

POTENTIAL OF GRANULAR ACTIVATED CARBON FILTERS FOR IRON REMOVAL FROM GROUNDWATER

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ABSTRACT

The most commonly used iron (Fe) removal mechanism from groundwater involves oxidation-precipitation and adsorptive-filtration worldwide. In this study the oxidation-floc formation mechanism was examined for granular activated carbon (GAC) filter using synthetic groundwater (SGW). Batch experiment including kinetic and isotherm study were carried out to find out the adsorb ability of GAC. Column test was conducted at different phases to identify the influence of initial concentration of Fe, hydraulic retention time (HRT) and aeration supply to the system. Widely used up-flow mode was used to supply SGW using peristaltic pump. It was observed that the experimental results for kinetic experiment best fit to the pseudo-first order kinetics model with the adsorption amount of 8.54×10^{-5} mg/g and the reduction of adsorption amount with the increment of GAC weight was identified from the result of isotherm study. Column experiments concludes that the effluent Fe concentration reduced from 0.05 to 0.03 mg/L when increasing the concentration of Fe approximately from 1 to 3 mg/L. The reduction of HRT from 7 hours to 3.5 hours reduced the iron removal efficiency from 99% to 98.4%. The air supply to the system with the flow rate of 3.5 L/min did not show any improvement in Fe removal efficiency. Overall, the effluent achieved the World Health Organization (WHO) drinking water standard at all the phases which shows that granular activated carbon filters are more suitable for Fe removal from groundwater.

Index Terms— Aeration, iron removal, granular activated carbon, synthetic groundwater

1. INTRODUCTION

Groundwater resources play a crucial role in the production of clean and adequate drinking water supply all around the world. The comprehensive use of groundwater can be explained by the ease of access, better protection from pollution sources, higher water purity as compared to surface water (Hallberg & Martinell 1976), less subject to seasonal and perennial changes, uniformly spreading over large areas (UNESCO 2004) and also lower capital cost of production (Sharma, Petruseveki & Schippers 2001). These benefits have resulted in groundwater use for water supply at large scale. Most groundwater and surface water sources that are used to supply public water systems contain a variety of organic and inorganic chemicals. Inorganic contaminants are usually present at much higher concentrations than their organic counterparts. Iron is the second most ample metal in the earth crust and a common inorganic constitute in the groundwater (WHO 1996). Fe exists in two forms, which are soluble ferrous iron [Fe(II)] and insoluble ferric particulate iron [Fe(III)]. Fe in groundwater is generally present in the ferrous state.

The presence of Fe ions in groundwater is generally attributed to the dissolution of Fe-bearing rocks and minerals, which are primarily oxides (hematite, magnetite, and limonite), sulphides, carbonates and silicates under anaerobic conditions in the presence of reducing agents such as organic matter and hydrogen sulphide (O'Connor 1971; Hem 1989). The high concentration of iron in ground water leads to clogging of distribution systems, shortened lifespan of major appliances and more energy requirement for pumping water through clogged pipes and for heating water in industries. The World Health Organization

has approved the removal of iron when concentration is higher than 0.3 mg/L (WHO 1996). Therefore, there is a need to carry out a study which endeavors to alleviate the problem of high Fe concentration in groundwater. The study area has been selected as Vallipuram coastal area which is located in Jaffna Peninsula in Northern Province, Sri Lanka. Groundwater supply through collector wells in Vallipuram water treatment plant which has higher iron concentration affects the treatment plant process and the population in Point Pedro where the groundwater is distributed for drinking purpose.

Different mechanisms (physical, chemical, and biological) may contribute to the removal of Fe in filters but the treatment method domains the removal mechanism depends on water quality and process conditions applied. Under the commonly applied treatment conditions in iron removal plants, the oxidation-floc formation mechanism (floc filtration) is commonly believed to be dominant. In this floc filtration mode, commonly applied in many groundwater treatment plants, soluble Fe^{2+} is first oxidized to insoluble Fe^{3+} by aeration or chemical oxidation and the flocs formed are subsequently removed in a rapid sand filter (O'Connor 1971). In several conventional plants, however, oxidation is only partially achieved before filtration and, as a consequence, besides oxidation-floc formation, adsorption-oxidation plays a role as well.

