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ORIGINAL ARTICLE

Adsorption of Arsenic using Multan mitti

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ABSTRACT
In recent years the researchers debate that the adsorption technique is an economical method for groundwater treatment to remove the toxic metals or inorganic effluents like Arsenic which cause health hazards to the living organisms. The adsorption techniques are categorized into physical, chemical, and Biological methods. Adsorption, ion exchange, and coagulation/filtration are physical methods. The studies revealed that among all these methods, Adsorption is the best fitting and low-cost for the high percentage removal of Arsenic from the water. It is known as the efficient unit operation in the chemical engineering processes employed for the segregation of the wastewater pollutants to meet the demand for drinking water in the most populated areas. Multan mitti which has a high adsorptive nature is selected for the removal of Arsenic in these studies. The efficiency of adsorption on Multan mitti was explored with various parameters such as contact time 30 min, dosage 2.0 gm with 50 µg/L concentration of Arsenic, and pH 7 was identified as the optimum conditions for the maximum Arsenic adsorption. The highest removal of Arsenic is 81% with 2.0 gm of dosage. The experimental studies reveal that Langmuir and Freundlich's isotherms were found good fitting isotherm models for the Arsenic removal on Multan mitti.
Keywords: Multan mitti**,** *Arsenic, Groundwater treatment*

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INTRODUCTION

The groundwater of several countries contains high levels of Arsenic and it is highly toxic in its inorganic form. The inorganic arsenic, being the most significant chemical contaminant in drinking-water globally causes cancer with its consumption.

The contaminated groundwater with arsenic causes the greatest threat to public health. The high levels of inorganic arsenic are present in the groundwater of industrial areas and it is widespread in the countries of Argentina, Bangladesh, Chile, China, India, Mexico, and the United States of America.

Arsenic, an alloying agent is utilized in the processing of glass, pigments, textiles, paper, metal adhesives, wood preservatives, and the hide tanning process and, to a limited extent, in pesticides, feed additives, and pharmaceuticals industries.

It is reported that at least 140 million people in 50 countries have been drinking water containing arsenic of 10µg/L [1]. To prevent further exposure to arsenic the small, low cost and effective methods like adsorption, coagulation, ion exchange and reverse osmosis, etc are practiced. Taking these hazards of life into consideration the studies of adsorption on Multan mitti had given been performed to remove the arsenic from the contaminated groundwater for the provision of a safe water supply to mankind, the flora, and the fauna of industrial regions.

MATERIAL AND METHODS

Selection of Adsorbents:

Multan mitti is a type of clay consisting of Aluminium Silicate with other impurities in minimal proportions. It is known as fullerene mud and rich in lime [2]. Fuller's earth is lighter and more porous than other clays [3]. Electronic microscopic studies have shown these crystals to be very small,

approximately 0.4 x 0.004 microns. They contain the complex multi-center crystalline structure of oxides and hydroxides of magnesium, Aluminium, zinc, and silicon. Despite this basic crystalline structure, the powder behaves as though it were amorphous. It's high adsorptive, Base Exchange and bonding properties give its importance as an industrial substance [4]. Due to its adsorptive nature, Multan mitti has also been traditionally used on TajMahal to maintain the shine on marble [5-10] by removing air pollutants. The high porosity of Multan mitti played a major role in the work of Arsenic adsorption.
In the screening tests, 90% Arsenic adsorption is observed on Multan mitti, this proves that it can adsorb the inorganic pollutants from the water. Hence the adsorption studies are carried with various parameters contact time, Dosage, Concentration, and pH. The physicochemical characterization of Multan mitti has been presented in Table-1.

