M. Alamgir, S.M.T. Islam and J. A. Saju (Eds.)
ISBN: 978-984-35-4034-8

Proceedings of the Waste Safe 2023 – 8th International Conference on
Integrated Solid Waste and Faecal Sludge Management
25-26 February 2023, Khulna, Bangladesh

ADSORPTION ISOTHERM STUDY OF As(III) ONTO Fe FOR ACCOMPLISHING A TREATMENT PLANT TO ERADICATE As FROM CONTAMINATED INDUSTRIAL WATER

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ABSTRACT

The core target of this work is to ensure an efficient and low-cost As-removal technique that will remove arsenic acceptably and proficiently. Among Langmuir and Freundlich isotherm models which model is fitted well with the experimental data is also ensured in this research. From the kinetic study, it is known that pH 7 and 3 hours of contact time is the best option for the adsorption of As, and from the isotherm study with different amounts of iron and As, the required amount of iron for higher adsorption of As is evaluated. The adsorption capacity (Ce/qe) for 10 ppm iron concentration was acquired to be 1.111, and the equilibrium concentration of As at the aqueous phase (Ce) was 0.05 ppm for the initial Arsenic concentration of 0.5 ppm. However, for 5ppm Iron, Ce/qe was found to be 0.95238, and Ce was 0.05ppm for an initial As the concentration of 0.5 ppm after two cycles of column study. The adsorption isotherm model is fitted well with the Langmuir isotherm model and not fitted with Freundlich's isotherm.

INTRODUCTION

Water scarcity is a major problem in the world and there is no other way for Bangladesh. Bangladesh is facing high rainfall every monsoon but when it is to accessing pure drinking water there is a huge deficiency. The water crisis is an immense problem in the world to get safe drinking water. Arsenic (As), as an element can be categorized as a metalloid, which can act both as metal and non-metal and exerts toxic effects on public health. As a consequence of industrial and agricultural activities, soil/rock erosion, and other processes, arsenic is detected in groundwater as well as Food and water that has been tainted with this metalloid are the main exposure routes (Garza-Lombó et al., 2019). There are so many mining activities, As (Arsenic) herbicides, fungicides, and pesticides, wood preservatives, which contribute a huge amount of As in the groundwater, and eventually by food or direct consumption of groundwater it causes disaster to public health.

As a result of the competitive exchange of phosphate anions, arsenic anions that have been sorbed to aquifer minerals are being shifted into solution and causing arsenic pollution in groundwater. The overuse of phosphate fertilizer in agriculture, the fermentation or decay of buried peat deposits and other naturally occurring organic compounds, etc. are cited as the sources of phosphate. These posited mechanisms have yet to be verified, though. Arsenicosis is spurred on by long-term exposure to arsenic and may entail several organ diseases. In Bangladesh, many of the negative health impacts of chronic toxicity are visible. In addition to dermatological manifestations, noncommunicable disorders like cancer, unfavorable pregnancy outcomes, and a decline in children's IQ are also reported to be on the rise. As cancer cases from long-term low-dose arsenic exposure from drinking contaminated water increase, Bangladesh is becoming increasingly concerned about this issue. The cornerstone of arsenicosis prevention and case management is ceasing to consume arsenic-contaminated water. Due to a shortage of reliable sources of arsenic-safe water, a greater percentage of individuals are currently still eating this tainted water. (Ahmad, S. A., et al., 2018).

There are many techniques for arsenic removal such as reverse osmosis (Moreira, V. R., et al. 2021), chemical precipitation, chemical oxidation, coagulation, chemical process, ion exchange, and adsorption of arsenic in aqueous solutions (Alka, S., et al., 2021). Most of them are expensive, require high operational costs, and ultimately produce a huge amount of waste. But among them, the adsorption process is relatively more effective, low cost, and usage of less toxic and easily available materials. This process can be exploited easily and there is the availability of a huge range of adsorbents (Rahdar, S., et al., 2019).

