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Thermal Response for the Adsorption of Arsenic(III) Removal on Mixed Adsorbents

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The study regarding suitability of low cost and easily available materials such as red mud and mixture of red mud with haematite, china clay and fly ash and china clay with fly ash for the removal of As^{3+} from solution was conducted by adsorption technique in the batch experiment. The adsorption equilibrium data for adsorption of As(III) at different temperatures (30°C, 40°C and 50°C) favoured the applicability of Langmuir model of isotherm and the adsorption capacity of all used adsorbents (except red mud-haematite) during the removal of As(III) which increased with increasing solution temperature.

Key words: Mixed adsorbent; adsorption isotherm; temperature effect; thermodynamic parameter

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Arsenic ingestion disturbs skin, lungs, gastrointestinal and nasopherangel system. Arsenic(III) exerts its toxic [1−4] action by attacking a group of an enzyFme and inhibits the enzyme action and hence cellular energy generation in the citric acid cycle which is adversely affected and proteins are precipitated. The effect of temperature on adsorption isotherm and the thermodynamics involved during adsorption of cation by mixing adsorbent have been studied by several investigators [4, 5]. The kinetics and effect of pH on the removal of As(III) have been reported earlier [4,6]. In the present investigation the study of adsorption isotherm and influence of temperature in adsorption process of Arsenic(III) with low cost mixed adsorbent such as red mud, mixture of 1:1 ratio of china clay—fly ash, red mud—hematite, red mud—fly ash and red mud—china clay has been made.

MATERIALS AND METHOD

The parent adsorbents, red mud, china clay, fly ash and haematite were obtained from different sources [6, 7] and the mixed adsorbents were prepared by mixing of two in equal ratio 1:1 by weight, for experimental work. Batch experiments were conducted by taking 1.0 g of adsorbent having particle size <53 µm in 50 ml of arsenic solution of 5.0 mg/l concentration, at pH 8.0 and agitated at 220 r.p.m in a temperature controlled agitator at 30°C, 40°C and 50°C for 24 h to ensure the complete equilibrium. The centrifuged supernatant liquid was analysed spectro-photometrically by using iodine monochloride method [8].

RESULT AND DISCUSSION

Adsorption Isotherm

The maximum possible adsorption of the adsorbate species at the solid surface is a function of its concentration at constant temperature:

$$q_e = f(c_e)$$

Where, q_e (mg g^{-1}) is the amount of adsorbate adsorbed at equilibrium and c_e (mg l^{-1}) is the equilibrium concentration of the adsorbate in solution. The equilibrium data for the adsorption of As(III) on adsorbents used at various temperature were calculated with the help of Langmuir adsorption isotherm equation, which is based on the monolayer coverage [9, 10] of adsorbate on the surface of adsorbent. The re-arranged linear form of Langmuir equation is written as:

$$\frac{c_e}{q_e} = \frac{1}{Q^\circ.b} + \frac{c_e}{Q^\circ}$$

where, Q° and b are the Langmuir constants indicating adsorption capacity of the adsorbents and the energy of adsorption, respectively. The straight line plots of c_e/q_e vs. c_e (Figure 1) for the adsorption of As(III) for all systems confirm the applicability of Langmuir equation. The values of Q° and b obtained from slope and intercept of respective plot at 30°C, 40°C and 50°C in each system were given in TableI. It was clear that the adsorption capacity of red mud, and its mixed adsorbents except red mud−haematite for the adsorption of As(III) increased with increasing adsorbate solution temperature depending upon the nature of adsorbents. The higher value of adsorption capacity (Q^o) of adsorbents showed their better suitability for the removal of As(III) by adsorbent at 50°C and suggested to be more efficient for the removal. The essential characteristics of a Langmuir isotherm can be described as:

$$R_L = \frac{1}{1 + b'C_i}$$

where, C_i is the initial concentration of adsorbate. The value of R_L, for different adsorbate-adsorbent has been shown in Table I and found to be less than one indicates that process is much favourable [11]. However the constants Q° and b may not completely define the absolute monolayer coverage or a true heat of adsorption. The apparent heat change or net enthalpy, (ΔH) of adsorption is related with Langmuir constant, b, as follows [12]:

$$b = b'e^{\Delta H / RT}$$

or, $$\ln b = \ln b' - \Delta H / RT$$

where b' is constant. The value of ΔH for which the adsorption of As(III) on various adsorbents were calculated from the slopes of the respective