Based on the low efficiency of the 'iron removal plants', researches were intensified to identify appropriate filter media and mechanisms that can achieve improved water quality of the treatment plants. Granular Activated Carbon (GAC) prepared using charcoal, a porous form of carbon made from hardwood, as the base material has been identified, investigated and found capable of achieving a substantial iron and manganese removal from sample groundwater sources in a batch test (Siabi & Ghana 2003). The choice of carbon as a filter medium for water treatment is increasingly becoming important as a result of the new knowledge acquired through research regarding its high capacity for removing manganese and iron, and other minerals through filtration process.

This research mainly focused on proposing and analyzing an alternative cost effective and easily operatable conventional treatment technique for the suspended and dissolved Fe removal from groundwater. Oxidation and precipitation removal mechanism using granular activated carbon filters will be focused throughout the study.

2. METHODS

2.1. Sample collection

The physical-chemical properties of groundwater from collector well were tested on October, 2018 by collecting samples from top and bottom using standard sampler made of stainless steel having 300 mL capacity in day time. The top sample was collected approximately 10 cm from the top surface which was opened to atmosphere. The measured parameters were given in the Table 1 bellow which was used to prepare Fe contaminated synthetic groundwater. The highest Fe concentration was found at the bottom of the collector well than the top surface.

Table 1. Groundwater Collector well properties at 32°C

Parameter	pH	TDS	EC	Turbidity	Salinity	DO	Fe^{2+}	Ca^{2+}	Mg^{2+}
Unit	–	mg/L	μS	NTU	mg/L	mg/L	mg/L	mg/L	mg/L
Top sample	7.85	1200	1812	1.27	840	5.3	0.04	60.26	2.85
Bottom sample	7.8	1700	2390	47.6	1230	<0.01	0.2	31.14	2.18

2.2. Preparation of SGW

Synthetic ground water was used in this study due to the seasonal variation of Fe concentration throughout the year which was not suitable for the experimental study. Laboratory reagent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used to prepare the synthetic groundwater. Required amount of reagent was mixed with 500 mL distilled water and then added with groundwater for the batch and column test.

2.3. Granular activated carbon preparation

A coconut shell based granular activated carbon with the product type of PUC-PAC having the sieve range of 8×20 supplied from Enviro Equipments Pvt. Ltd. was used as filter media. 1 kg of GAC particles were sieved through sieve size range of 2.36 to 0.8 mm using sieve shaker. The particle size distribution curve used to identify the mean size was given in the Fig.1 below. According to the curve the mean size was found as 1.2 mm which was used to carry out the batch experiment. The sieved particles were separately rinsed several times with constant amount of distilled water until getting a clear color and constant pH. Finally the pH of washed water was found nearly 8.5. Then the samples were dried at 105°C for 24 hours using the oven. Then it was stored safely to avoid contamination from the environment.

