

Sustainable bio-adsorbent for treatment of Nitrate, Fluoride and TDS in groundwater

ABSTRACT

The quality of groundwater and surface water bodies have been analyzed globally and showed that 23% of primary drinking water sources have more than permissible limits of pollutants' concentration. A major part of the world suffers from high concentrations of Nitrate, Fluoride and total dissolved solids (TDS) in drinking water. Therefore, the present work focuses on the treatment of these three parameters. There are many processes available to remove and reduce the higher concentration of the aforesaid pollutants in water with advantages and disadvantages. One of the main disadvantages of these processes is the sustainability and availability of treating materials. In this regard, the work explores different agricultural materials (nine to be exact) for reduction of Fluoride, Nitrate and TDS in water. It is found that most of the materials have the potential to reduce either of one contaminant. However, only potato gel has shown potential in reduction of all three contaminants', i.e. Fluoride, Nitrate and TDS, concentration. The Isotherm plots indicate that Nitrate and TDS biosorption mechanism follows the Langmuir Isotherm while Fluoride biosorption follows the Freundlich Isotherm. Optimization is carried out, using batch and continuous study, in terms of time and mass of adsorbent against the concentration of the contaminant. Adsorption column tests indicate the reduction of 89%, 92% and 86% in the concentration of Fluoride, Nitrate and TDS respectively by potato gel.

Keywords: Nitrate; Fluoride and TDS; Bio-adsorbent; Potato gel; Langmuir Isotherm; Freundlich Isotherm; Optimization.

1. INTRODUCTION

The study focuses on worldwide contaminants vis. Nitrate, Fluoride and TDS. They are hazardous to health if present in high concentration. The quality of groundwater and surface water have been analyzed globally by many international agencies (Montgomery, 1985) and showed that 23% of primary drinking water sources violate permissible standard in terms of concentrations of pollutants. Elevated Nitrate, Fluoride and TDS concentrations in drinking water sources present a potential risk to public health and found to be present in drinking water supplies in the European Economic Community, United States, Canada, Africa, Middle East, Australia, New Zealand and Asia (Croll and Hayes, 1988; Fried, 1991; Nixon, 1992). A survey conducted by the U.S. Environmental Protection Agency (Briskin, 1991) indicated that up to 1,130 public and approximately 250,000 private domestic water supply wells may have been exceeding the maximum contaminant level for Nitrate. Similar situations have

been discussed by WHO (WHO, 2005) with higher concentrations of Fluoride and TDS in water globally. The availability of potable water will be one of the major concerns in developing countries in near future and severe shortage of water would lead to a number of individuals being affected due to bad health (Miller, 2003; WHO, 2005). The commonly observed contaminants such as Nitrates and heavy metals etc. are added to our water resources by various human activities including domestic sewerage; agricultural practices and industrial effluents [38].

Excess Nitrite can result in brain damage and death. Other health problems include headache, dizziness, weakness or difficulty in breathing. Prolonged intake of nitrate is linked to gastric problems due to the formations of nitrosamines. N-nitrosamine compounds have been shown to cause cancer in test animals. Blue-Baby syndrome is also associated with high nitrate intake (Fraser et al., 1980). Mirvish, (1995) reflected the pro-carcinogenic nature of nitrate, i.e. it reacts with other chemicals (amines and amides) to form carcinogenic compounds (N-nitroso) compounds. N-nitroso compounds have been associated with 15 different types of cancers, including tumours in the bladder, stomach, brain, esophagus, bone & skin, kidney, liver, lung, oral & nasal cavities, pancreas, peripheral nervous system, thyroid, trachea, acute myelocytic leukemia and T & B cell lymphoma (Mirvish, 1995).

Dental fluorosis is a tooth enamel defect characterised by opaque white areas, caused by excess exposure to fluoride while the teeth are forming in the jaw and before they erupt into the mouth. Dental fluorosis reflects overall fluoride absorption from all sources at a young age, and is a known effect of drinking water containing naturally very high concentrations of fluoride (ATSDR, 2003; Public Health England, 2014). Because fluoride accumulates in bones, the risk of bone defects or fractures has also been extensively analyzed. There are published studies suggesting associations exist (of water fluoridation, 2014).

As per annexure of WHO report, consumption of water with TDS less than 100 *mg/l* disturbs the body's water and salt balance, promoting the release of sodium, potassium, chloride, and calcium ions from the body of animals or humans, imposing a stress on the mechanism of homeostasis, promoting changes in the gastrointestinal muscles and mucosa, and reducing the thirst quenching capacity of the water (Rozelle, 1993; Rozelle 1997; Guyton, 2006). The palatability of drinking water with a TDS level less than 600 *mg/l* is generally considered to be good. Drinking water supplies with TDS levels greater than 1200 *mg/l* are unpalatable to most consumers. An aesthetic objective of upto 500 *mg/l* should ensure palatability and prevent excessive scaling. However, it should be noted that at low levels of TDS contributes to the palatability of drinking water (WHO, 2005).