Table-1: Characterization of Multan mitti

S.No	Parameters	Result
01.	Surface area	16.8 cm^2
02.	Particle size	210 mesh
03.	Particle density	0.56
04.	Moisture content	0.5%
05.	Porosity	41
06.	Bulk Density	650-750 Gm/cc
07.	p^H	7.5 – 8.5

RESULTS AND DISCUSSION

Effect of contact time between Arsenic and Multan mitti

As contact time is one of the most effective factors in the batch adsorption process through Arsenomolybdate method [11, 12]. The effect of contact time on the adsorption of Arsenic using Multan mitti was investigated. The percentage of Arsenic metal ion removal with respect to time is represented in Figure-1. Adsorption rate gradually increased from 0 min to 30 min and the optimal removal efficiency was from 30 min to 40 min. Further increase in contact time did not show any significant change as adsorption sites are completely covered with the adsorbent. This shows that the adsorption phase reached equilibrium.

Determination of adsorbent dosage:

Taking the concentration of 50 µg Arsenic, 1 gm. of adsorbent the adsorption studies are performed at optimum contact time 30 min. As the active sites are more at lower adsorbent, the Arsenic removal efficiency increases with increase in adsorbent dosage and becomes constant at dosage of 2 gm signifying the equilibrium shown in the figure-2. With the increase in adsorbent dosage aggregation of particles take place, as a result efficiency of Arsenic uptake decreases. The optimum dosage is reported as 2gm from the investigation.

Effect of concentration on Arsenic removal:

Varying the initial concentrations of Arsenic from 10µg to 80µg the effect of change in adsorption efficiency is studied. Keeping time and adsorbent dosage constant the batch experiment is performed to observe the Arsenic removal efficiency. This study gave conclusion that the increase in Arsenic concentration is directly proportional to the increase in Arsenic removal efficiency as shown in the figure-3.This shows that initial concentration has only a very little effect on adsorption and the increase in concentration showed a better impact on the removal efficiency.

Determination of Optimum pH:

The pH value is one of the important impact factors during the adsorption process that can help the heavy metal ions binding to the adsorbent surface. Since the pH value affects the binding sites on the surface of the adsorbent, the hydrogen ions could combat with heavy metal ions at low pH values [13, 14].
Maximum removal efficiency of Arsenic was increased gradually from 3 to 7 as shown in the figure. The highest removal efficiency was between pH 7 to 8 and then decreased slowly after neutral condition.
Because of the competition between the heavy metal ions and H+ ions, the surface active sites of Multan mitti become positively charged at a low pH value, increasing the Arsenic removal efficiency. However, these surface active sites became more negatively charged with the increasing pH value and later the low tendency of competition helped to enhance the adsorption of the positively charged metal ions to combat with OH^- ions through electrostatic force [15, 16].

Effect of Temperature on Removal efficiency:

With Arsenic concentrations of 14µg, 28.6µg, 42.6µg the effect of temperature on adsorption of the Arsenic was studied by conducting different sets of experiments at different temperatures, that is, at 0°C, 20°C, 40°C, 60°C and 80°C. It was observed that the adsorption of Arsenic increases with the increase in the temperature. Same results were obtained on the sorption of Pb^+ and Cd^+ by Caladium bicolour biomass [17].

Adsorption Isotherm Models:

The adsorptive removal of Arsenic by Multan mitti particles was studied using the adsorptive isotherm like the Langmuir, Freundlich, Temkin isotherm models.

Langmuir Adsorption Isotherm Model:

The Langmuir adsorption isotherm predicts the capacity of Arsenic adsorption with brick powder is stronger or weaker following its phenomenon and equation [18, 19].

A plot of q_e/c_e against c_e yielded a straight line graph with values of Q_0 and b_L calculated from the slope and intercept respectively as shown in figure- 6.

Table-2 shows R^2 value as 0.960 – 0.990 and the values of slope and intercept were determined as -0.004 and 0.502 respectively. The figure-6 showed the non linear form as lines were not originated from the axis indicating that the adsorption of Arsenic on Multan mitti was unfavourable process. Hence, the adsorption studies of Arsenic removal on Multan mitti does not fit for the Langmuir Isotherm.

Freundlich Adsorption Isotherm Model:

Freundlich Isotherm describes the Arsenic adsorption characteristics for the heterogeneous surfaces and active sites of brick powder with different energies [18, 20] and slope and intercept of the plot is calculated using the equation [19, 21].