In groundwater, Arsenic is found as As(III) and As(IV) in inorganic form. Among them, the toxicity of As(III) is the most. (Kobya, M et al., 2022) In this paper As(III) is taken for all experiment and the adsorption properties of Arsenic onto Iron is used. Adsorption is used in many fields of filtration due to its efficient removal of waste or toxic material from the wastewater, contaminated water, or gaseous phase. It is mainly popular for its sustainability and low cost and also for recyclable materials. It has a huge scope for use in industrial work at adsorption-based filtration work. For adsorption study, evaluation of kinetic and isotherm models is essential. For the isotherm adsorption study, Freundlich's and Langmuir's models are popularly used for the adsorption process for the equilibrium phenomenon. (Azizian, S. et al., 2018). Removal of As(III) is harder than As(V) as in normal pH (6-8) As(III) is not found as an ion whereas when the treatment is based on adsorption ionized adsorbate is needed.

This paper aims to use zero-valent iron scrap available in the workshop as an efficient adsorbate for the adsorption of arsenic and proceed with the adsorption kinetic and isotherm study for the equilibrium aqueous stage. The main goal is to study the adsorption isotherm model and to know which adsorption isotherm model will be fitted well among Langmuir's and Freundlich's. With help of the linear regression coefficient, the best-fit isotherm model with experimental data is evaluated. The suggestion of the filtration technique with available filter media will assuage the contamination of arsenic from industrial water.

MATERIALS AND METHODS

Preparation of As (III) and Fe (III) Solutions

For the isotherm study, stock solutions of As and Fe of 500 ppb and 50 ppm respectively were prepared to conduct further experiments (Figure 1).

For the preparation of As stock solution of 500 ppb solution, 3.3mg of $\mathrm{As_2O_3}$ (anhydrate and powdered form, 99.9% As and 0.1% Fe) was poured into 40 ml of 10% NaOH and then 1 ml of 98% $\mathrm{H_2}SO_4$ was mixed. NaOH was used to dissolve the powdered As with distilled water very well as natural water and $\mathrm{H_2SO_4}$ was used to neutralize the basic solution. Then the mixture was diluted in 0.5 L distilled water and the solution was stored properly. The solvency of As depends on pH mostly. Thus, the 500ppb solution of As was made and further concentration was prepared from it by diluting it with distilled water. To ensure that the solution was prepared accurately As test was conducted with the HACH tool and 500 ppb concentration was confirmed.

$\mathrm{FeCl_3}$ was used for preparing a stock solution of Fe which will be used for mixing with As solution in the batch adsorption study. 0.1454 g of $\mathrm{FeCl_3}$ was used for preparing 1L of 50 ppm Fe. After the preparation of the solution, two Fe test was conducted on the sample, and the result was 50 $\pm$ 5 ppm.

Stock solutions were kept in a safe position and the used all instruments were washed well with distilled water as the chemicals ($\mathrm{As_2O_3}$, $\mathrm{FeCl_3}$, NaOH and $\mathrm{H_2SO_4}$ etc.) have come with cautious signs. And the basin was cleared with enough water.

Batch Study

A batch adsorption isotherm study was conducted with different amounts of Fe with a specific amount of As. From the stock solution of 500 ppb of As and 50 ppm of Fe, using this $V_1S_1 = V_2S_2$ formula a 200 ppb and 100 ppb As solutions and 1 ppm, 5 ppm, and 10 ppm Fe solutions were prepared.

The different initial concentration of As was mixed with various amount of iron to see the adsorbent capacity of arsenic onto the iron. 27 As-iron solutions were prepared for batch adsorption kinetic and isotherm study which were placed on a magnetic steerer at 650 rpm speed and the temperature was kept at 25ºC for 1,2, and 3 hr contact time respectively. After steering, the solution was kept for a moment and then filtered to separate the iron with adsorbed As.

Instead of using filter paper to separate the As-Fe compound from the water, a laboratory-based filter was prepared. It is a simulation of the column that would be used for the treatment of raw water samples.