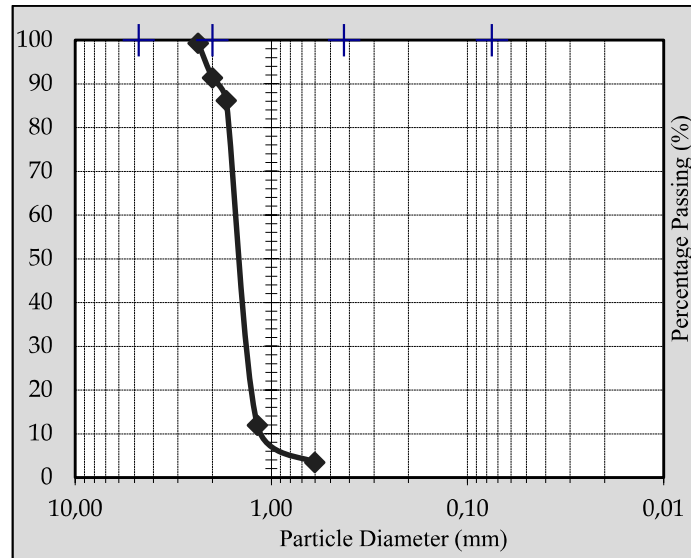


Fig. 1. Particle size distribution for GAC

2.4. Kinetic study

The kinetic experiment was conducted for 100 mL SGW with 5 g GAC for the time range of 10 to 300 minutes and the equilibrium Fe concentration was measured. The sorption kinetics was studied using pseudo-first order and pseudo-second order kinetics models using the equations 1 and 2 respectively, and the best fit values were calculated using the linear plots.

$$\ln(Q_e - Q_t) = \ln Q_e - Kt \quad (1)$$

where, Q_e (mg/g) is the mass of Fe adsorbed at equilibrium, Q_t (mg/g) is the mass of Fe adsorbed at time t (min) and K is the first order reaction rate constant (min^{-1}). The pseudo first order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites.

$$t/Q_t = 1/(K_2 \times Q_e^2) + t/Q_e \quad (2)$$

where, t is the reaction time (min), Q_t is the mass of Fe adsorbed at time t (mg/g), Q_e is the mass of Fe adsorbed at equilibrium (mg/g) and K_2 is the second order reaction rate constant (g min/mg).

Column Design

2.5. Isotherm study

Since GAC has the adsorption ability, it was needed to find out the adsorption capacity of GAC on Fe removal. GAC particles passed through 1.7 mm and retained in 1.18 mm sieve was used in this experiment. An equilibrium isotherm experiment was conducted using a series of conical flasks containing 100 mL SGW with 1 mg/L Fe concentration and GAC doses of 0.5,1,2,3,4,5,10,15 g by mixing in sterilizer with 150 rpm for 180 minutes. The amount of Fe adsorbed (Q) per unit mass of GAC was calculated using the equation 3:

$$Q = (C_o - C_e) \times V/W \quad (3)$$

where, Q is the amount of Fe removed from SGW (mg/g) at time t , C_o is initial concentration of Fe (mg/L), C_e is equilibrium concentration of Fe (mg/L), V is the volume of SGW (mL) and W is the weight of GAC used (g).

Temkin and Freundlich isotherm models were used to analyze the adsorption behavior of GAC on Fe removal as given by the equations 4 and 5 respectively.

$$Q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (4)$$

where, b is Temkin constant which is related to the heat of sorption (J/mol) and K_T is Temkin isotherm constant (L/g). R is the universal gas constant (8.314 J/mol.K) and T is temperature.

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

Where Q_e is the amount of Fe ion adsorbed (mg/g), C_e is the equilibrium concentration of Fe ion in solution (mg/L), and K_f and n are constant integrates, the factors affecting the adsorption capacity and intensity of adsorption, respectively.

2.6. Column experimental study

The column having the height of 1.5 m and 15 cm diameter was designed using acrylic tube for its transparency. The diameter was selected greater than 50 times the mean media size to avoid channeling effect. The smaller diameter was not used to avoid excess wall effects. The column height was selected according to column bed/height ratio $\cong 1/10$. For the column test the GAC particles were placed according to its particle size range where the largest to smaller in size was packed from the bottom to top. The schematic diagram of the experimental setup was given in the Fig.2.

The sampling ports were placed throughout the column height with 20 cm interval for the sample collection. The air supply and SGW were given concurrent from the bottom. The aquarium air pump was used to supply 3.5 L/min air flow rate to the column from the bottom. The widely used up-flow configuration was used to supply influent SGW in this study. The peristaltic pump was used to supply SGW. The filter media were packed partially for 80 cm height starting 40 cm from the bottom.

