bath shaker for 3 hours at 80 °C. The sample was then filtered using whatmann filter paper and washed several times with DM until the pH is neutralized (i.e. comes around 6) and the chloride content of the filtered solution is nil (i.e. free chloride is completely removed from the treated bentonite). Finally, sample was dried at 105 °C in oven until it attains constant mass. The sample was then grounded to pass 150 μm sieve and stored in air tight container for further use.

Nitrate stock solution of concentration 1000mg/l was prepared by dissolving 1.63 g of potassium nitrate in 1000 ml of distilled water. After that subsequent dilution was used for preparation of nitrate solutions of various con concentration. From this standard solution nitrate, solution of 91 mg $\text{NO}_3\text{-L}$ by dilution of the standard was prepared, for column experiment.

Sand was mixed with the adsorbent to increase the permeability of the adsorbent material so that it can be used in as a fixed bed adsorption media for column operation. There were two types of sand which was used (S-1) and (S-2), and their effect on the adsorption was also studied. For test column 1, 2, 3, and 4 sand of type S-1 was used, the grain size distribution is shown in Fig.1 . For test column 5 sand of type (S-2) was used the grain size distribution of the is shown Fig.2

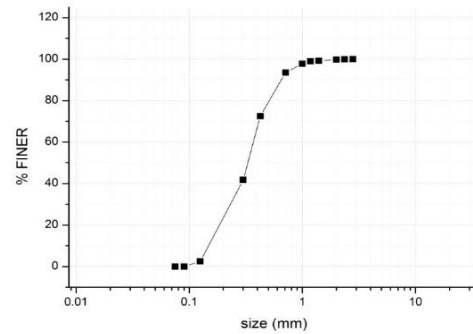


Fig.1 Grain Size distribution of sand S-1

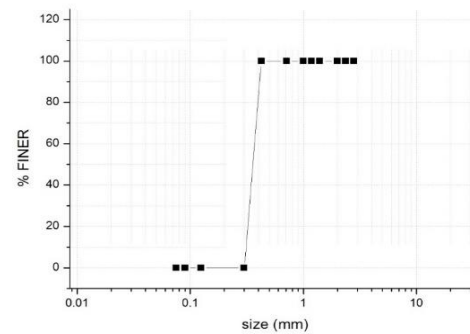


Fig.2 Grain Size distribution of sand S-2

III. EXPERIMENTAL SETUP

Five parallel columns were run with the ratio of bentonite to sand equals 1:10. the glass column used for column 1, 2, 3, and 5 was 60 cm long with internal diameter of 3.2 cm. the column with height of 100 cm and with internal diameter of 3.5 cm was used for column 4. The columns 1, 2, 3 and 4 had height of the bed 11.5 cm, 22.5 cm, 34 cm, and 65 cm respectively. The column 5 had a fixed bed of height of 33 cm.

The column was prepared by providing a 4-5 cm sand bed below the adsorbent bed in the column so as to prevent the leakage of adsorbent from the fixed adsorbent bed during column operation. Glass beads were placed above the adsorbent bed to obtain uniform flow. The experimental setup is shown in Fig.3.

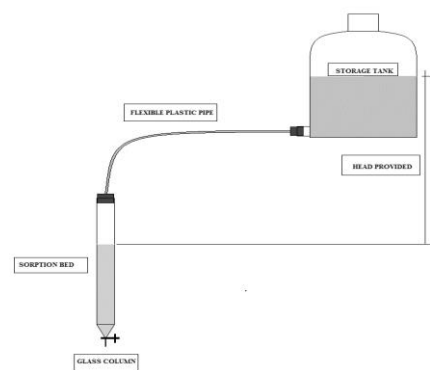


Fig.3 Experimental setup.