There are many processes available to remove and reduce the higher concentration of elements present in water. The general classification (Punmia et al., 2012; ENAM, 2009; Luo et al., 2011) is indicated in Table 1 for the water purification and illustrates the disadvantage (Al-Subaie, 2007; Della et al., 2007; Brown and Aaron, 1991) of these processes. The present study aims to evaluate the sustainable bio-adsorbent for treatment of Nitrate, Fluoride and TDS in groundwater.

Table 1. Disadvantages of the water treatment processes

Water treatment process	End products	Disadvantages
Chemical Process	Change in characteristics of water, Odour, deposition of salts, sludge generation	Unfit for direct consumption, costly
Physical Process	Non-selective in removal, improve physical characteristic of water	Need large space, not handy, energy consumption,
Biological Process	Treated pickling liquor free from heavy metals	Disposal problem of metal contaminated exhausted

Water treatment process	End products	Disadvantages
		biosorbents
Others	Deposition of metal and ions	Costly and not easy to operate, backwashing, wastage of water
Membrane separation	Deposition of metal and ions	Expensive , fouling of the membranes

It is a need that in purification process water should not get wasted and should be easy to operate. Choices of technology will depend on appropriateness where factors such as availability of materials, cost, level of contaminant treatment required and technical expertise available to the community. The present work explores the easily available material which can be used for purification purpose at low cost with high sustainability.

2. METHODOLOGY

The methodology followed for removal of Nitrate, Fluoride and Total Dissolved Solids is shown in Figure.

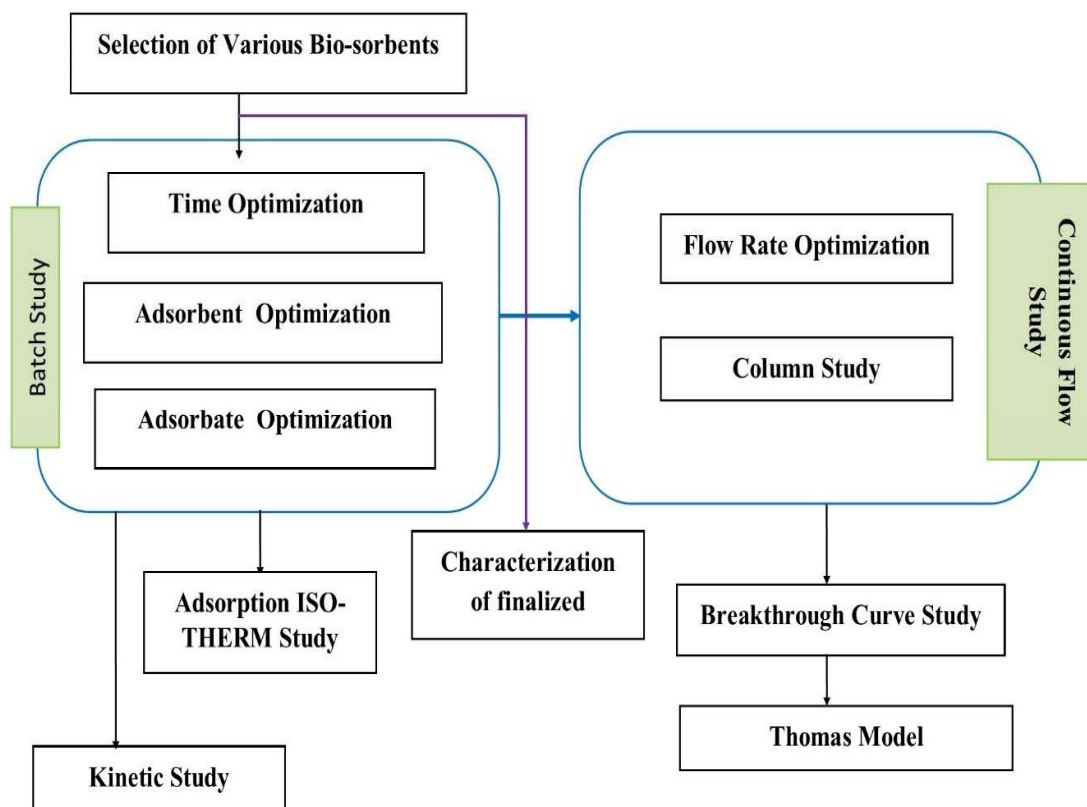


Figure 1. Methodology adopted for reduction of Nitrate, Fluoride and TDS concentration

To bring the concentrations of Nitrate, Fluoride and TDS present in groundwater under permissible limits, namely nine natural materials are used, which are indicated in Table 2.

