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As (v) Removal from Waste Water Using Class F Fly Ash as an Adsorbent

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ABSTRACT

Arsenic occurs in both organic and inorganic forms in snatural waters but organic arsenic is of little importance as it goes through biotransformation and detoxifies through methylation. Inorganic arsenic occurs in -3, 0, +3, and +5 oxidation states in aquatic systems. Inorganic species of arsenic [As(III) and As(V)] represent a potential threat to the environment, human health, and animal health due to their carcinogenic and other effects.

The fly ash carbons occur in the residual coal ash as a result of the incomplete combustion process. Due to the increasing applications of activated carbons, fly ash carbon may take a special place amongst the carbon materials that are produced as a major co-product in the pyrolysis of different starting materials for the production of liquids and gases.

Fly ash collected from Kota thermal power plant(Rajasthan) was found to be class F fly ash as amount of $SiO_2 > 60\%$.

Batch methods were used in this study to investigate arsenic adsorption using a clean, washed ash. ashStock solutions of As(V) were prepared by dissolving sodium salt heptahydrate of arsenic (Na2HAsO4·7H2O) . Experimental results indicated that pH had a significant effect on arsenic adsorption. Experimental equilibrium data of arsenic adsorption onto fly ash agglomerates can be fitted by Freundlich and Langmuir isotherm, while kinetics follows a pseudo second order model.

The negative values of ΔG^o *and* ΔH^o *indicated that adsorption was spontaneous and exothermic process. The developed adsorption system is useful and can be used for the removal arsenic from contaminated water.*

INTRODUCTION

The present work examines the possible use of fly ash, a by-product of coal power stations, as a means of removing arsenic (V) from water, or equivalently, of restricting its movement in the industrial effluents. From previous studies it was found that fly ash has significantly higher affinity towards heavy metals mainly present as cationic or non charged species compared to those present as anionic species.

Arsenic (As) poses a significant water quality problem and challenge for the environmental engineers and scientists in the world. Long-term exposure to arsenic in drinking water(1,2) is mainly related to increased risks of skin cancer, but also some other cancers, and other skin lesions such as hyperkeratosis and pigmentation changes. Occupational exposure to arsenic, primarily by inhalation, is causally associated with lung cancer. Clear exposure–response relationships and high risks have been observed.

The element arsenic occur in environment in different oxidation states and form various species, e.g., As as As (V), As (III), As (0) and As (-III). In oxidized environment, As appears mostly as oxyanions. Arsenic cannot be easily destroyed and can only be converted into different forms or transformed into insoluble compounds in combination with other elements. As (v) in +5 oxidation state is more stable than +3 oxidation state.

Fly ash(3,4) is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys of coal-fired power plants, and together with bottom ash removed from the bottom of the furnace is in this case jointly known as coal ash.

It was found that fly ash has significantly higher affinity towards heavy metals mainly so it can be used for removal of heavy metals (5) from waste water.

Classification of Fly Ash:

1. **Class F fly ash**

The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash, also called acidic fly ash. This fly ash contains more than 70% (SiO_2 + Al_2O_3) and less than 20% (CaO).

2. **Class C fly ash**

Fly ash produced from the burning of younger lignite or sub-bituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash(also called basic fly ash) hardens and gets stronger over time. Class C fly ash generally contains less than 70 %(SiO_2+ Al_2O_3) and more than 20% (CaO).

The batch adsorption studies(6) conducted to remove arsenic using fly ash was highly pH dependent and the optimum pH for maximum adsorption was found to be at pH 6.0. Also the effect of contact time, initial adsorbate concentration and adsorbent dose was studied.

The equilibrium study(7) depicts that Freundlich isotherms had higher coefficients of determination and lower chi-square values at all temperatures, suggesting that the Freundlich isotherm(8) was the best-fitting isotherm.

Kinetic(9) parameters fitted for pseudo second order kinetic model.

Thermodynamic study(10,11) depicts the endothermic and non spontaneous nature of the adsorption process.