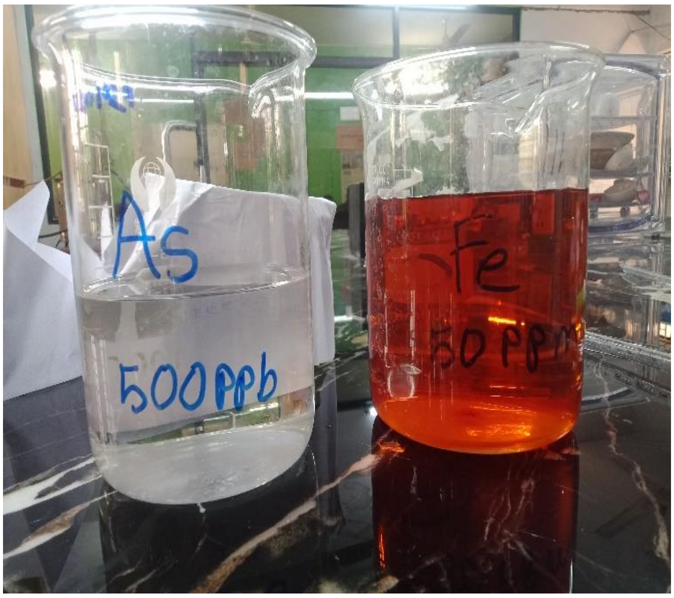


Figure 1: Kinetic Study for the adsorption of As

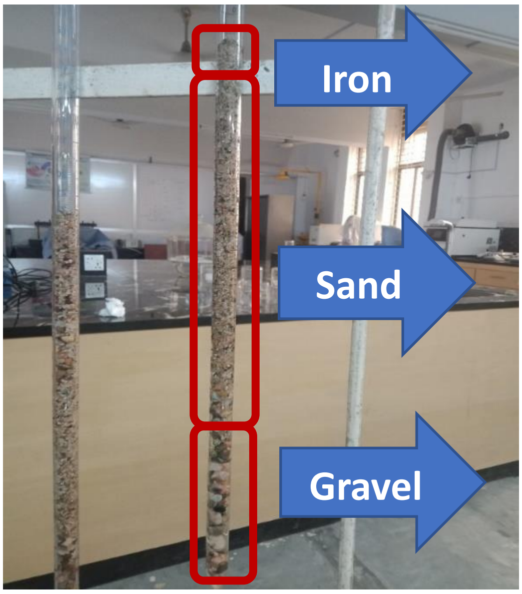


Figure 2: Filtration to separate As and iron from the water.

Column Study

The contaminated water was made to flow downwards through the filter media of sand, gravel, and iron bed. (Figure 2) The column was prepared with 0.005m^3 sand and 0.007m^3 gravel. As iron bed, scrap iron of 10 cm thickness, from the workshop was placed between the sand and gravel layer. The size of sand and gravel are respectively #16 passing #8 retained and 5/8'' passing ½'' retained. Water drifted downstream at 3 cycles to get the desired concentration of As (0.05 ppm) according to the ECR 1999. The column was backwashed after around 20-25 cycles and around 2 cm of sand was removed from the upper part of the filter media after 100 cycles of filtration. In the backwashing process, initially filter media was washed with arsenic-free normal water after that with distilled water (processed in the Environmental Engineering laboratory).

After filtration, the concentration of As was measured (Ce) using the Hack tools for As test. The amount of equilibrium concentration of As adsorbed at the adsorbate phase (qt) was determined by the subtraction of Ce from the initial concentration of As before the adsorption process (Co). The qe was found as the ratio of the amount of adsorbate (Fe) and the amount of adsorbent (As).

Fitting into Adsorption Isotherm Model

With the experimental data found from the column study Langmuir's and Freundlich's linear and non-linear model was fitted using the following equations.