Table 2. List of materials used in present study

S.No	Material Name	Scientific Name	Material Code	Form of material
1	Wheat Husk	<i>Triticum</i>	WH	Powder
2	Rice Husk	<i>Oryza sativa</i>	RH	Powder
3	Banana peel Husk	<i>Musa</i>	BH	Powder
4	Bagasse	<i>Saccharum officinarum</i>	SH	Powder
5	Coconut Coir	<i>Cocos nucifera</i>	CC	Chopped fiber
6	Amla Seed	<i>Phyllanthus emblica</i>	AS	Powder
7	Aloevara Gel	<i>Aloe Barbadensis Miller</i>	AG	Gel
8	Amla Bark	<i>Phyllanthus emblica</i>	AB	Powder
9	Potato	<i>Solanum tuberosum</i>	PG/PF	Gel/ Flakes

These materials are prepared for the experimentation as indicated below:

- a) Washing the material with distilled water at room temperature for removal of dust and other dirt particles.
- b) Materials are oven dried at Temp. 103 ± 3 °C to remove moisture content (Reeb and Milota, 1999).
- c) Oven dried samples are ground and meshed to the size of 10 μm ; Coconut coir and Aloevara gel are not grinded and used in their normal form.
- d) Potato gel is prepared by suspending potato slurry in distilled water in beakers followed by gentle heating and holding the temperature at 55-60 °C for 24 hour (Hans et al., 2004).

The groundwater used for experimentation is collected from the field. These samples are analyzed in the Environmental Engineering Laboratory of BITS- Pilani, Rajasthan.

Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to bind contaminants on its cellular structure (Velasquez and Dussan, 2009). This process doesn't require energy and amount of contaminants removal by sorbent is dependent on kinetic equilibrium and composition of sorbent's cellular surface. Biosorption is largely influenced by pH, the concentration of biomass, the time of reaction and the interaction between different metallic ions (Ahalya et al., 2003; Velasquez and Dussan, 2009).

Batch and Continuous study

The batch study is carried out to optimize the various parameters namely Time, Weight and Concentration for removal of nitrate, fluoride and total dissolved solids, separately. In the

study, samples are used as influent for a high concentration of nitrate, fluoride and total dissolved solids. The samples are prepared based on the description provided in standard methods, 1995 (APHA, 1995) for chemical analysis. To check the potential of the method, field samples are tested in column tests with continuous flow of water with different concentrations of contaminants.

Isotherms

In general, adsorption is described through isotherms. An isotherm is an important curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution in a dynamic balance with the interface concentration. Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents (Foo and Hameed, 2010). There are many isotherms available to identify the adsorption mechanism and here we are using following two isotherms due to their universal acceptance.

(i) Freundlich isotherm (Reynolds and Richard, 2009) is the mathematical relationship that describes the non-ideal and reversible adsorption and it is not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. In multilayer adsorption, the stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of adsorption process (Foo and Hameed, 2010). The standard form of this isotherm is expressed by equation 1 and its linear form by equation 2.

$$\frac{x}{m} = X = KC_e^{1/n} \quad (1)$$

$$\log \left(\frac{x}{m} \right) = \log X = \log K + \frac{1}{n} \log C_e \quad (2)$$

where, x = mass of solute adsorbed (mg), m = mass of adsorbent (mg),
 X = mass ratio of the solid phase: the mass of adsorbed solute per mass of adsorbent,
 C_e = equilibrium concentration of solute (mg/l)
 K and n = experiment constants (Reynolds and Richard, 2009)

(ii) Langmuir empirical model (Langmuir, 1918) assumes monolayer adsorption occurs at a finite (fixed) number of definite localized sites with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. Homogeneous adsorption is referred in Langmuir isotherm which suggests that each molecule possesses constant enthalpies and sorption activation energy and no transmigration of the adsorbate in the plane of the surface occurs (Foo and Hameed, 2010). The standard form of this isotherm is expressed by equation 3 and its linear form by equation 4.

$$Q = \frac{Q_{\max} KC_e}{1 + KC_e} \quad (3)$$

$$\frac{1}{Q} = \frac{1}{KQ_{\max} C_e} + \frac{1}{Q_{\max}} \tag{4}$$

where, K = experiment constant or relative energy of adsorption (L/mg), C_e = equilibrium concentration of solute, mass/volume (mg/l), $Q=(x/m)$, mass ratio of the solid phase, i.e., the mass of adsorbed solute per mass of adsorbent, x = mass of solute adsorbed (mg), m = mass of adsorbent (mg), and, Q_{\max} = ultimate adsorption capacity (mg/g)

To know the order of reaction (Averill and Eldredge, 2006; Bures, 2016), 3 graphs viz., (i) Time (T) vs concentration difference (ΔC), (ii) T vs log of concentration difference ($\log \Delta C$) and (iii) T vs inverse of concentration difference ($1/ \Delta C$) are plotted. The order of reaction is determined as,

- i. If T vs ΔC is straight line then it is of Zeroth order reaction.
- ii. If T vs $\log \Delta C$ is straight line then it is of First order reaction.
- iii. If T vs. $1/ \Delta C$ is straight line then it is of Second order reaction.

Batch study is carried out to optimize parameters namely Time, Weight and Concentration to bring down the concentrations of nitrate, fluoride and TDS, and discussed subsequently.