EXPERIMENTAL SESSION

1. **Activation of fly ash (adsorbent preperation)**

Fly Ash collected from the Thermal Power Plant, Kota (Rajasthan) India was washed several times with distilled water and left to dry in oven at 120^0 C for 90 min. and then subjected to chemical activation.

Fly Ash sample was soaked in N/2 H_2SO_4 solution for 24 hrs. Then it was filtered and dried into oven at 500^0 C for overnight.

2. **Arsenic Solution (Absorbate)**

Stock solutions of As (V) were prepared by dissolving sodium salt heptahydrate of arsenic (Na2HAsO4·7H2O) in double-distilled water (at a concentration of 1g/L) and the experimental solutions were obtained by diluting the stock solution to the required concentrations (50 – 300ppm.). The solution pH (2,3,4,5,6,8) was adjusted with 0.1 N HCl or 0.1 N NaOH. The pH of solution was measured using a pH meter.

The residual arsenic concentration in the solutions was analyzed by UV-Vis spectrophotometer.

3. **Batch Experiment**

The process consist of contacting a whole volume of adsorbate/feed solution (hydrated sodium hydrogen arsenate solution) with a quantity of adsorbent (chemically activated fly ash) in volumetric flask. The mixture is stirred using a magnetic stirrer to facilitate mass transfer. After desired period of time generally when equilibrium has been attained, the adsorbent and solution are seperated, by filtration.

OBSERVATION

1. **EFFECT OF CONTACT TIME**

The contact time is one of the most important parameters for practical application. The effect of contact time onto the adsorption of arsenic (+5) on fly ash at room temperature,adsorbent dose of 5 g and at pH6 is shown in plot 1

The maximum removal 90.7% for removal of As (v) was obtained at 200 min. A further increase in contact time had an insignificant effect on the amount of adsorption (adsorption capacity). This phenomenon is attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

2. EFFECT OF pH

Effect of Ph on % removal of arsenic (+5) using fly ash is shown in plot 2.

In order to determine the preferred pH for adsorption of As(v) over fly ash, the uptake of As (v) as a function of hydrogen ion concentration was studied.

adsorption usually increases as the pH is increased. Lower adsorption of metal ion at acidic pH is probably due to the presence of excess H^+ ions competing with the cation groups on the metal ion for adsorption sites. At higher pH, the surface of activated carbon particles may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction.

As pH of the solution increases % removal of metal ion also increases. Maximum removal found to be at pH 6, which was chosen as an optimum pH condition for further experiments. pH parameter is very important since it strictly depends upon the nature of adsorbate and adsorbent. Also, it is an established fact that As(V) is more strongly adsorbed when where pH is acidic. One reason for the change of pH may be the ion exchange process.

3. EFFECT OF ADSORBENT DOSE

Effect of adsorbent dose on removal of arsenic (+5) is shown in plot 3 the removal of arsenic increases with increase in adsorbent dose from 1 to 5 g/L respectively. keeping initial solute concentration at 50ppm. It is found that after dosage of 5g/L, there is no significant change in percentage removal of arsenic.

The increase in percentage removal could be attributed to the availability of more number of adsorption sites at the solid phase. Availability of specific surface area and micropore volume plays a vital role for surface adsorption process. However, in present investigation, with further increase in adsorbent dose, the removal extent remains almost constant indicating the saturation of adsorption sites. The saturation of the active sites may also be due to the overlapping of active sites at higher dosage as well as the decrease in the effective surface area resulting in the accumulation of exchanger particles. So,5g/L.is considered as the optimum dose and is used for further study.

4. EFFECT OF INITIAL METAL ION CONCENTRATION

Effect of initial metal ion concentration on % removal of As(v) is shown in plot 4.

The initial concentration provides an important driving force to overcome all mass transfer resistance of the adsorbate between the aqueous and solid phases.

As the concentration of metal ion increases, more and more surface sites are covered and hence at higher concentrations of metal ions the capacity of the adsorbent get exhausted due to non-availability of the surface sites.It is therefore evident that at low concentration ranges the percentage of adsorption is high because of the availability of more active sites on the surface of the adsorbent.