From the figure-7 and Table-2 it is reported that the results of Freundlich isotherm model showed a better fit to this experiment giving linear line in the graph. The data gives the values of R^2 0.999 which illustrates that the adsorption of Arsenic to Multan mitti particles was favourable and spontaneous process on heterogeneous surfaces.

Temkin Adsorption Isotherm Model:

The Characterization of the adsorption can be described by Temkin isotherm model equation by presuming that the heat of Arsenic molecules decrease precisely with the increase in coverage of the adsorbent (Multan mitti) surface and the type of binding energies distribution [21-23] with its equation.

The heat of adsorption is used to describe the adsorption process in Temkin isotherm model [24-26]. Temkin Isotherm also showed good fit with Arsenic adsorption process as shown in Figure-8. a_T and b_T values were 0.280 and 1.007 respectively (Table-2). R^2 value is 0.954 which is less than 1. Since the values of slope and intercept are positive the adsorption process was exothermic.

Adsorption Kinetic Models:

The experimental data were tested with the pseudo-first-order kinetic model, pseudo-second-order kinetic model, Elovich kinetic model, and intraparticle diffusion models to analyze the kinetic parameters of Arsenic removal using Multan mitti. The chemical reaction of functional groups present on the surface of adsorbate and adsorbent is observed by the mechanism of adsorption.

Pseudo first-order kinetic model:

The relationship between the rate the sorption sites of the adsorbents occupied and the number of unoccupied sites is given in Pseudo first order kinetic model by using the Lagergren equation [27]

$\log q_e - q_t = \ln (q_e\text{-}q_t)$

The linear plot of $\ln (q_e\text{-}q_t)$ against time determines the rate constant k.

The plot of Pseudo first order did not show a linear relationship in Figure-9. The rate constant k_1 is low initially as Arsenic concentration increased from 10µg to 40µg the rate constant also increased but R^2 values are high initially and decreases with increase in concentrations as in the Table-3. Hence, Pseudo first order kinetic does not fit to the Arsenic adsorption studies as reported in the Chromium adsorption studies using Multan mitti.

Pseudo second – order kinetics:

Pseudo second order kinetic model explains the dependency of the adsorption capacity of the adsorbent on time. The applicability of the pseudo-second-order kinetics has to be tested for the estimation of q_e with rate equation given by Ho 1995 [28].

A linear relationship is given from the plot of t/q_t versus t which determines the k_2 and q_e form the slope and intercept respectively.

Figure- 10 shows the plot of pseudo second order kinetic model with linear relation. The R^2 values of pseudo second order are higher than pseudo first order in Table -3. This proves that the adsorption of Arsenic on Multan mitti apt to the pseudo second order kinetic.

This assumes that each Arsenic ion is adsorbed on to adsorption sites allowing a stable bi nuclear bond to form. The same result had been reported in the studies of Chromium adsorption using Multan miiti.

Table-2. Statistical comparison values of adsorption isotherm models for Arsenic adsorption by Multan mitti

S.No	Parameters	Langmuir Adsorption Isotherm				
	Temperature ^{0}C					
		0	20	40	60	80
01.	R^2	0.960	0.998	0.996	0.991	0.999
	ASS	0.128	0.025	0.036	0.060	0.016
	Q_0	-0.005	-0.003	-0.004	-0.004	-0.005
	b_L	0.409	0.372	0.425	0.462	0.502
	Freundlich Adsorption Isotherm					
02.	R^2	0.994	0.999	0.998	0.982	0.999
	ASS	0.002	0.000	0.000	0.000	0.000
	Log k_f	0.418	0.589	0.620	0.648	0.632
	l/n	0.205	-0.001	-0.0008	-0.008	0.003
	Temkin Adsorption Isotherm					
03.	R^2	0.883	0.951	0.944	0.952	0.954
	ASS	0.060	0.024	0.028	0.024	0.023
	a_T	0.173	0.209	0.283	0.259	0.280
	b_T	1.083	0.793	0.883	0.905	1.007