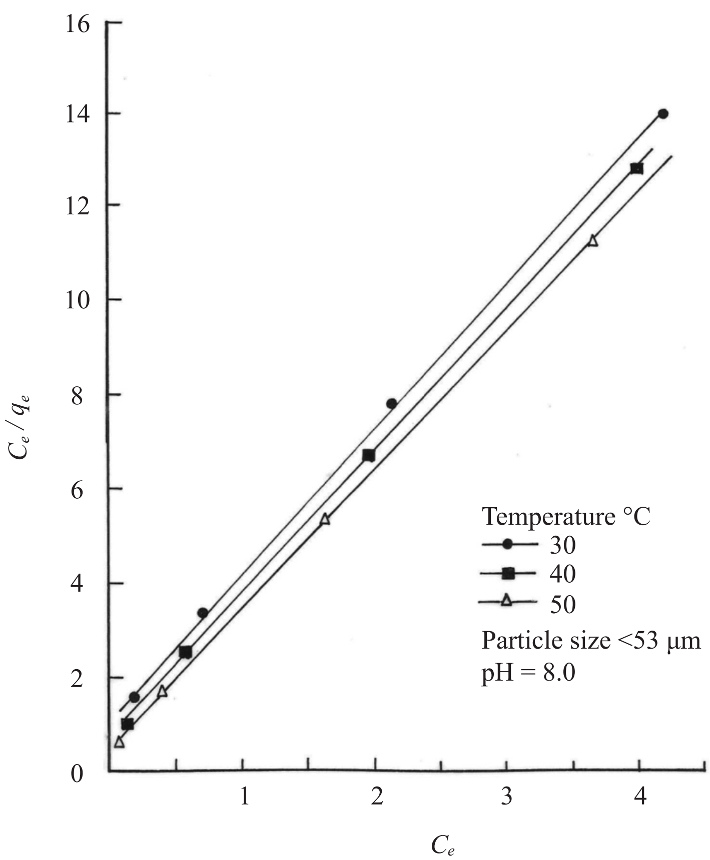

Figure 1. Langmuir adsorption isotherm plot for As(III) on red mud at different temperatures.

Table 1. Langmuir constant and separation factor for As(III) on adsorbents.

Adsorbent	Temperature (°C)	$Q°$	$b(lg^{-1})$	R_L
Red mud	30	0.31	3.42	0.055
	40	0.32	4.33	0.044
	50	0.33	6.80	0.029
China clay–fly ash (1:1)	30	0.39	1.59	0.112
	40	0.40	2.06	0.088
	50	0.40	3.55	0.053
Red mud–haematite (1:1)	30	0.30	0.99	0.167
	40	0.29	0.99	0.168
	50	0.26	0.71	0.219
Red mud–China clay (1:1)	30	0.37	1.33	0.130
	40	0.38	1.65	0.108
	50	0.40	2.07	0.088
Red mud–fly ash (1:1)	30	0.36	1.23	0.140
	40	0.37	2.50	0.118
	50	0.38	2.12	0.086

Table 2. Thermodynamic parameters for adsorption of As(III) on various adsorbents.