3. TIME OPTIMIZATION

Time optimization has been done for the removal of Nitrate, Fluoride and TDS by taking nine different materials and details are given in Figure 2, Figure 3, and Figure 4 respectively. Adsorbent materials were kept in contact with water and concentration were determined at different times as indicated in figures.

It is noted that Nitrate is removed only by the potato flakes for all the contact time and by aloe vera gel at specific time. The potato flakes were changed by potato gel to remove the color and odor, which produced better results.

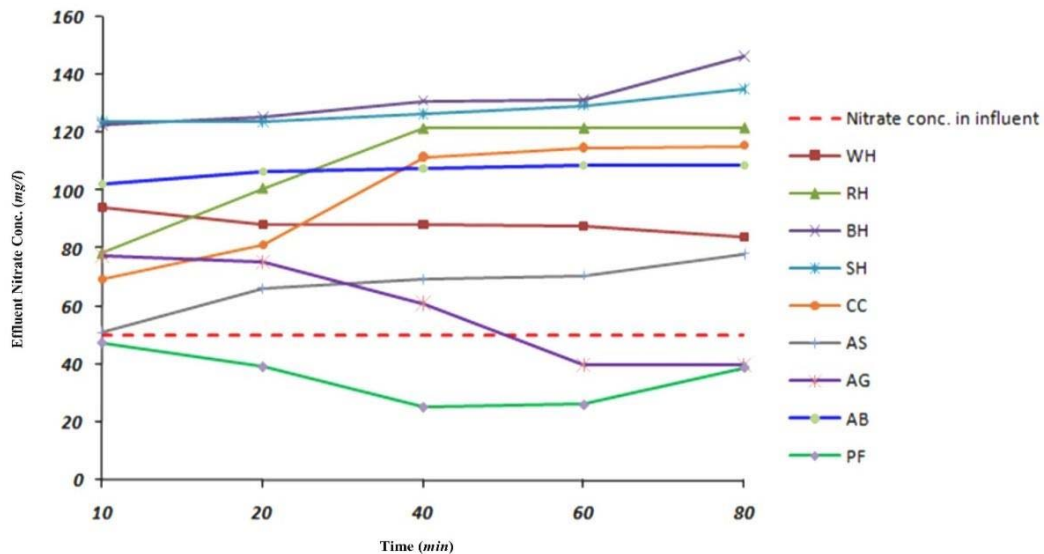


Figure 2. Changes in Nitrate concentration for different adsorbent material

It is observed that wheat husk, rice husk, banana peel husk, bagasse, coconut coir, amla seeds and amla bark show increase in Nitrate concentration in the effluent. The probable reason for the same is the presence of Nitrogen compound in plants (Turner, 1960; Brady and Weil, 1999). The maximum reduction (51.42%) is observed at 40 *min* contact time for potato gel/ flakes.

The details of material response for time optimization for reducing the Fluoride with nine materials are given in Figure 3. Potato gel is taken in place of potato flakes for time optimization study to reduce Fluoride to avoid the odor and colour problem associated with potato flakes. It is noted that Fluoride is removed by the potato gel, bagasse and aloevera gel for all the contact times. Figure 3 reveals that some adsorbent material demonstrates the rise in the concentration of Fluoride. The reason for the same is the presence of Fluoride compound in plants through pesticides and form C-F bonds. (Gribble, 2002; Hagan et al., 2002). Aloevera gel, bagasse and potato gel have shown the reduction in Fluoride concentration. The maximum Fluoride reduction (39.33%) is observed at 40 *min* contact time for potato gel.