From table 4 it is clear that the percentage of arsenic ions removed at 50, 100, 150, 200,250 and 300 ppm. levels at 50 min are 66.8, 64.9, 63.4, 61.5, 59.7 and 57.7% respectively. Adsorption study at 45 min. reveals that % removal of 50, 100, 150, 200,250 and 300 ppm. Solutions are 67.9, 66.4, 64.5, 63.7, 62.8 and 60.2 % respectively.

Table 1: Freundlich isotherm constants for adsorption of As (v) ions at 200 min.

m = 1/n	n	C = log Kf	Kf	R	r2
0.635	1.574	0.908	8.09	0.994	0.99
0.686	1.457	0.704	5.05	0.995	0.991
0.654	1.529	0.669	4.67	0.99	0.981
0.673	1.485	0.478	3.01	0.982	0.966
0.684	1.461	0.527	3.36	0.984	0.969
0.649	1.54	0.637	4.33	0.9899	0.98

Table 2: Langmuir isotherm constants for adsorption of As(V) ions at 200 min

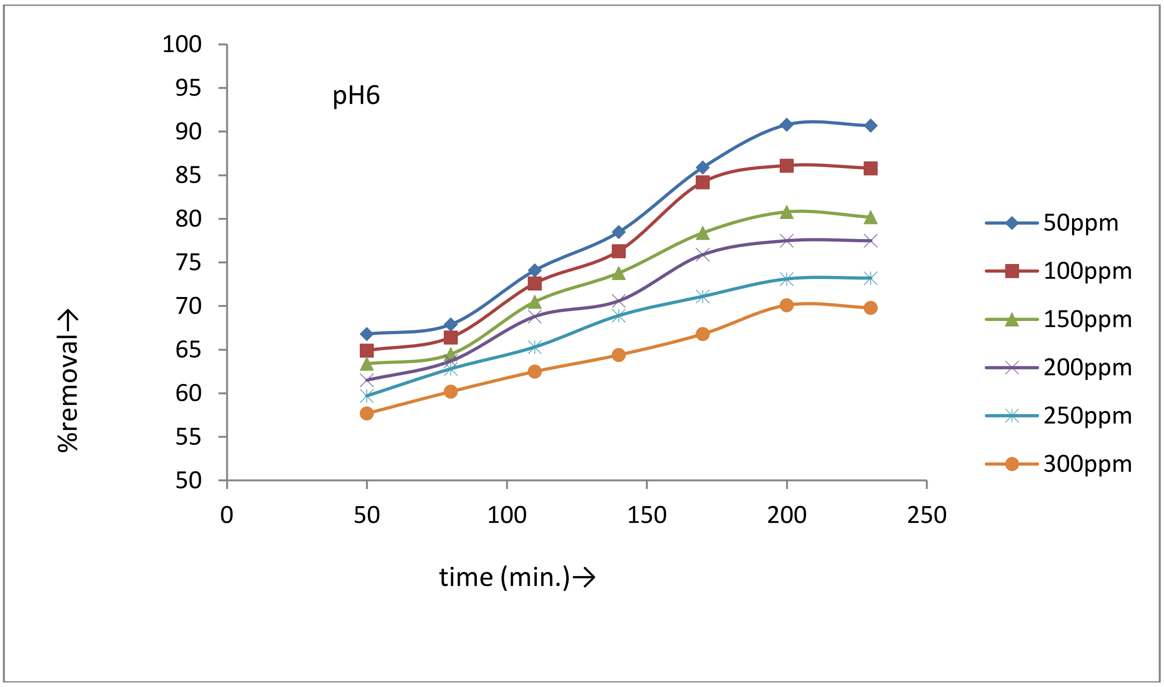
m	q_o=1/m	C=intercept	q_o.C	b	b.Co	1+bCo	R_L=1/1+b.Co	R^2
0.003	333.33	0.404	134.67	0.007	0.37	1.37	0.73	0.999
0.007	142.85	0.541	77.28	0.012	0.65	1.65	0.61	0.989
0.01	100	0.762	76.2	0.013	0.66	1.66	0.6	0.994
0.013	76.92	0.739	56.85	0.017	0.88	1.88	0.53	0.94
0.018	55.55	0.569	31.61	0.0316	1.58	2.58	0.39	0.95
0.022	45.45	0.683	30.99	0.032	1.61	2.61	0.38	0.953
0.025	40	0.804	32.16	0.031	1.55	2.55	0.39	0.949