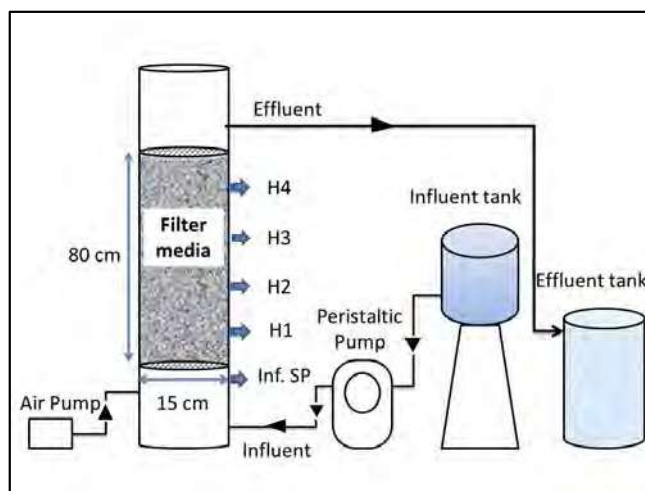


Fig. 2. Schematic diagram of experimental setup

2.1. Column operational conditions

The column was operated at 3 different phases to identify the effect of initial concentration of Fe in SGW, HRT and air supply to the system on Fe removal efficiency. Phase 1: Fe concentration increased approximately from 1 mg/l to 3 mg/l at 7 hours HRT, phase 2: HRT was reduced from 7 hours to 3.5 hours for the initial Fe concentration of 3 mg/l and phase 3: with the air supply of 3.5 L/min to the column having 3 mg/l Fe and 7 hours HRT.

The porosity of the filter media GAC was measured using volumetric method. Initially the distilled water was sent up to the filter media height. Then the system was allowed to get saturated for 20 minutes. Finally the distilled water was drained from bottom and the porous volume was measured. The procedure was continued for 3 times to get the average porous volume. Finally the porosity was measured as 0.28 from which the flow rate was calculated according to the HRT. The column was operated continuously and the samples were collected from the sampling ports with 4 hours' time interval for the measurement. The column was backwashed at the end of each phase using clean water with the flow rate of 1.2 L/min for 30 minutes. The parameters pH, Temperature, TDS were measured using PC2700 multi meter, DO was measured using DO meter and the total Fe was measured using DR900 calorimeter.

3. RESULTS AND DISCUSSION

3.1. Batch experimental results

Laboratory batch studies are useful in obtaining and providing fundamental equilibrium adsorption and kinetic data for potential adsorbents. The importance of obtaining isotherms and kinetics curves lies in developing a model which accurately represents the results obtained and could be used for design purposes. Moreover, the models applied to describe the breakthrough behavior have a key role in the scale-up procedure from laboratory experiments through pilot plant to industrial scale.

To find out the mechanism of Fe adsorption and the potential rate controlling steps, like diffusion mass transport and chemical reaction process, it is required to characterize the adsorption mechanism. In order to understand the kinetics of Fe removal using GAC as an adsorbent pseudo first and pseudo second order models were plotted with the experimental data.

Fig.3 shows the Pseudo first order and second order model describe the sorption kinetics with R^2 values of 0.987 and 0.963 respectively. So, both models reach the adsorption regardless of the type and amount of GAC used. It is observed that the pseudo-first order model yields a somewhat higher fit than the pseudo-second order model. The parameters Q_e and K were calculated as 8.54×10^{-5} mg/g and 0.019 respectively from the linear plot results.