IV. RESULTS AND DISCUSSION

A. FTIR characterization

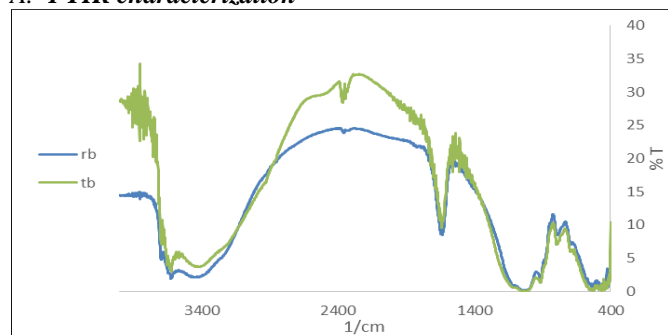


Fig.4 FTIR analysis of Raw bentonite (rb) and acid activated bentonite (tb).

It was observed that the intensities of stretching bands observed at 3623, 3432, 1641, 920 cm^{-1} which is associated with O-H along with Al-OH vibrations decreased after activation, also stretching vibration at 3630 cm^{-1} which represents Al-Al-OH coupled by Al-Mg-OH vibrations decreased, this may be attributed to partial depletion of Al, Mg, Fe from clay. The bands 3425, 3200 cm^{-1} decreases, which represents absorption by interlayer water, also the bands at 3435, 1635 cm^{-1} decreases, which are designated for stretching of -OH groups of the water molecules adsorbed on the clay surface due to acid attack, this may be due to removal of octahedral cations resulting in loss of water and -OH group, associated with them. It is also seen that Absorbance band in the range 1000-1100 cm^{-1} represents Si-O vibration, also absorbance at 1035 cm^{-1} represents Si-O plane stretching. Absorbance band at 1066, 1116, 1043, 999 cm^{-1} are corresponding to Si-O-Si (2 bands in plane) and Si-O (out of plane) bending vibrations, remains the same after acid attack. The band at 792 cm^{-1} which represents cristobalite not only sustains the acid attack, but its intensity is increased. Transformation of tetrahedral sheets was found at 792 cm^{-1} this may be due to the formation of amorphous silica which is indicated by increase in the peak intensity after activation, which may expose more sites for adsorption. Results obtained are similar as that obtained by literature[23].

B. SEM Analysis

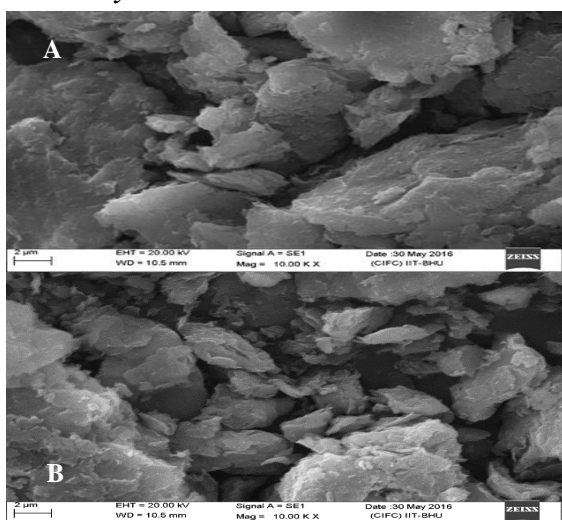


Fig.5 SEM Analysis, (A) Raw Bentonite; (B) Bentonite after activation (@10K magnification)

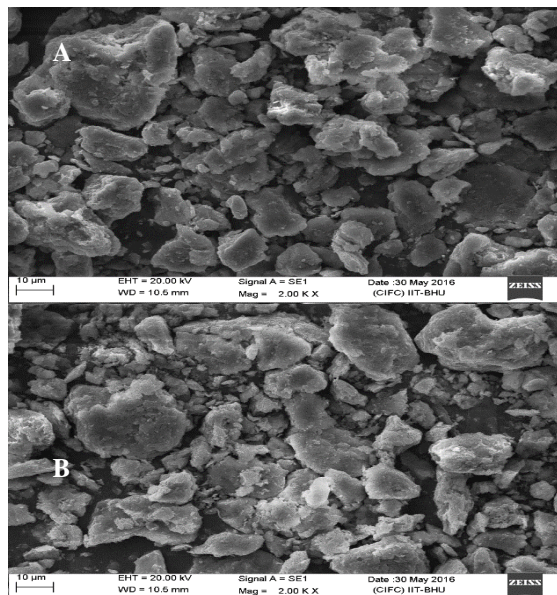


Fig.6 SEM images of raw, (A) Raw Bentonite; (B) Bentonite after activation (@2K magnification)