Linearized and Non-linearized Langmuir's equations are given below,

$$\mathrm{q_e} = \frac{\mathrm{Q_{max}} * (\mathrm{K} * \mathrm{C_e})}{1 + (\mathrm{K} * \mathrm{C_e})} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\text{Or,} \quad \frac{\mathrm{C_e}}{\mathrm{q_e}} = \left(\frac{1}{\mathrm{Q_{max}}}\right) * \mathrm{C_e} + \left(\frac{1}{\mathrm{Q_{max}} * \mathrm{K}}\right) \ldots\ldots\ldots (2)$$

Linearized and Non-linearized Freundlich's equations are given below,

$$\mathrm{q_e} = (k' * \mathrm{C_e})^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$\ln \mathrm{q_e} = \left(\frac{1}{n} * \ln \mathrm{C_e}\right) + \ln K' \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

After plotting the graph for the experimental, Langmuir's, and Freundlich's model, using the linear regression coefficient (R^2), the fitness of the model with the experimental data was evaluated. Among the linear and non-linear models the non-linear curve shows the better result. When the difference of coefficient between the experimental and adsorption model is unity or near unity, was considered the best-fitted graph.

With help of Microsoft Excel using the LINSET function linear regression coefficient for linear Langmuir's and Freundlich's isotherm model. R^2 is also used for non-linear isotherm model fitting. In this case, R^2 was found as follows,

R^2 = 1-(sum of squared differences between model and experimental qe/sum of square differences between model and average of model qe)

Here model qe was found from equation (1) and the value of $\mathrm{Q_{max}}$ and K had been found by comparing equation (2) with y = mx+c.

A similar case was applied to Freundlich's isotherm model and in this case, K' and n can be found from the slope and intercept of the linearized form of equation 4 which will be plotted on a graph.

Here, $\mathrm{Q_{max}}$ and K is Langmuir constant for Langmuir's isotherm model whereas K' and n are Freundlich constant for Freundlich's equation that depends on the nature of the adsorbate and adsorbent at a particular temperature.

RESULTS AND DISCUSSION

The results found from the test were tabulated in table 1 and the equations used for evaluating qt and qe are (Co-Ce) and x/m or, Co/m respectively.

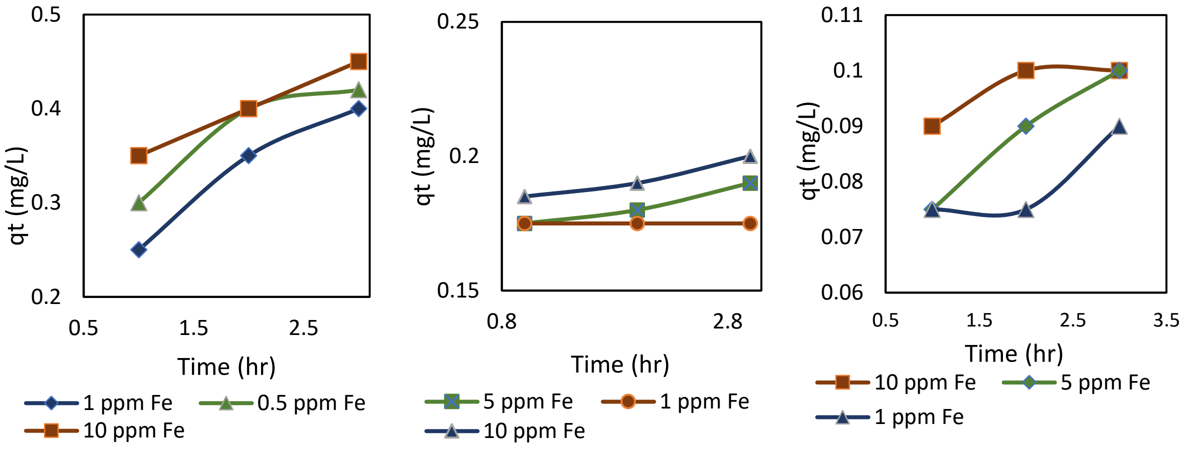
Here Ce/qe is the adsorption capacity of the iron for As. The kinetic study was conducted at pH 7 for different conduct times i.e., 1hr, 2hr, and 3hr.