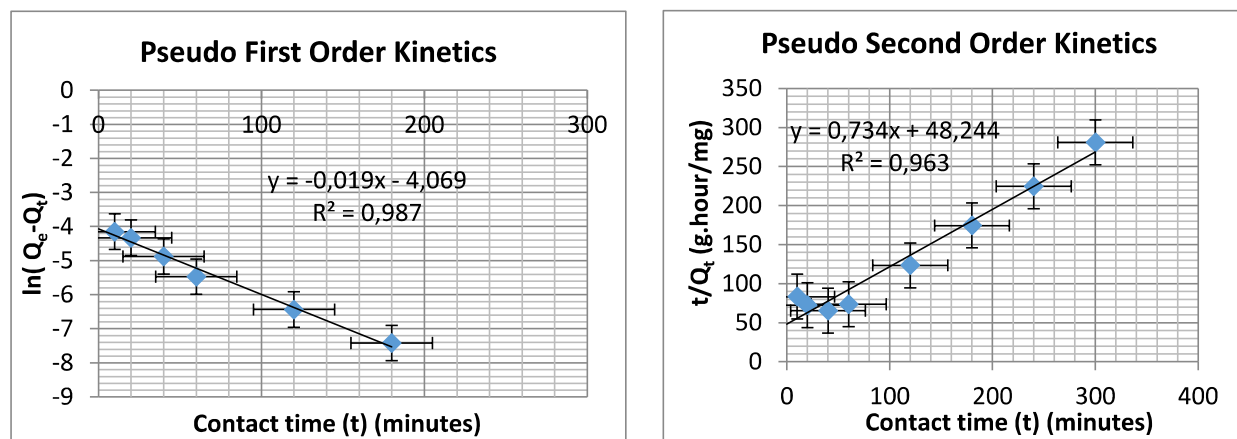


Fig.3. Pseudo first order and second order kinetics model for Fe contaminated groundwater

The adsorption experimental results for 1 mg/L Fe contaminated groundwater by GAC media at 25 °C at equilibrium contact time of 240 minutes was plotted in terms of equilibrium Fe concentration in liquid phase (C_e) Vs. amount of Fe adsorbed on GAC (Q_e) as shown in Fig.4. A nonlinear relationship between the amount of Fe adsorbed on GAC and Fe contained in solution at equilibrium was observed. At studied operating conditions the maximum value of Q_e (0.17 mg/g) was obtained at a C_e equal to 0.17 mg/L Fe.

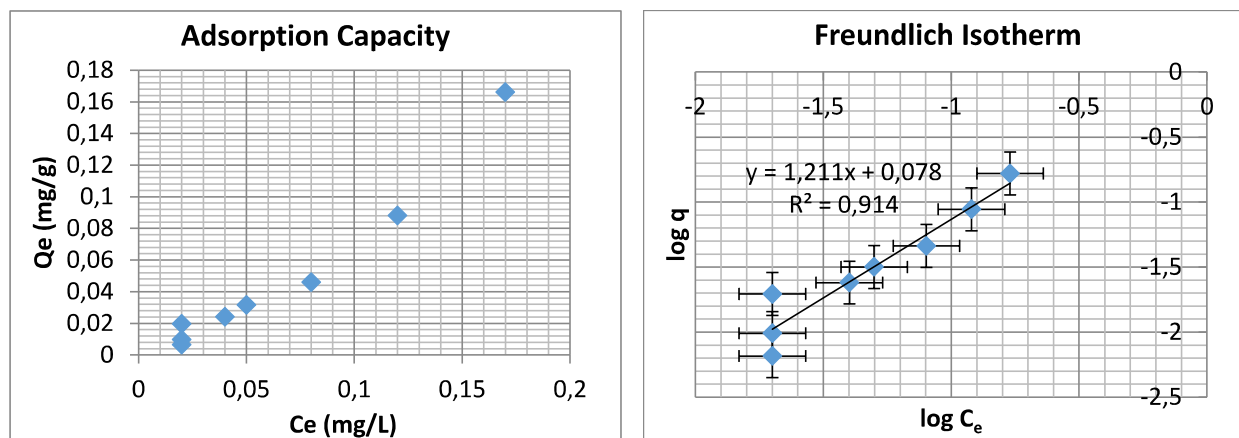


Fig.4. Adsorption capacity diagram and Freundlich isotherm model

Taking into consideration the values of correlation coefficient (R^2) for Fe contaminated groundwater as shown in Fig.4, it is observed that the Freundlich model gives the best fit of 0.914 compared to Temkin model with correlation of 0.783. The Freundlich constants K_f and n were calculated as 1.198 and 0.825 respectively from linear plot. Okeola et al. (2011) also got the best fit to Freundlich model for Fe removal using GAC media to conform the heterogeneous adsorption process. The adsorption parameters b and KT obtained from Temkin model were 1.9×10^4 J/mol and 50.19 L/g respectively. Here the constant related

to heat of sorption (b) has a positive value which indicating that the adsorption process is endothermic where the head energy was adsorbed from the surrounding.