Table 3: Pseudo second order kinetic parameter for As(V) on fly ash

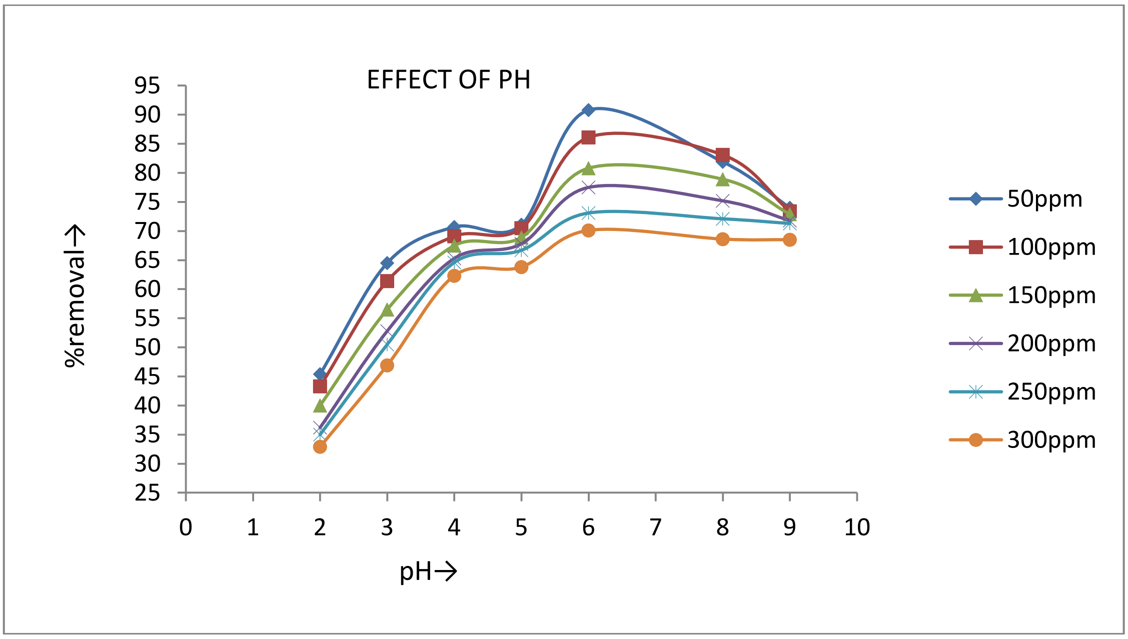
PSEUDO SECOND ORDER KINETIC MODEL				
s. no.	parameter	50ppm	100ppm	150ppm
1.	K_2(g/mg min)	2.8x10-3	1.4x10-3	1.35x10-3
2.	R^2	0.99	0.99	0.99
3.	q_e(mg/g)	10.2	20	27.02