Table 1 shows the experimental values that are observed from batch adsorption and column study. Using these data linearized, non-linear Langmuir's and Freundlich's isotherm model was plotted. The pH of the solution before and after putting on the magnetic steerer is around 7. The adsorption capacity of arsenic is found higher for 10 ppm iron while the initial concentration of iron was 0.5 ppm.

Table 1. Batch adsorption isotherm study

Time (hr)	Amount of As before adsorption (Co) (ppm)	Amount of Fe to be mixed (m)(ppm)	pH	Ce (mg/L)	qt (mg/L)	qe (mg/mg)	Ce/qe
1	0.1	1	7	0.025	0.075	0.075	0.33333
	0.1	5	6.9	0.025	0.075	0.015	1.66667
	0.1	10	7	0.01	0.09	0.009	1.11111
2	0.1	1	7	0.025	0.075	0.075	0.33333
	0.1	5	7.1	0.01	0.09	0.018	0.55556
	0.1	10	6.9	0	0.1	0.01	0
3	0.1	1	7.1	0.01	0.09	0.09	0.11111
	0.1	5	7	0	0.1	0.02	0
	0.1	10	6.9	0	0.1	0.01	0
1	0.2	1	7	0.025	0.175	0.175	0.14286
	0.2	5	7.1	0.025	0.175	0.035	0.71429
	0.2	10	7.1	0.015	0.185	0.0185	0.81081
2	0.2	1	6.9	0.025	0.175	0.175	0.14286
	0.2	5	7.1	0.02	0.18	0.036	0.55556
	0.2	10	7.1	0.01	0.19	0.019	0.52632
3	0.2	1	7	0.025	0.175	0.175	0.14286
	0.2	5	7	0.01	0.19	0.038	0.26316
	0.2	10	6.9	0	0.2	0.02	0
1	0.5	1	6.9	0.25	0.25	0.25	1
	0.5	5	7	0.2	0.3	0.06	3.33333
	0.5	10	6.9	0.15	0.35	0.035	4.28571

2	0.5	1	7.1	0.15	0.35	0.35	0.42857
	0.5	5	7	0.1	0.4	0.08	1.25
	0.5	10	6.9	0.1	0.4	0.04	2.5
3	0.5	1	7.2	0.1	0.4	0.4	0.25
	0.5	5	7.1	0.08	0.42	0.084	0.95238
	0.5	10	7.1	0.05	0.45	0.045	1.11111



(a) (b) (c)

Figure 3: Kinetic Study for the adsorption of As

Figure 1 shows the graphical presentation of the equilibrium concentration of adsorbed As over different contact hours. It shows the influence of As adsorption over different contact times clearly. Figure 1(a), (b), and (c) shows the batch adsorption kinetic study for 0.1 ppm, 0.2 ppm, and 0.5 ppm As concentration respectively. In the range of 1-3 hr(60-180 min) contact time arsenic was removed by the adsorption onto the iron of different concentrations. With an increasing rate of iron concentration the arsenic adsorbed on iron is increased as the surface area was increased. But for 0.2 ppm initial concentration of arsenic, the curve was going downward for the increment of iron concentration. Mainly at a 3-hour contact time adsorption capacity is the most effective. Nevertheless for adsorption of 0.5 ppm As onto 10 ppm iron 2 hr contact hour at 293k temperature was most effective for arsenic removal. As most of the cases show that 3 hr contact hour was effective, for further work 3 hr contact time was considered especially for plotting Langmuir’s and Freundlich’s isotherm model. For suggesting treatment plant design if the amount of available iron scrap is abundant then for faster treatment, 2 hr contact time will be decent otherwise for economic cases 3 hr contact time will be utilitarian.