It can be easily seen in the above image of Bentonite before and after activation that the particle size of the bentonite after activation is reduced after activation of raw bentonite. Also change in surface morphology can be observed, after acid treatment the surface of the bentonite at 10K magnification looks eroded; small pits and undulations can be seen easily.

C. BET analysis

It was seen that the specific surface area of bentonite clay was increased to 126.97 m^2/g from 73.06 m^2/g after acid activation. The increase in the specific surface area is the result of reduction in size of the adsorbent after acid activation and formation of pits of cavities by corrosion of surface due to the action of the acid as seen in the SEM images.

Table1 Specific surface area of bentonite before and after activation.

Absorbent	Specific surface area (m^2/g)
Raw bentonite	73.06
Acid activated bentonite	126.97

There is direct correlation between adsorption and surface area, the adsorption capacity of bentonites could be improved by activation process, by increasing the surface area, porosity or pore volume. In acid activation not only leaches out cations from octahedral and tetrahedral sheets but also soluble impurities like calcite, or other cations are exchanged with hydrogen ions [24]. Exchangeable cations (e.g. Na^+ , K^+ , Ca^{2+}) are replaced by H^+ and partial dissolution of octahedral cations (e.g. Al^{3+} or Mg^{2+}) occurs thereby some vacancies are created [25][26]. There by increasing the specific surface area of the adsorbent and also increasing the adsorption capacity as these vacant sites act an active site for adsorption.

D. Energy Dispersive X-Ray Spectroscopy (EDS)

The approximate elemental analysis of the Bentonite was analysed before and after acid activation, also the composition was analysed of the spent adsorbent, i.e. activated Bentonite after column adsorption experiment. The point of incidence of the spectrum and the resultant EDS spectrum for each tests is attached in the appendix and the elements found are shown in Table2.

Table2 EDS results of raw, acid activated, spent acid activated bentonite.

Element	Raw Bentonite		Acid Activated Bentonite		Spent acid activated Bentonite	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
N K	2.80	3.94	-	-	19.35	24.62
O K	56.08	68.96	54.67	69.70	52.20	58.14
Na K	2.12	1.82	0.33	0.29	0.22	0.17
Mg K	1.42	1.15	0.91	0.76	0.95	0.69
Si K	20.45	14.32	24.74	17.97	15.87	10.07
K K	0.34	0.17	0.56	0.29	0.26	0.12
Ca K	0.29	0.14	0.30	0.15	0.79	0.35
Cl K	0.27	0.15	0.29	0.16	-	-

From Table2 , it can be seen that in the raw bentonite small amount of nitrogen is present which is removed during the process of activation. The reappearance of nitrogen in the spent sample conforms that nitrate adsorption has taken place, as nitrate in the aqueous solution is the only source from where the nitrogen can come into the spent adsorbent sample. It is also seen that the amount of sodium (Na) has reduced in the adsorbent sample after activation which is responsible for swelling of the bentonite on contact with water, thus making the adsorbent suitable for column operation. The absence of Cl in the spent sample indicates that Cl might be exchanged with nitrate from the aqueous solution.

E. Nitrate Column Experiments

The rate of flow of the column was maintained in the range of 0.9-1.3 mL/min. The maximum breakthrough time observed was 120 min. in column 4, with bed height of 65 cm. And exhaustion occurred at about 200 min. of filter operation. It was also observed that the efficiency of the filter greatly depends also on the type of the sand mixed with the acid activated bentonite used for the preparation of the fixed bed adsorption bed of the filter. As for the same height of the bed the test column 3 and test column 5 have different breakthrough time and exhaustion time.