Table-3. Data of kinetic parameters for Arsenic adsorption using Multan mitti

S.No	**Parameters**	**Arsenic Concentration (10 μg/L)**	**Arsenic Concentration (20 μg/L)**	**Arsenic Concentration (30 μg/L**	**Arsenic Concentration (40 μg/L)**
	Pseudo first order kinetic model				
01.	R^2	0.973	0.910	0.932	0.848
	ASS	0.001	0.011	0.007	0.026
	K_1	-0.107	-0.127	-0.079	-0.090
	Pseudo second order kinetic model				
02.	R^2	0.985	0.966	0.955	0.899
	ASS	0.000	0.002	0.004	0.013
	K_2	0.128	0.139	0.162	0.193
	Elovich model				
03.	R^2	0.936	0.946	0.838	0.091
	ASS	0.006	0.005	0.029	0.091
	α	-6.034	-7.380	-4.387	-4.749
	β	19.02	20.76	14.66	14.66
	Intraparticle diffusion model				
04.	R^2	0.975	0.953	0.891	0.754
	ASS	0.001	0.004	0.015	0.056
	k_{id}	-1.090	-1.308	-0.794	-0.882
	I	16.21	17.19	12.54	12.58

Table-4: Thermodynamic report of Arsenic adsorption by Multan mitti

S.No	**Temperature**	**ΔG (KJ/mol)**	**ΔS (KJ/mol)**	**ΔH (KJ/mol)**
1.	273	-72.63	-5.71	-0.006
2.	293	-51.15		
3.	313	-49.44		
4.	333	-55.37		
5.	353	-58.69		

Table-5: Equilibrium (R_L) values at different concentrations and temperatures.

S.No	**Temperature (°C)**	**Concentration of Arsenic (μg/L) and R_L values**		
		10μg/L	**30μg/L**	**50μg/L**
01.	0	0.1005	0.033	0.200
02.	20	0.1003	0.033	0.200
03.	40	0.1004	0.033	0.200
04.	60	0.1004	0.033	0.200
05.	80	0.1005	0.033	0.200

Elovich Model:

The chemisorptions of gases onto heterogeneous surfaces and solid systems had been studied using the Elovich kinetic model and now the study of the pollutants removal from aqueous solutions can be applied to this model. It describes the second order kinetics assuming that the solid surface has heterogeneous energy but does not support any mechanism for adsorption [29].

Though the Elovich equation could also be used to explain Arsenic adsorption on to Multan mitti the figure – 11 i.e., the plot of q_t and log t does not yield a straight line from the origin. The R^2 values are low (0.838) and slope (α) and intercept (β) are determined with negative and positive values respectively as shown in Table–3. This denotes that the Elovich kinetic model is extensively applicable for chemisorptions kinetics [30].

Intraparticle Diffusion Model:

The rate-limiting step is the main feature of intraparticle diffusion model in adsorption studies. This is achievable by plotting a graph between the amount of ion adsorbed and the square root of time that yields a straight line. The equation given by Weber and Morris in 1963 supported to calculate the amount of Arsenic adsorbed (mg/g) at time t (min)[31, 32].

When the kinetic data was analysed using the intraparticle diffusion model, it was observed that the plot did not pass through the origin indicating that intraparticle diffusion was not the only rate-limiting step but also does not fit to the experimental data as shown in figure-12 and Table-3.

Thermodynamic of Adsorption:

Thermodynamic parameters of Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated to determine the adsorption process nature, spontaneity, and its applicability. The intercept gives the values of K_c. The Gibbs free energy is related to K_c as in the equation given below [33].

$\Delta G^\circ = - RT \ln K_c$

The changes in enthalpy (ΔH°) and entropy (ΔS°) for Arsenic adsorption were calculated from the slope and intercept of the plot following Van't Hoff equation [34].

ΔG° is a change in free energy. The negative values of ΔG° indicate a favourable and spontaneous [35].

An illustration of figure 13 gave a linear relationship with enthalpy (ΔH°) and entropy (ΔS°) evaluated from the slope and intercept respectively. The negative values of ΔG° shown in the Table-4 indicate the approving and instinctive process and the negative values of ΔH° express that Arsenic adsorption process by Multan mitti is exothermic. The results are similar to the study of Chromium adsorption on Multan mitti by Gandhi et al.