Adsorbent	Temperature (°C)	ΔG° (k Cal mol^{-1})	ΔH° (k Cal mol^{-1})	ΔS° (Cal $mol^{-1}K^{-1}$)	ΔG° (k Cal mol^{-1})
Red mud	30	–1.093	–	–	
	40	–1.300	5.190	20.74	7.193
	50	–1.567	7.063	26.72	
China clay–fly ash (1:1)	30	–1.045	–	–	
	40	–1.239	4.839	17.90	7.665
	50	–1.660	11.953	42.15	
Red mud–haematite (1:1)	30	–0.769	–	–	
	40	–0.527	–8.122	–24.27	3.088
	50	–0.287	–8.033	–23.98	
Red mud–China clay (1:1)	30	–0.873	–	–	
	40	–1.031	3.925	–15.83	4.226
	50	–1.279	6.713	24.74	
Red mud–fly ash (1:1)	30	–0.835	–	–	
	40	–0.986	3.755	15.15	5.296
	50	–1.220	6.329	23.37	

linear plots of ln *b* vs *l/T* (Figures 2 and 3) and reported in Table 3. The positive values of ΔH are indicative of endothermic nature of the adsorption process.

Effect of Temperature

The effect of temperature on removal of As(III) by all the adsorbents at various time variations was studied and shown in Figure 4 for red mud and results are reported in Table 2 for removal of As by all adsorbents. It was very clear from the results that the amount adsorbed by almost all adsorbents except red mud−haematite increased with the rise in temperature and 87% to 93% removal was achieved at 50°C. The decrease in adsorption with rise in temperature was mainly due to the weakening of adsorption forces between the active sites of adsorbent and adsorbate species and also between the adjacent molecules of adsorbed phase. The increase in adsorption with rise in temperature is mainly due to the increase in the number of adsorption sites caused by the breaking of some internal bonds near the edge of the active surface sites of adsorbent. Also at high temperature, the physical adsorption gradually changes into chemical adsorption which favours [13] the increase of uptake of adsorbate species with the increase in temperature. The increase in uptake of adsorbate with the increase in temperature may be due to the diffusion [14] of adsorbate species from the bulk phase into the pores of adsorbent and it favours the adsorbate transport within the pores of adsorbent, which is endothermic process. This has further explained on the basis of ion-exchange reactions [15] between adsorbate and adsorbent.

The change in thermodynamic parameters such as free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) has been calculated using the following relationships [16, 17].

$$\Delta G^0 = -RT \ln K_e \quad (1)$$

$$\Delta G^0 = R\left[\frac{T_2 \,.\, T_1}{T_2 - T_1}\right] \ln \frac{K_{c_2}}{K_{c_1}} \quad (2)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (3)$$

where, R is gas constant, T is absolute temperature and K_c, K_{c1} and K_{c2} are the equilibrium constants

Table 3. Effect of temperature on the removal of As(III).

Adsorbent (Concentration = 5.0 mgl⁻¹)	Temperature (°C) (Particle size < 53 μm)	Removal (%)	Amount adsorbed (mg g⁻¹) pH = 8.0
Red mud	30	86	0.215
	40	89	0.222
	50	92	0.230
China clay–Fly ash (1:1)	30	85	0.212
	40	88	0.220
	50	93	0.232
Red mud – Haematite (1:1)	30	79	0.197
	40	70	0.175
	50	61	0.152
Red mud–China clay (1:1)	30	81	0.202
	40	84	0.210
	50	88	0.220
Red mud – Fly ash (1:1)	30	80	0.200
	40	83	0.207
	50	87	0.217

at temperatures T, T_1, T_2 respectively. The values of equilibrium constant at each temperature were calculated from limiting slopes of adsorption isotherm at zero concentration. The values of thermodynamic parameters are presented in Table 2. The negative value of free energy change ($\Delta G°$) for various adsorbate-adsorbent systems at different temperatures (30°C, 40°C and 50°C) is inductive of the spontaneity of the adsorption process. In such cases, the adsorption forces are strong enough to overcome the potential barrier. The positive values of standard enthalpy change, ΔH° (Table 2) indicated the endothermic nature of As(III) removal by almost all adsorbents at various temperatures. It was evident from the Table 2 that the negative values of free energy change for the most of the cases indicated stronger binding energy between ions adsorbed and the active surface sites of the adsorbents. In such cases there was possibility of simultaneous occurrence of physical and chemical adsorption to various extents. Adsorption, fixation or immobilization of adsorbate on the interface between two phases resulted in loss of the degree of freedom,