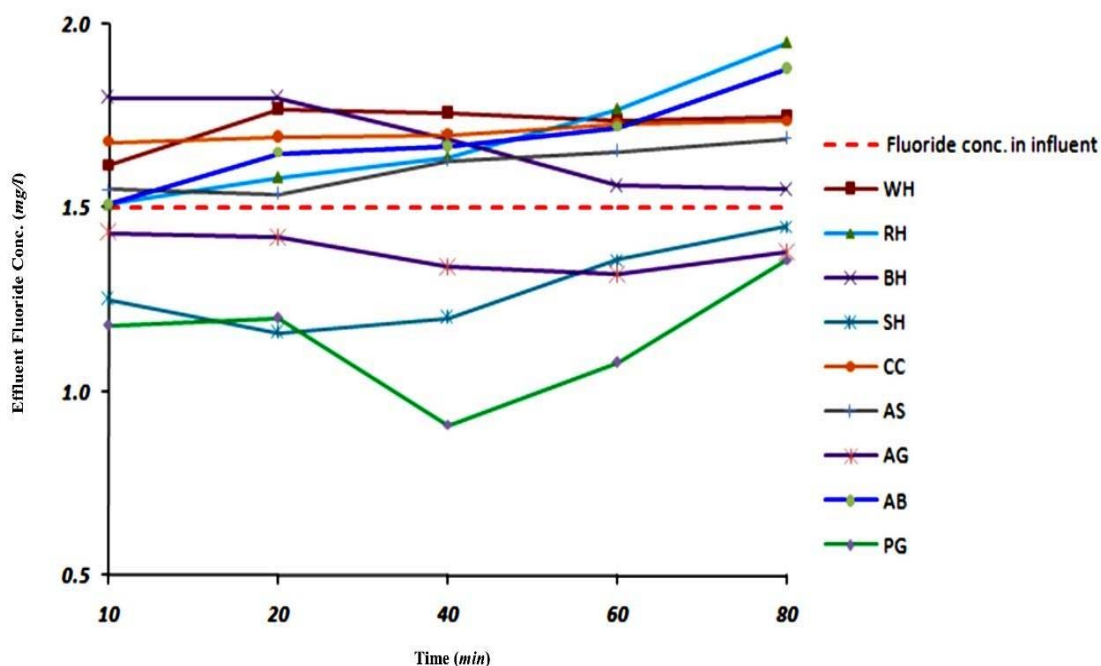


Figure 3. Changes in Fluoride concentration for a different adsorbent material.

The details of material response for time optimization for reducing TDS with nine adsorbent materials are given in Figure 4. It is noted that TDS is reduced by all the materials tested at all contact times. Wheat husk, coconut coir, aloevera gel and potato gel have shown very good reduction in TDS concentration. Even all materials have depicted the reduction potential for TDS from effluent but the maximum reduction is achieved by potato gel. The maximum TDS reduction (31.06%) has been observed at 40 *min* contact time in potato gel.

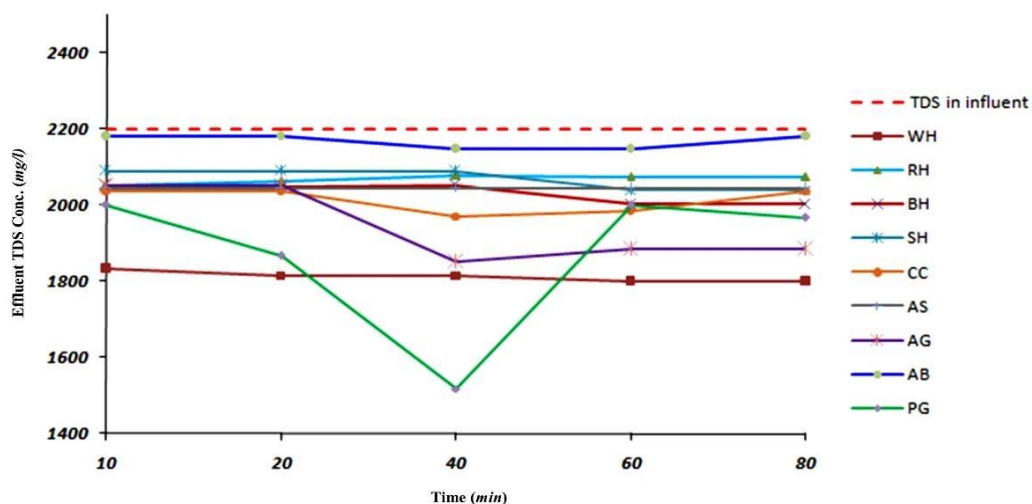


Figure 4. Changes in TDS concentration for a different adsorbent material

The time optimization study with nine materials showed that potato gel gives the best result in the reduction of Nitrate, Fluoride and TDS collectively as compared to other materials. Hence, potato gel as the adsorbent material is considered for optimization of other parameters in this study.

4. ADSORBENT WEIGHT OPTIMIZATION

Adsorbent weight optimization is conducted after deciding the time optimization, which is kept at 40 mins as indicated in all three studies. Seven samples of the different weight of potato gel are prepared and kept for 40 min contact time with sample water with known concentrations. Concentrations of Nitrate, Fluoride and TDS were obtained after 40 mins for each sample.

Nitrate reduction in effluent varies between 26.3% and 65.78% for different weights of potato gel with contact time 40 mins. Maximum reduction (65.8%) is observed at 0.1 g weight of adsorbent. The reductions of 65.78% and 65.56% in Nitrate are obtained with weights of 0.1 g and 0.5 g of potato gel respectively. The difference in reduction achieved by 0.1 g and 0.5 g is small. So either of the weights could be used as an optimized amount of adsorbent.

Fluoride reduction in effluent varies between 11.33% and 72% for different weights of potato gel and maximum reduction (72%) is observed at 0.1 g weight of adsorbent. The reductions of 72% and 71.33% is shown by the samples having a weight of 0.1 g and 0.5 g of potato gel respectively. This difference is quite small. So either of the weights could be used as an optimised amount of adsorbent.