The negative values of ΔS° suggest the adsorption process involves an associative mechanism that causes the decrease in randomness between adsorbate and adsorbent [36, 37] and does not show any significant change in the internal structures of the adsorbent during the adsorption process. ΔS is negative because the adsorbate molecules find no space to move about on the adsorbent surface.

Equilibrium parameter:

To find out the efficiency of the adsorption process, the dimensionless equilibrium parameter, R_L is calculated by using the following equation [38].

$$R_L = \frac{1}{1 + b\,C_o}$$

Where C_o is the initial concentration (mg/L), b is Langmuir isotherm constant. Values of the equilibrium parameter illustrate the differences in the shapes of the isotherm. The R_L values that lie between 0 and 1 indicate favourable adsorption. The R_L value above 1 indicates unfavourable. These values are presented in Table-5 and Figure-13.

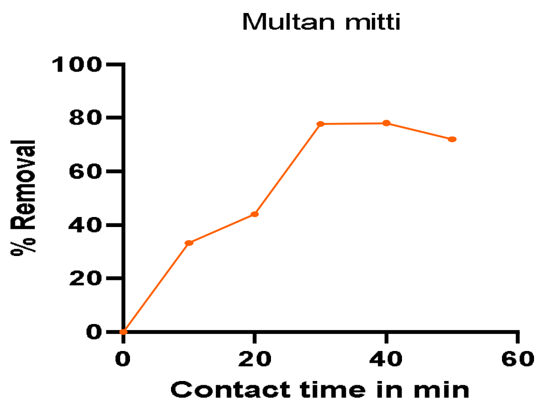

Figure-1: Variation of contact time between Arsenic and Multan mitti

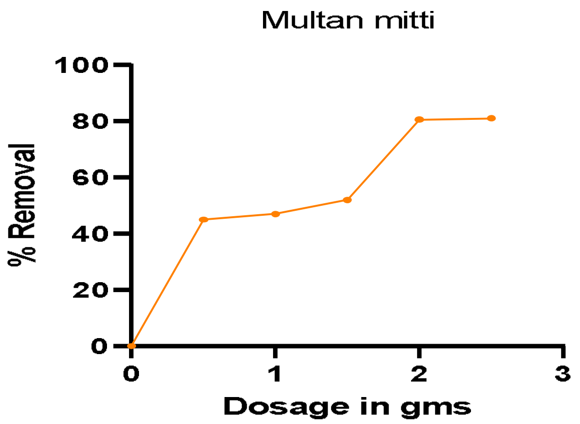

Figure-2: Variation of dosage between Arsenic and Multan mitti

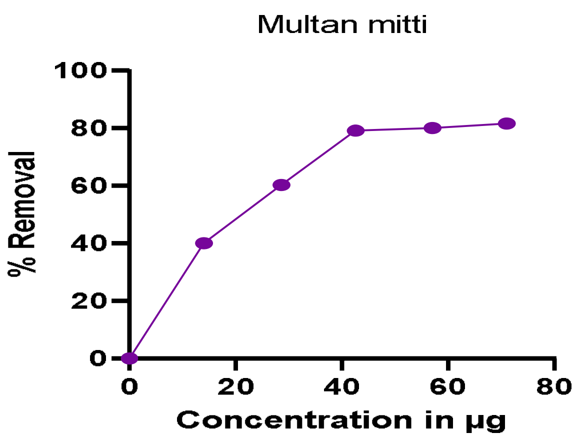

Figure-3: Variation of concentration between Arsenic and Multan mitti

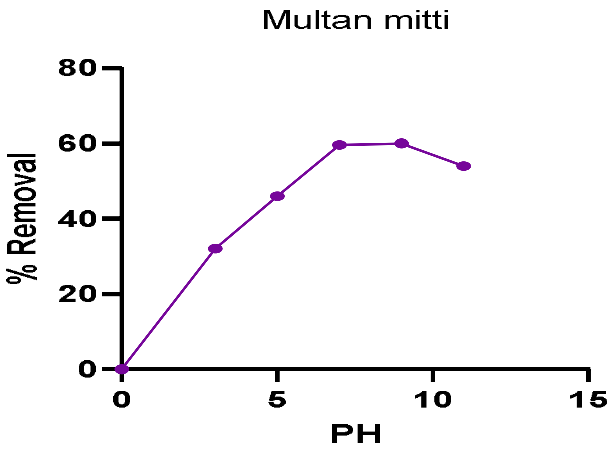

Figure-4: Variation of p^H between Arsenic and Multan mitti

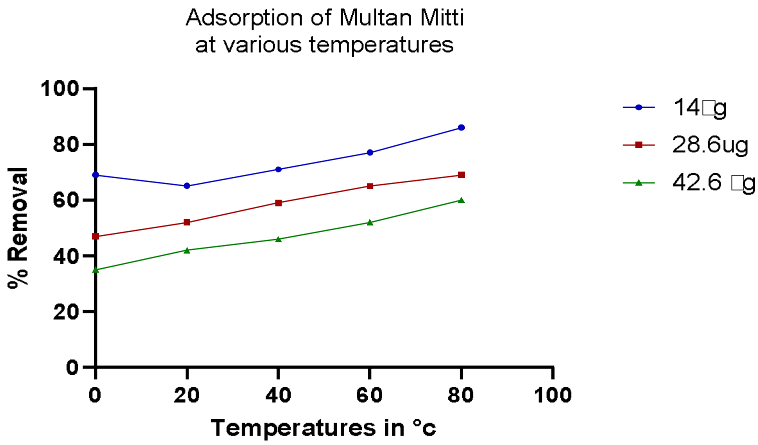

Figure- 5: Effect of temperatures on Arsenic removal

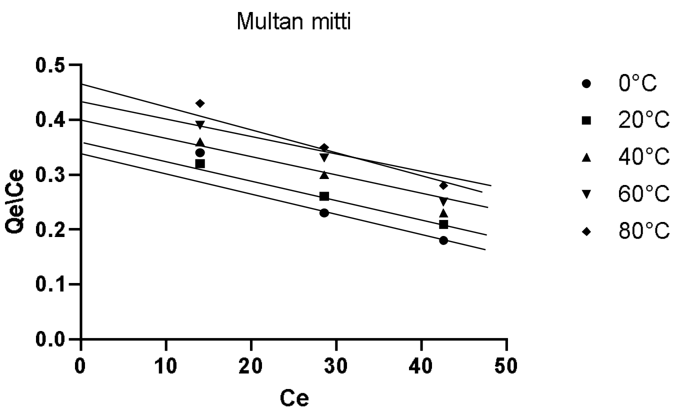

Figure- 6: Langmuir Isotherm removal of Arsenic by Multan mitti