2.1. Column experimental results

The results from each phase were discussed below. Under the applied condition 68% of Fe was entering the filter bed in dissolved form which was found from filtration method for influent SGW.

Phase 1: Influence of Initial Fe concentration on GAC filter run

The initial Fe concentration was increased from 1 mg/L to 3 mg/L at 7 hours HRT to check for the removal efficiency of GAC on Fe removal. The experimental lag time 48 hours with 30 minutes backwash time was indicated in the Fig.5. It shows that with the increment of initial feed Fe from 1 to 3 mg/l the removal efficiency increased approximately from 95 to 98.9 % for GAC column. When the initial Fe concentration increased, the percentage of suspended Fe particles entering the filter also increases from 32 % to 85 % which could promote the precipitation process of Fe ions on GAC filter media. Therefore total Fe removal efficiency is increased with increasing initial Fe concentration as a result of combined adsorption and precipitation process.

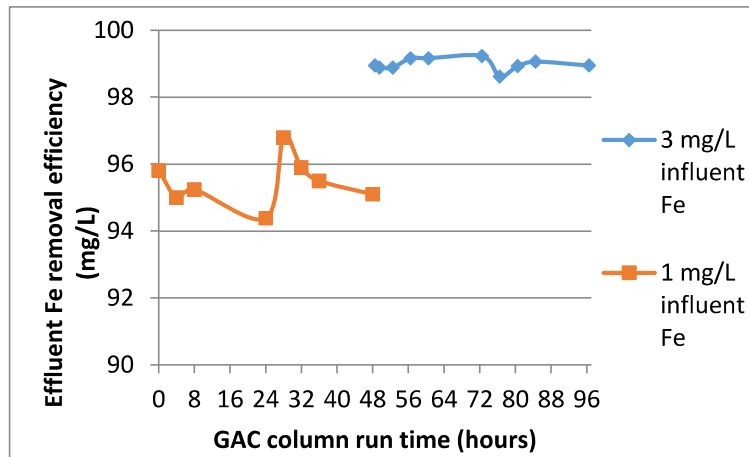


Fig.5. Effluent Fe removal efficiency of GAC at 1 and 3 mg/L influent Fe with 7 hours HRT

Phase 2: Influence of HRT on GAC filter run

The Fe removal efficiency was reduced from 99 to 98.4% when the HRT reduced by half for 3 mg/l average of total initial Fe concentration and the Fig.6 compares the pattern in the Fe removal efficiency at Phase 2 for GAC. But still both removals can be considered as acceptable since the effluent concentrations reached drinking water standards. However, as indicated by Tchobanoglous et al. (2003) the increased filtration velocity resulted in a factor 4 higher Reynolds number. More turbulence within the hydraulic pore may have accelerated the Fe ions to the effluent and reduced the Fe removal efficiency.