Table 4: Thermodynamic parameters for adsorption of As(V) on fly ash

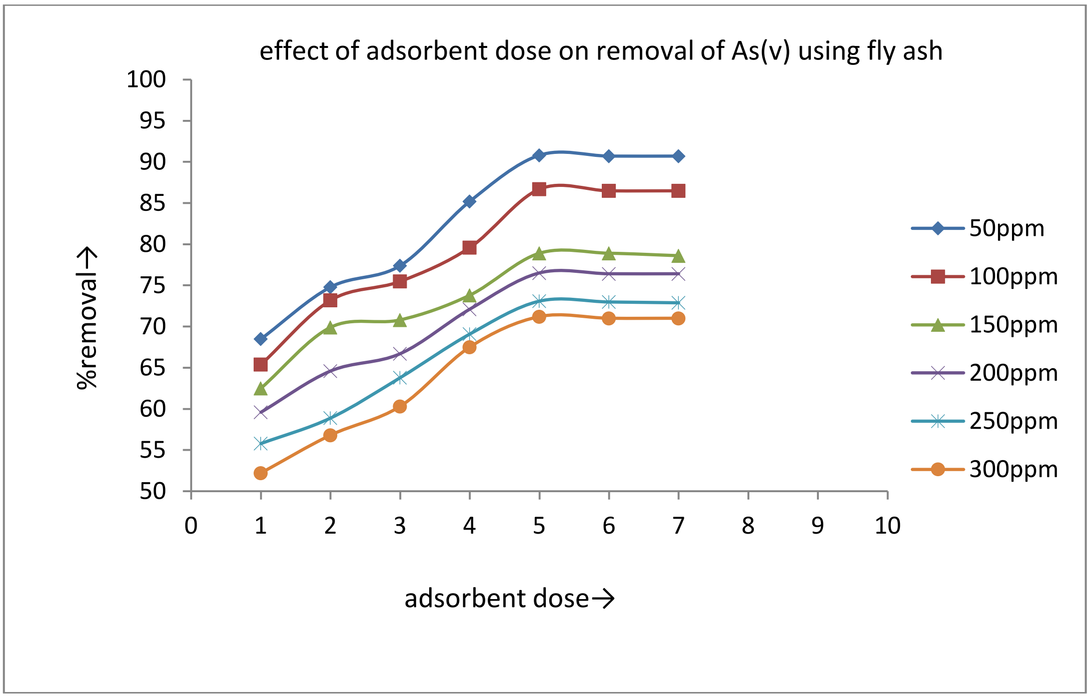
Temp.(K)	Equilibrium time 150min.,adsorbent dose 2.5 g,PH5		
	ΔG(K J mol^{-1})	ΔH(K J mol^{-1})	ΔS (J K^{-1} mol^{-1})
303	-8.785	-27.968	-.06331
313	-8.15		
323	-7.518		



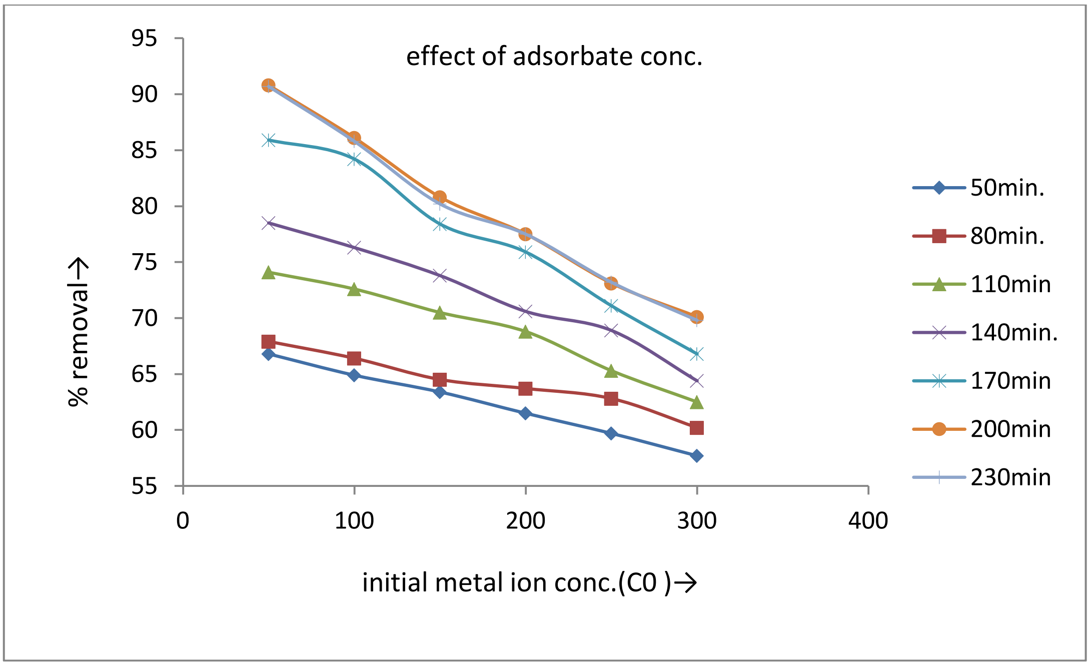
Plot 1. Effect of contact time on %removal of As(v) on class F fly ash at Ph6