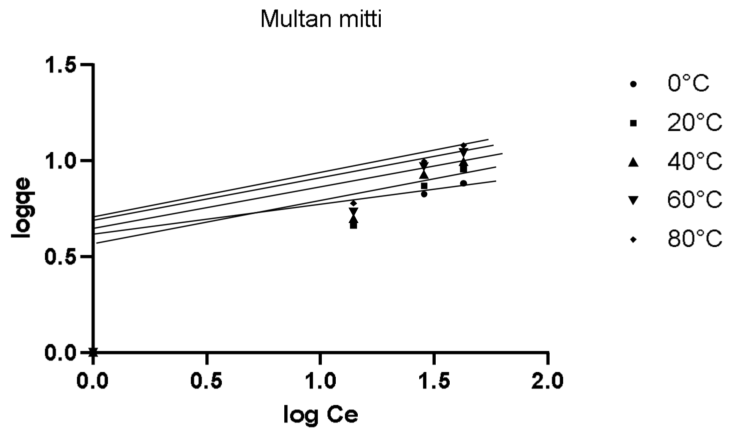

Figure-7: Freundlich Isotherm removal of Arsenic by Multan mitti

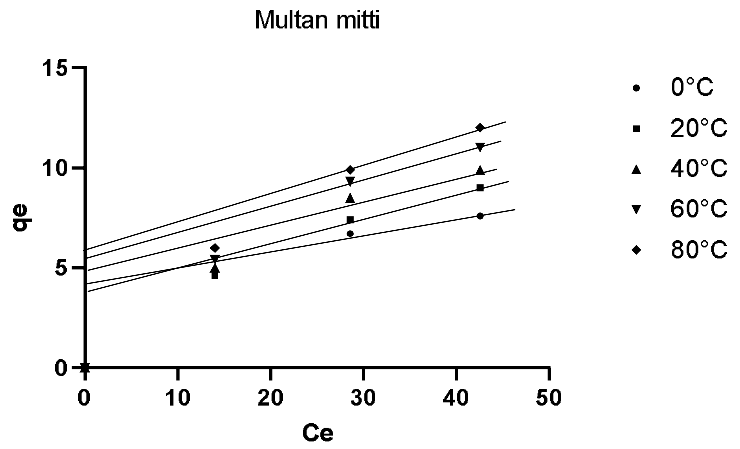

Figure-8: Temkin Isotherm removal of Arsenic by Multan mitti

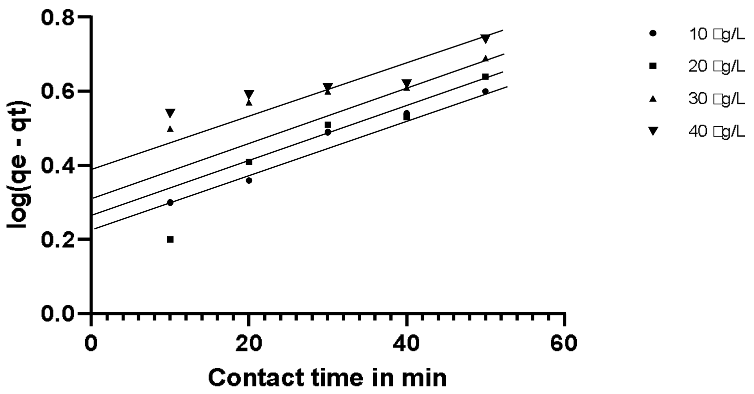

Figure-9: Pseudo first order kinetic model

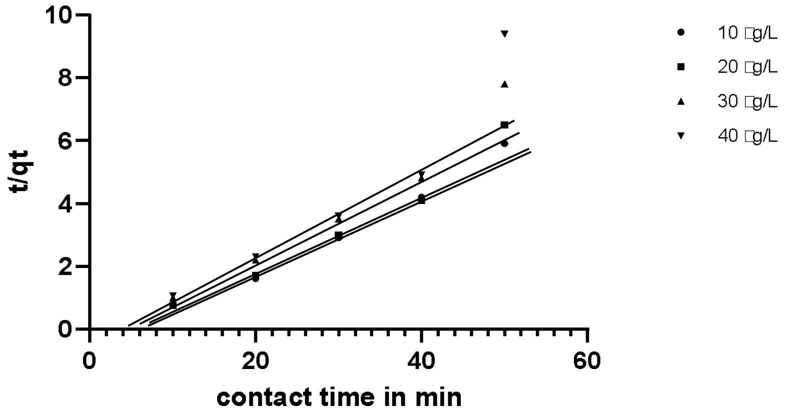

Figure-10: Pseudo second order kinetic model

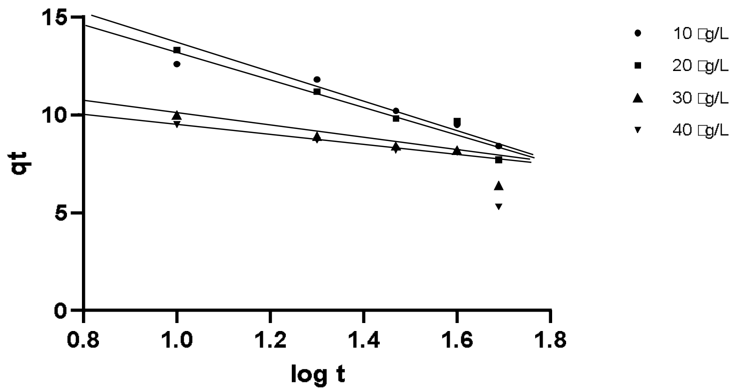

Figure-11: Elovich kinetic model

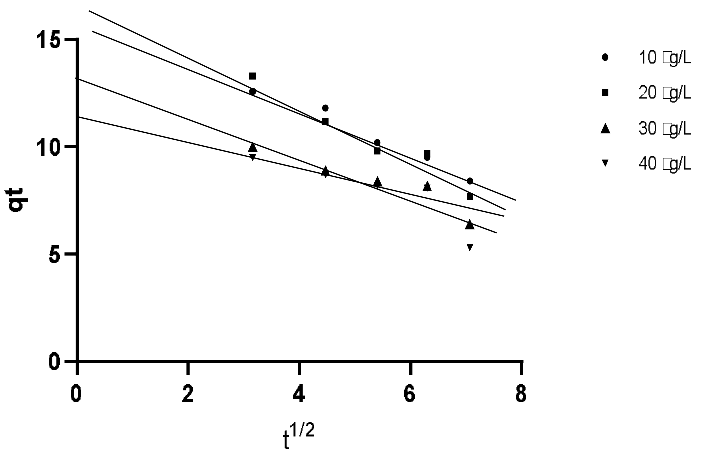

Figure-12: Intra particle diffusion model

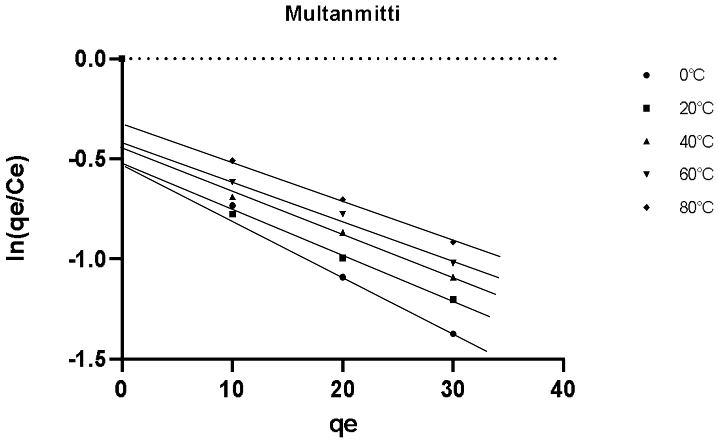

Figure -13 : Relationship between ln (q_e/c_e) and q_e for the removal of Arsenic by Multanmitti

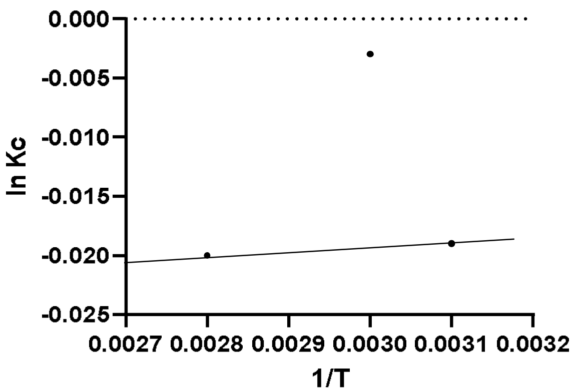

Figure-13: Relationship between ln (K_c) and 1/T for the removal of Arsenic by Multanmitti

CONCLUSION

The demonstration of Arsenic adsorption revealed that the low cost adsorbent Multan mitti showed its efficiency for the removal of Arsenic from industrial ground water. The batch experiment showed the adsorption process was affected by the parameters like contact time, initial concentrations of Arsenic, dosage, p^H and temperature. The isotherm models explained the efficiency of Arsenic adsorption process on Multan mitti and kinetic studies played a role in adsorption process with various mechanisms. Thermodynamic and equilibrium parameters investigation reported that the Arsenic adsorption using Multan mitti is suitable, exothermic and spontaneous in nature.

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