TDS reduction in effluent varies between 17.9% and 27.3% for different weights of potato gel and maximum reduction (27.31%) has been observed at 0.5 g weight of adsorbent. It is established that the difference in reductions of Nitrate and Fluoride at 0.1 g and 0.5 g are negligible whereas maximum reduction in TDS is achieved at 0.5 g. Hence, 0.5 g of adsorbent weight is chosen as optimised weight for next parameter optimization.

5. ADSORBATE CONCENTRATION OPTIMIZATION

A number of samples are tested for adsorbate (potato gel) concentration after the optimization of contact time and adsorbent weight.

To optimize the adsorbate concentration, six samples of Nitrate concentration viz. 50 *mg/l*, 90 *mg/l*, 145 *mg/l*, 200 *mg/l*, 260 *mg/l* and 301 *mg/l* are prepared. Optimized weight of potato gel i.e. 0.5 *g* is mixed thoroughly and kept for a contact time of 40 *min*. Nitrate concentration reduction varies between 57.9% and 76.5% for all influent concentration. Maximum reduction (76.45%) in Nitrate is obtained at adsorbate concentration of 260 *mg/l*.

To optimize the adsorbate concentration, six samples of Fluoride concentration viz. 1.50 *mg/l*, 2.65 *mg/l*, 3.52 *mg/l*, 5.30 *mg/l*, 7.13 *mg/l* and 8.37 *mg/l* are prepared. Optimized weight of potato gel i.e. 0.5 *g* was mixed thoroughly and kept for contact time of 40 *min*. Fluoride reduction varies between 51.3% and 68.3% for all influent concentration. Maximum reduction (68.30%) in Fluoride was shown at an adsorbate concentration of 5.30 *mg/l*.

To optimize the adsorbate concentration, seven samples having concentration viz. 400 *mg/l*, 600 *mg/l*, 860 *mg/l*, 1000 *mg/l*, 1250 *mg/l*, 1500 *mg/l* and 2200 *mg/l* are prepared. The process is repeated as followed in case of Nitrate and Fluoride. TDS reduction varies between 46.7% and 53.3% for all influent concentration. Maximum reduction (53.33%) in TDS was shown at an adsorbate concentration of 600 *mg/l*.

After process parameters optimization, Isotherm and Kinetic study are carried out to understand the mechanism of adsorption occurring in potato gel.

6. ISOTHERMS

of biosorption is through isotherms. The quantity adsorbed is normalized by the mass of the adsorbent to allow comparison of different materials. Langmuir and Freundlich isotherm are universally accepted isotherms (Foo et. al., 2010) to describe such mechanism.

The Freundlich and Langmuir isotherm has been developed for the Nitrate reduction on the basis of batch study data shown in Table 3. It is observed in experiments that Nitrate concentration is reduced from 57.9% to 76.45% for different concentrations of adsorbate while the contact time was the same. Freundlich and Langmuir isotherms are plotted. Both the isotherm graphs follow the straight line but Langmuir is more promising as the regression coefficient is higher. The adsorption of Nitrate is taking place on the single layer of adsorbate surface.

The Freundlich and Langmuir isotherm constants are derived for reduction taking place in Nitrate and is shown in Table 3.

The Freundlich and Langmuir isotherm is developed for the Fluoride reduction on the basis of the batch study. It has been observed in the studies that Fluoride concentration is reduced from 51.33% to 68.3% for the different concentration of adsorbate while the contact time was the same. Freundlich and Langmuir isotherms are plotted. Freundlich isotherm graph follows the straight line and Langmuir from the linear trend. The adsorption of Fluoride is taking place in multilayer on the surface of the adsorbate. It also indicates that quantity adsorbed rises more slowly and higher concentrations are required to saturate the surface. The Freundlich and Langmuir isotherm constants are derived for reduction taking place in Fluoride and shown in Table 3.

TDS concentration is reduced from 42% to 53.3% for different concentrations of adsorbate while the contact time was kept the same. Freundlich and Langmuir isotherms graphs follow the straight line but later is found more promising (Table 3). The adsorption of TDS has been taking place on the single layer over the surface of the adsorbate. The Freundlich and Langmuir isotherm constants are derived for reduction taking place in TDS and shown in Table 3.

Table 3. Freundlich and Langmuir isotherms constants for Nitrate reduction

Parameter	Nitrate		Fluoride		TDS	
	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir
Slope (m)	0.6416	4.4096	0.3479	5.061	0.1304	4.6876
Intercept (c)	-7.6509	-0.0409	0.0029	-1.2376	26.74	0.0011
n	1.558603	-	2.8744	-	7.6687	-
K	0.000476	-	1.0029	-	4.1x10 ¹¹	-
Q _{max}	-	-24.4499	-	-0.8080	-	909.091
K	-	-0.00928	-	-0.2445	-	0.00023
R ²	0.9201	0.9846	0.9194	0.8914	0.9648	0.967

$$\frac{1}{Q} = \frac{1}{0.2268C_e} + \frac{1}{24.4499} \tag{5}$$

7. KINETIC STUDY

The kinetic study is the study of reaction rates (order of reaction). Here kinetic study is undertaken to know the order of reaction taking place on the surface of potato gel (Averill and Patricia, 2006). To know the order of reaction, 3 graphs for each contaminants viz., (1) Time vs. Concentration difference (T vs. ΔC), (2) Time vs. log of concentration difference (T vs. log ΔC) and (3) Time vs Inverse of concentration difference (T vs. 1/ ΔC) are plotted. The optimized conditions (adsorbent weight and adsorbate concentration) are used to experiment for time and concentration relation. For all the three parameters, the straight line pattern is followed in plot between time and concentration difference. Thus, indicating the zero order adsorption on the surface of potato gel. Table 4 shows the trend line equation and regression coefficients and help in determining the order of the reaction.