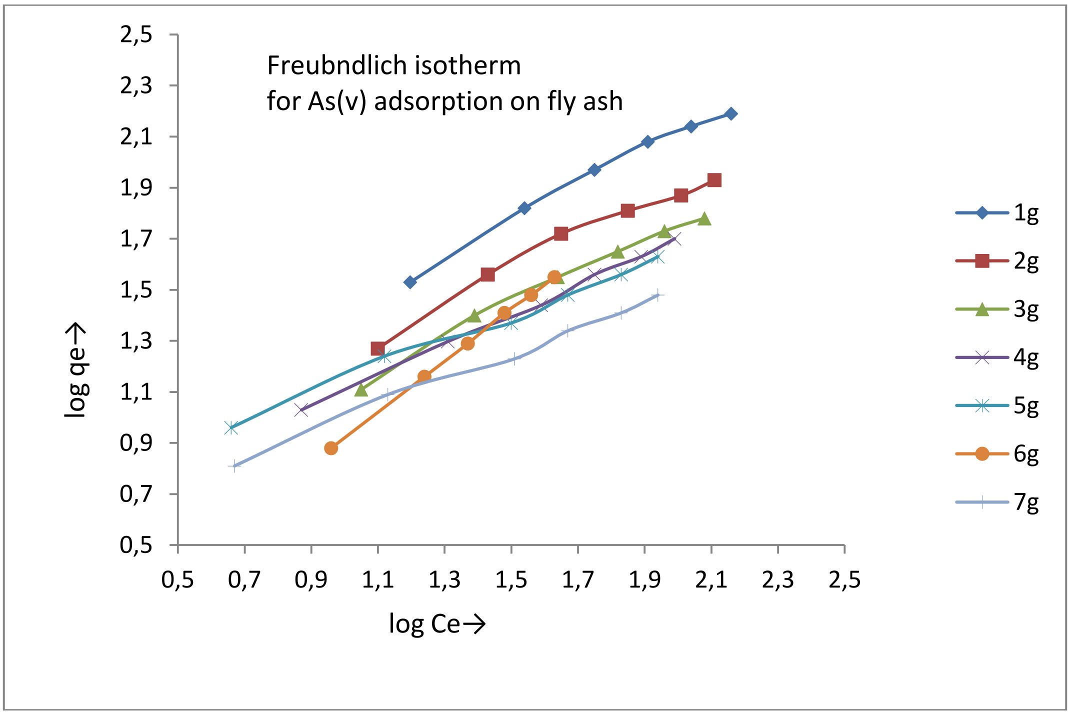
Plot 2: Effect of Ph on %removal of As(v) on class F fly ash at contact time 200 min.



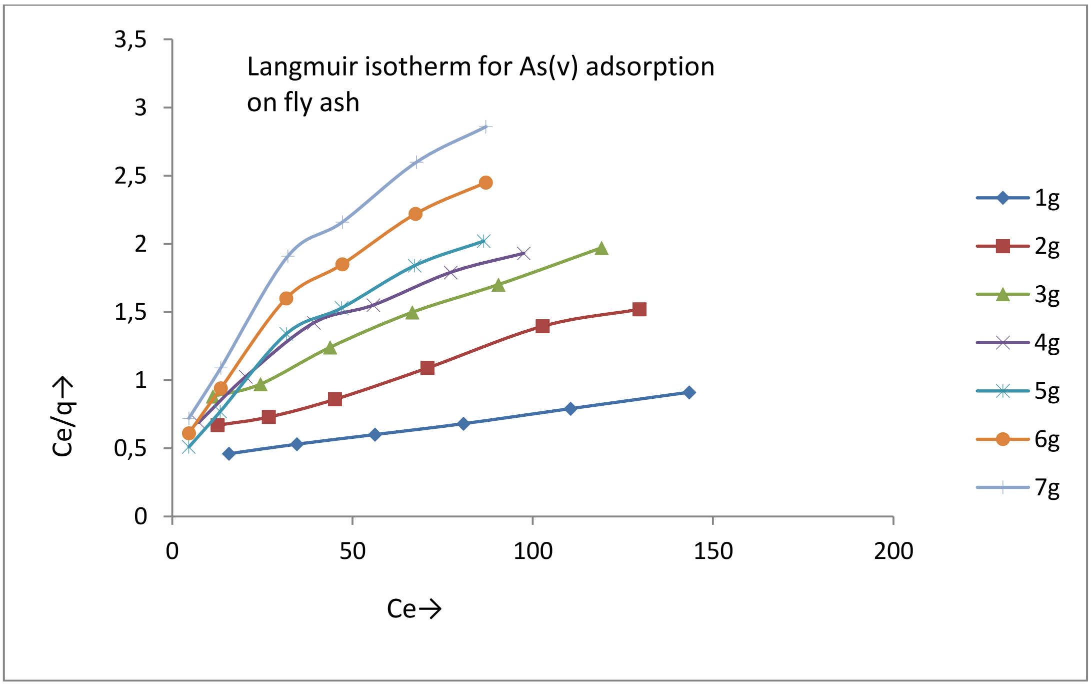
Plot 3: Effect of adsorbent dose on % removal of As(v) at Ph6, a contact time of 200 min.