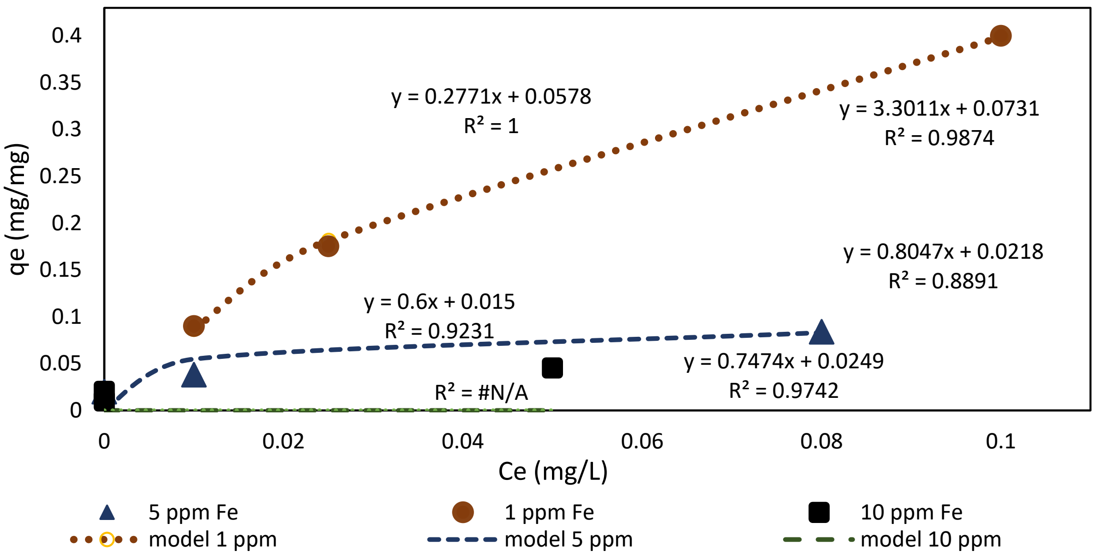


Figure 4: Experimental adsorption result showing the linear regression coefficient for fitting Langmuir's model qe with the experimental value

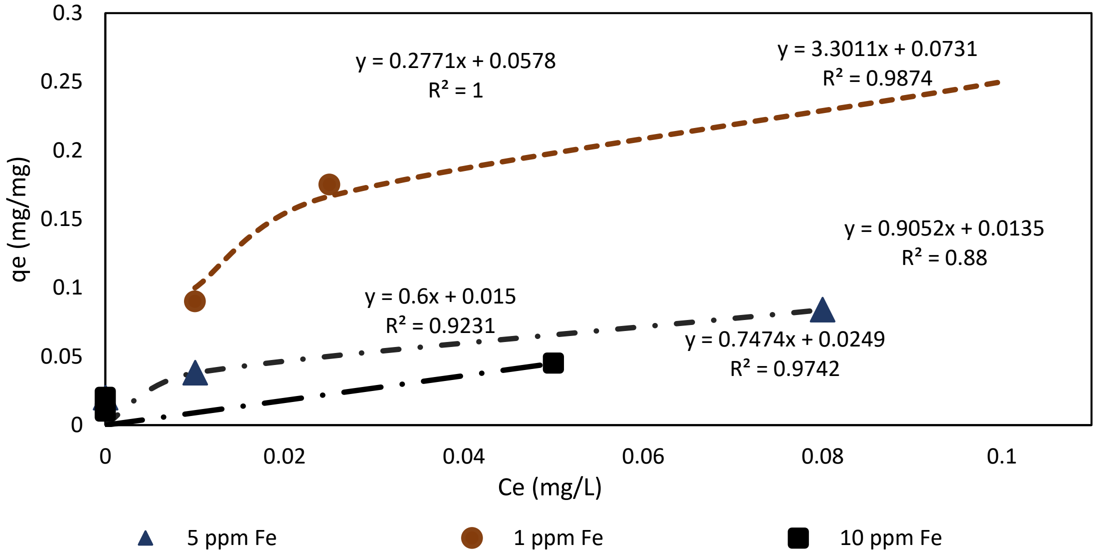


Figure 5: Result showing the linear regression coefficient for fitting non-linear Langmuir's model qe with the experimental value