Table 4. Trend line equations and R^2 for order determination

Plot type	Trend line equation	Regression coefficient
Nitrate		
Time and ΔC	$Y = 0.6845x + 63.814$	$R^2 = 0.9535$
Time and $\log \Delta C$	$Y = 0.0033x + 1.8186$	$R^2 = 0.9243$
Time and $1/\Delta C$	$Y = -9E-05x + 0.0149$	$R^2 = 0.8894$
Fluoride		
Time and ΔC	$Y = 0.0124x + 1.2876$	$R^2 = 0.9726$
Time and $\log \Delta C$	$Y = 0.003x + 0.1255$	$R^2 = 0.9652$
Time and $1/\Delta C$	$Y = -0.0039x + 0.7328$	$R^2 = 0.9422$
TDS		
Time and ΔC	$Y = -1.6273x + 161.26$	$R^2 = 0.9885$
Time and $\log \Delta C$	$Y = -0.01x + 2.3198$	$R^2 = 0.8936$
Time and $1/\Delta C$	$Y = 0.0004x - 0.0014$	$R^2 = 0.7499$

The examination of various plots and regression coefficient of respective plot suggest that the zero order reaction is taking place on surface three different adsorbate.

8. RESULT & DISCUSSION

The reduction of high concentrations of Nitrate, Fluoride and TDS in groundwater are achieved by series of experiments and validated by Breakthrough curve and Thomas model (Basmadjian, 1997; Thomas, 1944). The nine natural materials are used for reduction of Nitrate, Fluoride and TDS in water. Two materials (Aloevera gel & Potato gel) have displayed the potential to reduce Nitrate; three materials (Aloevera gel, Amla bark & Potato gel) have shown potentials in reduction of Fluoride; and all nine materials have reduced the TDS present in water. The potato gel is the only material that has shown reduction in all three chosen contaminants (Nitrate, Fluoride and TDS) during experiments. The odor associated with dry flakes of potato is removed by converting them into gel. Four parameters (Time, Weight, Concentration & Flowrate) are optimized through batch and continuous study for reduction of Nitrate, Fluoride and TDS using potato gel as adsorbent. The isotherm plots indicate that Nitrate and TDS reduction have followed the Langmuir model while Fluoride reduction has followed the Freundlich model. The single layer adsorption is suggested by Langmuir and multi layer adsorption by Freundlich (Foo and Hameed, 2010).

9. CONCLUSION

The batch study followed the Langmuir isotherm, indicating single layer adsorption for Nitrate and TDS while Fluoride reduction followed Freundlich isotherm indicating multilayer adsorption. Potato gel showed the potential in reduction of high concentrations of Nitrate,

Fluoride, and TDS in batch and continuous study. The optimum values in terms of contact time, weight and concentration of adsorbent are obtained. The zero order adsorption reaction is followed in reduction of three contaminant under study.

10. REFERENCE

1. Basmadjian Diran. (1997). *The Little Adsorption Book: Practical guide for engineers and scientists*. CRC press, Boca Raton, pp. 180.
2. Foo K. Y. and Hameed B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*. 156 (1), pp. 2–10.
3. Thomas, H. C. (1944). Heterogeneous Ion Exchange in a Flowing System. *Journal of the American Chemical Society*. 66, pp. 1664-1666.
4. Gribble Gordon W. (2002). Naturally occurring organofluorines - *The Handbook of Environmental Chemistry* (ISBN 3-540-42064-9). Springer-Verlag, pp. 121–136.
5. Hagan O. D., Schaffrath C., Cobb S. L., Hamilton J. T. and Murphy C. D. (2002). Biochemistry: Biosynthesis of an organofluorine molecule. *Nature*, 416 (6878), pp. 279.
6. Montgomery J. M. (1985). *Water treatment principles and design*. John Wiley & Sons Inc., New York, N.Y, pp. 696.
7. Croll B. T. and Hayes C. R. (1988). Nitrate and water supplies in the United Kingdom. *Environment. Pollution*. 50, 163-187.
8. Fried J. J. (1991). Nitrates and their control in EEC aquatic environment. Nitrate contamination: exposure, consequence and control. (ed.: I. Bogardi and R. D. Kuzelka), Springer-Verlag, Berlin, Germany, pp. 3-11.
9. Nixon N. (1992). English water utility tackles nitrate removal. *Water Engineering Management*. 139, pp. 27-28.
10. Briskin J. S. (1991). Pesticides, nitrates found in US wells. *Chemical Engg. News*. 46, pp. 46-50.
11. Miller J. E. (2003). Review of water resources and desalination technologies. Report: 2003-0800, pp. 25.
12. Fraser P., Chilvers C., Beral V. and Hill M. J. (1980). Nitrate and human cancer: a review of the evidence. *Int. J. Epidemiology*. 19(1), pp. 3-11.
13. Mirvish S..S. (1995). Role of N-nitroso compounds and N-nitrosation in etiology of gastric, esophageal, nasopharyngeal and bladder Cancer. *Cancer Letter*. 93, pp. 17-48.
14. ATSDR. (2003). Toxicological profile for fluorides, hydrogen fluoride, and fluorine. Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Service: Atlanta, GA, pp. 2-132.
15. Public Health England. (2014). Delivering better oral health: an evidence-based toolkit for prevention (3rd ed.). London, pp. 6-35.