From the column operation it was seen that the pH of the effluent remained in the range of 6.5 to 7.5, thereby eliminating the possibility of OH⁻ (hydroxyl ion) taking part in the removal process.

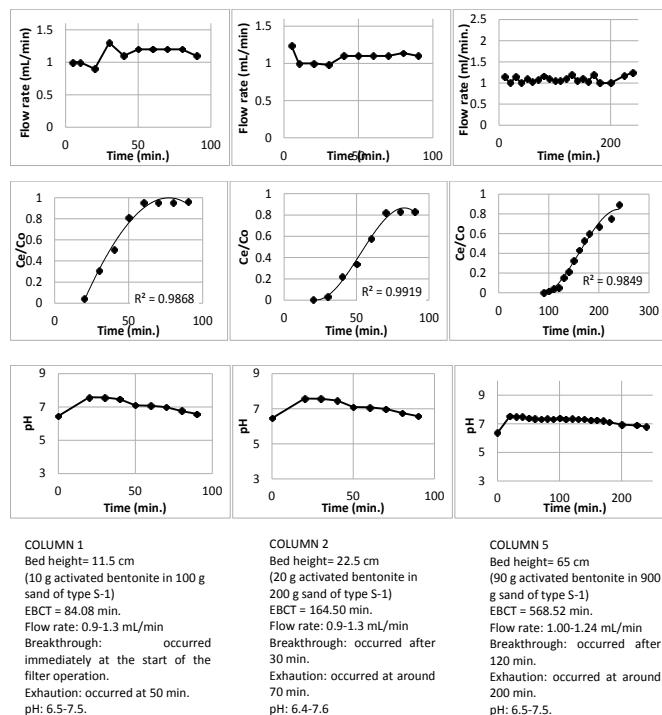


Fig.7 Effect of bed height/EBCT on nitrate removal.

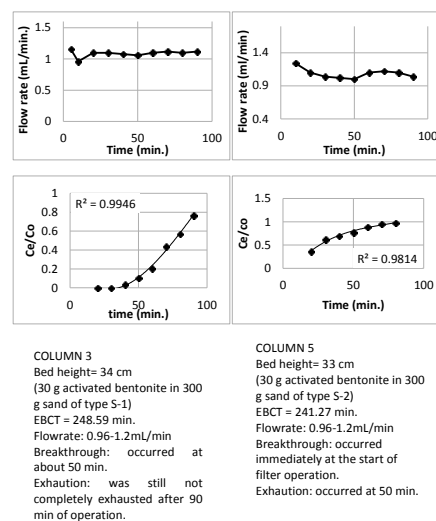


Fig.8 Effect of type of sand used for mixing with the adsorbent on nitrate removal.

V. CONCLUSIONS

Based on the experimental works, instrumental and computational analyses done during present study, following conclusions can be drawn: Acid activated bentonite clay shows potentials of an effective adsorbent for nitrate from aqueous solutions. During column operations it was observed that time of breakthrough increases with the increase in bed height or EBCT. The breakthrough time observed was immediate, 30 min, 50 min, 120 min for EBCT of 84.08, 164.50, 248.59, 568.52 min. (= cm³.min/mL) respectively, during column operations. Sand of lower effective size provides a better dispersing medium for activated bentonite, as it increases the contact time and thereby increasing nitrate

removal. It was observed that the pH of the treated water remained in the range of 6.5-7.5 during nitrate removal, indicating no hydroxyl ion exchange taking place from the adsorbent. EDS analysis shows reduction in the chloride content in the spent bentonite, thus there may be possibility of ion exchange taking place during the removal of nitrate. Similar observations were made in literature [21] with calcium bentonite for nitrate removal. SEM images show some reduction in the particle size and surface pitting of the activated bentonite by acid action. BET analyses show that activation of bentonite with 2N HCl results in increase in the surface area from 73.06 m²/g to 126.97 m²/g. FTIR analysis shows that there is a partial depletion of octahedral cations (Al³⁺, Fe³⁺, Mg³⁺) from the structure of the bentonite during acid activation. It also shows that the basic structure of the clay remains the same.

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