Figure 4 shows the adsorption capacity of As vs the concentration of As measured after adsorption onto the iron according to linear Langmuir's isotherm model and Figure 3
Figure 5 shows experimental data fitting with non-linear Langmuir's isotherm. In the figures, considering 3 hr contact time the experimental plottings were shown with points, and the isotherm models with the help of equation (1) and equation (2) were shown in the dotted line. In both figures, they each have three curves for 1 ppm, 5 ppm, and 10 ppm iron concentration. Analyzing the linear regression coefficient of each curve it was clear that all of them have a value of unity or near unity which means that Langmuir's linear and non-linear models fitted well with the experimental value. But in both

Figure 4 and
Figure 5 3, 5 ppm iron concentration showed some difference but it was quite near unity. So, it could be told Langmuir isotherm fitted well with the experimental value and Q_{max} can be used for the adsorption capacity.

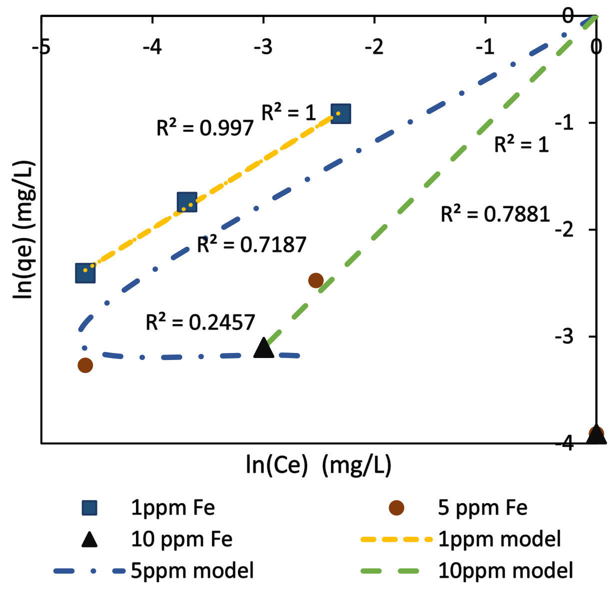


Figure 6: Experimental adsorption result showing the linear regression coefficient for fitting Linear Freundlich isotherm model qe with the experimental value.

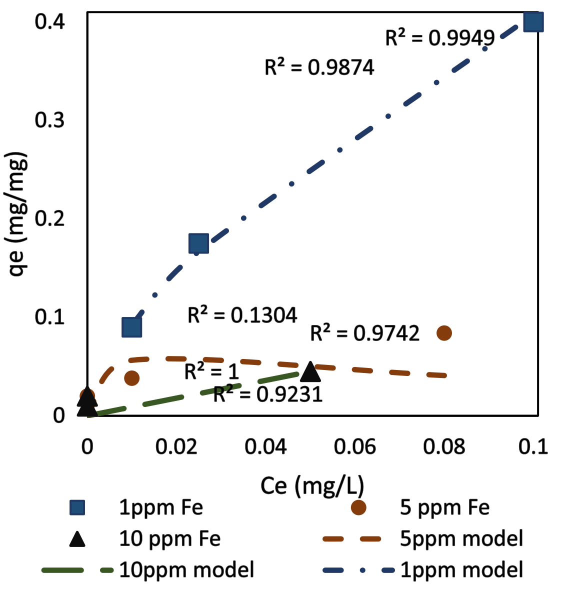


Figure 7: Result showing the linear regression coefficient for fitting Non-linear Freundlich isotherm
model qe with the experimental value.