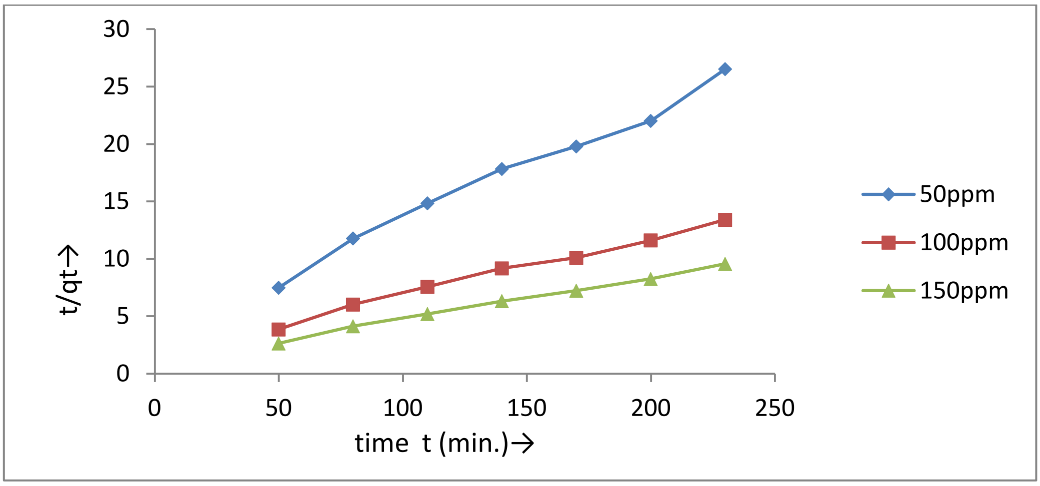
Plot 4: Effect of initial metal ion concentration on % removal of As(+5) at ph6



Plot 5: Freundlich isotherm for As (V)adsorption (Log (qe) vs Log (Ce)



Plot 6 : Langmuir adsorption isotherm for As (V) ions (Ce/q_e vs Ce)



Plot 7: Pseudo second order kinetic model for As(v) on fly ash

EQUILIBRIUM STUDY

Adsorption data are usually described by adsorption isotherms, such as Langmuir, and Freundlich isotherms. These isotherms relate metal uptake per unit mass of adsorbent, qe, to the equilibrium adsorbate concentration in the bulk fluid phase Ce .

A: FREUNDLICH ISOTHERM EQUATION

$q_e = k_f C_e^{1/n}$

Where

k_f = Freundlich constant

n= constant

q and C_e are same as in Langmuir isotherm

The linear form of the equation or the log form of equation is

Log q_e = log k_f +1/n log C_e

The linear plot of q_e Vs log Ce shows that adsorption follows freundlich isotherm model. The value of k and 1/n can thus be calculated from the intercepts and slopes of these curves.(plot 5 shows Freundlich isotherm and table 1 shows the values of Freundlich constant k_f and constant n. According to Freundlich isotherm, favourable conditions for adsorption are n should have values lying in the range of 1 to 10 and which is in accordance with table 1.

n should have values lying in the range of 1 to 10 and which is in accordance with above table 1

B. LANGMUIR ISOTHER M EQUATION

$q_e = q_{max.}$ b. Ce / 1 + b. Ce

The linear form of isotherm equation can be written as

$Ce/q_e = 1/q_0 b + Ce/q_0$.