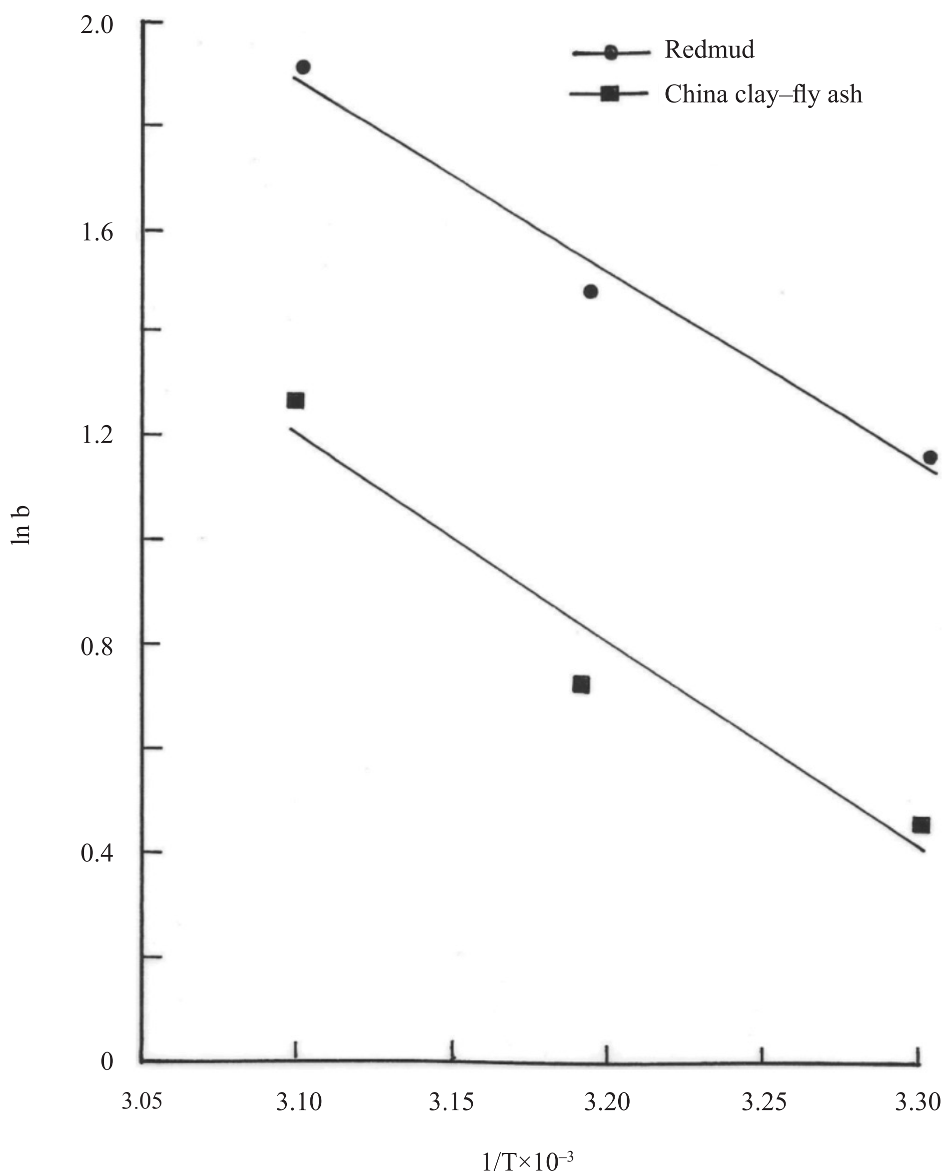

Figure 2. Plot of ln *b* vs *1/T* for red mud and China clay– fly ash (1:1) on adsorption of As(III).

thereby showing negative entropy effect. The positive values of ($\Delta S°$) for adsorption of As(III) in some cases might be attributed to an increase in translation entropy caused by randomness of displaced water molecules from the surface of the adsorbents.