Figure 6 and Figure 7 show the graph plotted for Freundlich's empirical adsorption isotherm equation both for linear and non-linear plotting. Using equations 4 and 5 and taking the logarithm function linearized form was considered for the linear plotting of the isotherm model. Here in each graph experimental curve was plotted using experimental data which was marked by symbols and using Freundlich's equation dotted line was plotted which indicates the model curve for 1 ppm, 5 ppm, and 10 ppm separately. From the figures, it was found that experimental data was not fitted well with Freundlich's isotherm model. By analyzing the linear regression coefficient value was not unity or near unity for 5 ppm iron concentration on the contrary for 1 ppm the coefficient was very near to unity and unity but for 10 ppm concentration coefficient was close but not very much close to unity. So, overall Freundlich's isotherm model was not fitted well with the experimental data as only one concentration fitted perfectly with the adsorption isotherm model.

Consequently, the adsorption isotherm model fitted well with Langmuir's isotherm model, and also the non-linear isotherm models fitted with the observed data.

Table 2: Linear regression coefficient for Langmuir's and Freundlich's isotherm model.

Iron Concentration	Langmuir's Isotherm Model			Freundlich's Isotherm Model		
	Q_{max}	k	R^2	n	K'	R^2
1ppm Fe	0.2	50	0.8582	1.554	1.79	0.98332
5ppm Fe	0.1802	59.7859	0.9972	6.472	0.027681	#NUM!
10ppm Fe	0.1725	26.5438	0.9308	2.588	0.014142	#NUM!

Table 2 shows the Q_{max}, k, and the linear regression coefficient of Langmuir's isotherm model and also n, K', and the linear regression coefficient from Freundlich's isotherm model. As Freundlich's adsorption isotherm model was not fitted well with the experimental data found from laboratory tests conducted on the adsorption of arsenic onto iron, only Langmuir's isotherm model will be considered. Q_{max} will be considered for the capacity calculation. It indicates the maximum capacity of the adsorbent and how much it can hold and keep the adsorbate on its surface. Though the value of Q_{max} is not dependent on the value of the initial concentration of adsorbent (iron) used, Q_{max} will be much more accurate with the increasing rate of the concentration of adsorbent as in this condition thermodynamic saturation condition is ensured. Q_{max} was found separately for different iron concentrations and similar for the K value and the linear regression coefficient.

Langmuir's constant K describes the adsorption equilibrium when the adsorbates are in contact with the adsorbent surface. Langmuir's adsorption isotherm model shows the fraction of the surface of iron that is adsorbed by arsenic molecules for a specific temperature and pressure of arsenic. This constant can describe the distribution of the adsorbate phase on the adsorbent phase.

From table 2, the higher value of Q_{max} was found for 1 ppm iron concentration but a higher K value was for 5 ppm concentration. As 5 ppm iron gives more surface area to adsorb than 1 ppm and the linear regression coefficient was more approaching the unity than 1 ppm concentration.

Adsorption capacity is related to the amount of adsorbed adsorbate on the adsorbent surface and which ultimately shows the removal efficiency of the adsorbent and the adsorption efficiency shows how faster the adsorption process will complete.

CONCLUSIONS:

Adsorption study of arsenic onto the iron at pH 6.9 to 7.1 and temperature 293 K gives the idea of the approximate amount of zero-valent iron needed for the proposed water treatment filter. With lower pH, the adsorption process does not work out as one test was conducted which shows a very small removal of arsenic. From the adsorption-contact hour relation, 3 hr contact time was taken as the most effective time. Analyzing the linear regression coefficient, Langmuir's isotherm model fitted well with the data. And calculating the Q_{max}, k, and the linear regression coefficient from the Langmuir isotherm model the adsorption was taken maximum for 5 ppm iron concentration. So maximum removal efficiency will be for 5 ppm iron concentration.

After two cycles of column study embedding zerovalent scrap iron as filter media along with sand and gravel, the concentration of Arsenic was 0 ppm and 0.05 ppm, respectively for the initial concentration of Arsenic 0.2 and 0.5 ppm which maintain the standard limit of As in drinking water according to IRC 1999. So, a treatment filter with iron scrap is proposed for arsenic removal from industrial wastewater.

ACKNOWLEDGEMENT:

We would like to express our humble gratitude to the Environmental Engineering Laboratory of KUET for their affable behavior to conduct required tests.

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