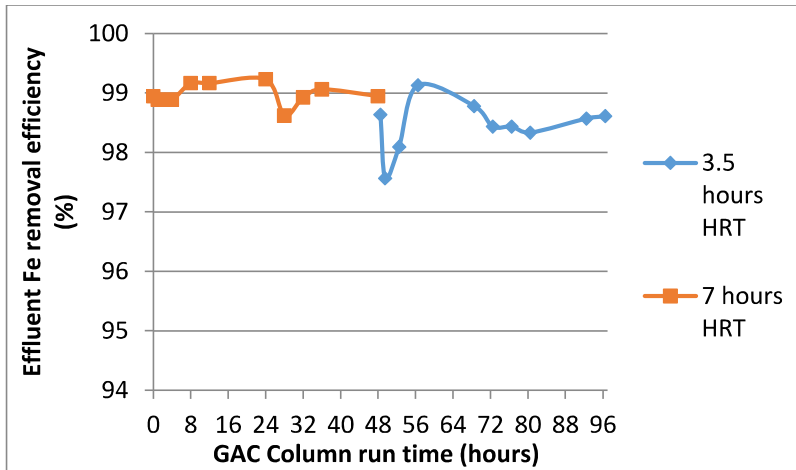


Fig. 6. The effluent Fe removal efficiency at Phase 2 for GAC filter media

Phase 3: Influence of air supply on Fe removal using GAC filter media

GAC filter shows almost same amount of Fe removal efficiency, which is in the range of 94 to 98% with the effect of aeration as shown in Fig.7. Effluents in both conditions reached the EPA drinking water standards of 0.3 mg/L (EPA, 2018). Oxygen transfer efficiency is the main factor determining the effective performance of the filter which in turn depends on the air to water ratio. In this study the air to water volume flow rate ratio reached to 100:1 which is less effective on Fe removal. Previous studies done by researchers say that 2 to 10:1 of air to water volume flow rate ratio gives the better removal of pollutant for aerated filters, and also increasing the air to water ratio can push down the air to water interface, where the uneven distribution of air is also possible (Kamarden et al., 2014).

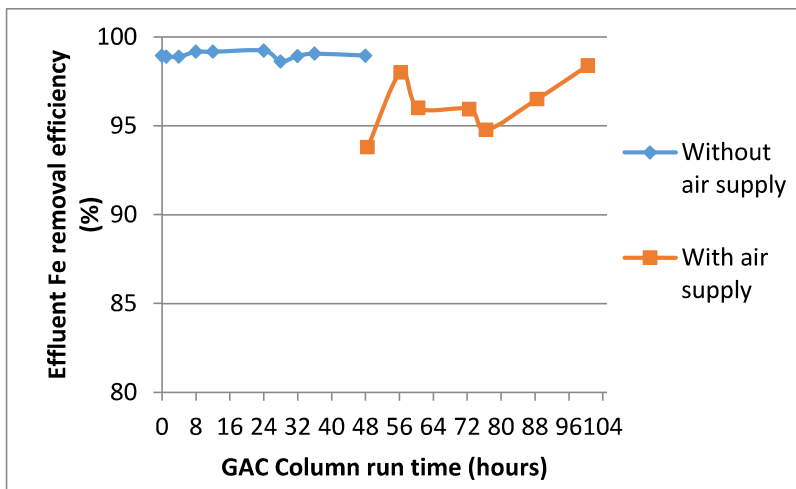


Fig. 7. Effluent Fe removal efficiency for GAC media at Phase 3

4. CONCLUSION

In this research a combined use of batch and column experiments were performed through the adsorption and oxidation- floc filtration process with aeration inside the same filter and thus reducing the operating space. A lab-scale GAC filter was developed and tested to investigate the effect of initial Fe concentration, HRT and air supply to the system on the removal of Fe ions from SGW. The kinetics

experiments showed that adsorption equilibrium data can be fitted to Pseudo-first order kinetics with a correlation coefficient of 0.987. It showed an lowest adsorption amount of 8.54×10^{-5} mg/g for Fe ions on GAC media at the equilibrium time 240 min. Results of the isotherm experiment for Fe contaminated groundwater showed that the Fe ions exhibited 98% removal efficiency towards GAC media. The isotherm data best fitted to Freundlich model with correlation coefficient of 0.914.

The column experiment results from Phase 1 conclude that, increasing the initial Fe concentration significantly reduces the effluent Fe concentration. The results of Phase 2 analysis show that reduction in HRT marginally reduces the Fe removal efficiency for GAC media. Result of phase 3 show that the aeration is not essential as the 98.9% removal was achieved without air supply and thus the operational cost can be reduced for GAC filter. As from the analysis of column experimental results, I suggest that the air: water volume flow ratio can be reduced to improve the Fe removal efficiency in Phase 3. Overall GAC filter showed a better removal of Fe from SGW.

5. REFERENCES

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