16. "Health effects of water fluoridation: A review of the scientific evidence," (ISBN- 978-1-877317-08-8), Published by Royal Society of New Zealand, 2014, pp. 22-55.
17. Rozelle L. T. (1993). Potential human health effects due to consumption of high purity water: Highlight investigation. Presented at Annual Water Quality Association Conference, pp. 47.
18. Rozelle L. T. (1997). All in the body's balance – Ill health effects are not connected to consumption of low TDS water. *Water Technology*. 20, pp. 126-132.
19. Guyton Arthur L. (2006). *Textbook of Medical Physiology*. (11th Edition), W.B. Saunders Company, Philadelphia, pp. 258.
20. WHO. (2005). *Nutrients in Drinking Water* (ISBN 92 4 159398 9). World Health Organization Geneva, pp. 322.
21. Punmia B C, Jain A K and Arun K Jain. (2012). *Environmental Engineering: Water Engineering* (2nd ed., reprint). Laxmi publications, New Delhi, pp. 530.
22. ENAM. (2009). *Facility classification standards. Standards under Environment Act, Environment & Natural Area Management (ENAM) Nova Scotia*, pp. 10.
23. Luo J, Wu C, Xu T, Wu Y. (2011). Diffusion dialysis-concept, principle and applications. *Journal of Membrane Science*. 366, pp. 1–16.
24. Al-Subaie K. Z. (2007). Precise way to select a desalination technology. *Desalination*. 206, pp. 29–35.
25. Della Rocca C., Belgiorno V. and Meriç S. (2007). Overview of in-situ applicable nitrate removal processes. *Desalination*. 204, pp. 46–62.
26. Brown M. D. and Aaron G. (1991). The effect of the point of use water conditioning systems on community fluoridated water. *Pediatric dentistry*. 13, pp. 35-38.
27. Reeb Jim and Mike Milota. (1999). Moisture content by the oven-dry method for industrial a testing. *WDKA*, pp. 66-74.
28. Hans Dieter Belitz, Werner Grosch and Peter Schieberle. (2004). *Food chemistry* (3rd ed.). Springer, pp. 318-323.
29. APHA. (1995). *Standard methods for the examination of water and wastewater* (19th ed., ISBN: 0-87553-223-3). edited by Andrew Deaton, Lenore S. Clesceri and Arnold E. Greenberg, American Public Health Association, Washington DC, pp. 963.
30. Reynolds T. D. and Richard P. A. (2009). *Unit Operations and processes in environmental engineering* (2nd ed.). PWS publishing, Toronto, pp. 795.
31. Langmuir I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40, pp. 1361-1403.
32. Averill A. Bruce and Eldredge Patricia. (2006). *Chemistry: Principles, patterns and Applications*. Pearson, pp. 1100.

33. Bures Jordi. (2016). A simple graphical method to determine the order in catalyst. *Angewandte Chemie*, 55(6), pp. 2028-2031.
34. Velasquez L., Dussan J. (2009). Biosorption and bioaccumulation of heavy metals on dead and living biomass of *Bacillus sphaericus*. *J. Hazard. Mater.* 167(3), pp. 713–716.
35. Ahalya N., Ramachandra T. V. and Kanamadi R. D. (2003). Biosorption of Heavy Metals. *Research Journal of Chemistry and Environment*. 7 (4), pp. 61-71.
36. Turner E. R. (1960). The Movement of Organic Nitrogen Compounds in Plants: With two Figures in the Text. *Ann. Bot.* 24(3), pp. 387-396.
37. Brady N.C. and Weil R.R. (1999). *The nature and properties of soils*. Prentice Hall Inc., NJ, pp.186.
38. Singh, S., & Mishra, P., 2018. Use of Different Bioadsorbents for the Nitrate Removal from Water. *International Journal for Research in Applied Science & Engineering Technology*, 6, 2781-2789.