Where

q = The amount of metal ion adsorbed per unit weight of an adsorbent was calculated using following formula:

$q = C_0 - C_e / m$ $(C = C_0 - C_e = X)$ or

q = x/m

C = amount adsorbed

C_0 = initial concentration of adsorbate

C_e = equilibrium concentration of adsorbate

% removal = C . 100/C_0

m= adsorbent dose

b = Langmuir constant

The linear plot of Ce/q_e Vs Ce shows that adsorption follows Langmuir isotherm model. The separation factor (R_l) can be used to predict affinity between the sorbate and sorbent in the adsorption system. The characteristics of the RL value indicates the nature of adsorption as favourable when (0 < RL < 1) and it is clear from table 2 that for present experiment all the adsorption conditions are favorable.

KINETIC STUDY

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system.

The overall rate of the adsorption process will be controlled by the slowest i. e. The rate limiting step. The nature of the rate limiting step in batch system can be determined from the properties of the solute and adsorbent.

Rate of adsorption is usually measured by detemining the change in concentration of adsorbate with the adsorbent as a function of time.

In present experiment metal ions whose concentrations were 50,100 and 150 ppm at optimum PH value (6) were used. The concentrations of metal ion were measured by UV- spectrophotometer.

By applying different kinetic models (pseudo first order, intra particle diffusion and pseudo second order kinetic models) on equilibrium data it was found that the adsorption of As(v) on fly ash followed pseudo second order kinetic model, which is as follows

- **Pseudo second order kinetic model:**

Pseudo second order equation is represented as

$t/q_t = 1/k_2 . q_e^2 + t. 1/ q_e$

a plot of t/q_t vs t gives a straight line with $1/q_e$ and $1/k_2 . q_e^2$ as slope and intercept respectively.(plot 7 and table 3)

table 3 depicts the values of R^2 for pseudo second order model were close to 1(.999). It indicates that the experimental data best fitted into pseudo second order. The q_e values also suggest that the process of adsorption follows pseudo second order kinetics.

THERMODYNAMIC STUDY

The effect of temperature on the adsorption of As (v) was studied by making 1000 ml of adsorbate solution was prepared in conical flask with initial concentration 50mg/L and adsorbent dose (5g/L) and put inside the incubator shaker. The final dye concentration readings were taken at 50, 80, and 110mins. The final concentration of the desired compound in the filtrate from each flask was then determined as described earlier. The same procedure was followed for temperatures 30°C and 40° C and 50^0 C.

The feasibility of the removal process is often evaluated by determining these thermodynamic parameters using the following equations:

$\Delta G° = -RT \ln k$

or

$\ln k = - \Delta G^0/RT$

or

$\ln k = \Delta S^0/ R – \Delta H^0/RT$ (as $\Delta G^0 = \Delta H^0 - T\Delta S^0$)

where $\Delta G°$ = Gibb's free energy of adsorption

ΔH^0 = enthalpy change

ΔS^0 = entropy change and

k= pseudo second order rate constant

a plot of ln k versus 1/T gives a straight line with $\Delta H^0/R$ as slope and $\Delta S^0/ R$ as intercept.(table 4)

Table 4 depicts the negative values of ΔH° indicate the exothermic nature of adsorption and it governs the possibility of chemical adsorption. Because in the case of chemical adsorption, while increasing the temperature of the system, the extent of metal ion adsorption decreases, there is no possibility of physical adsorption. The negative values of ΔG° are given in Table 4 indicate that the adsorption is spontaneous for arsenic ion. The negative values of S° in Table 4 show the decreased disorder and randomness at the solid solution interface of arsenic ion with fly ash adsorbent. The results indicate more efficient chemisorptions.

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