CONCLUSIONS

It was clear from the above findings that the the removal of As(III) from aqueous solution by almost all adsorbents except red mud–haematite was maximum at 50°C. The values of thermodynamic parameters provided information for understanding the nature of adsorption mechanism as well as in predicting the optimum conditions for the removal of As(III) pollutants from water. The adsorption equilibrium data for the adsorption of As(III) by all adsorbents are found fit well in the model proposed by Langmuir.

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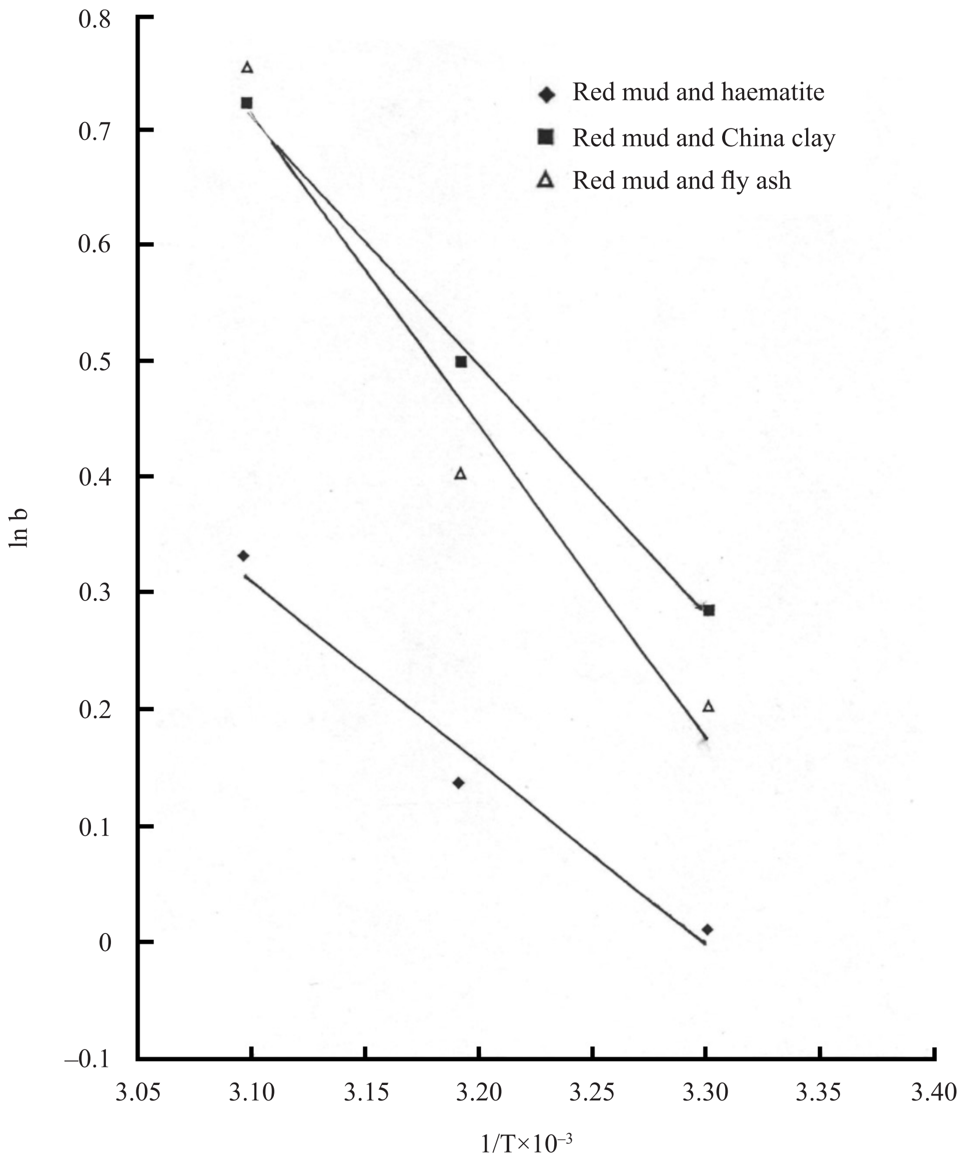

Figure 3. Plot of ln *b* vs *1/T* for different adsorbents on adsorption of As(III).

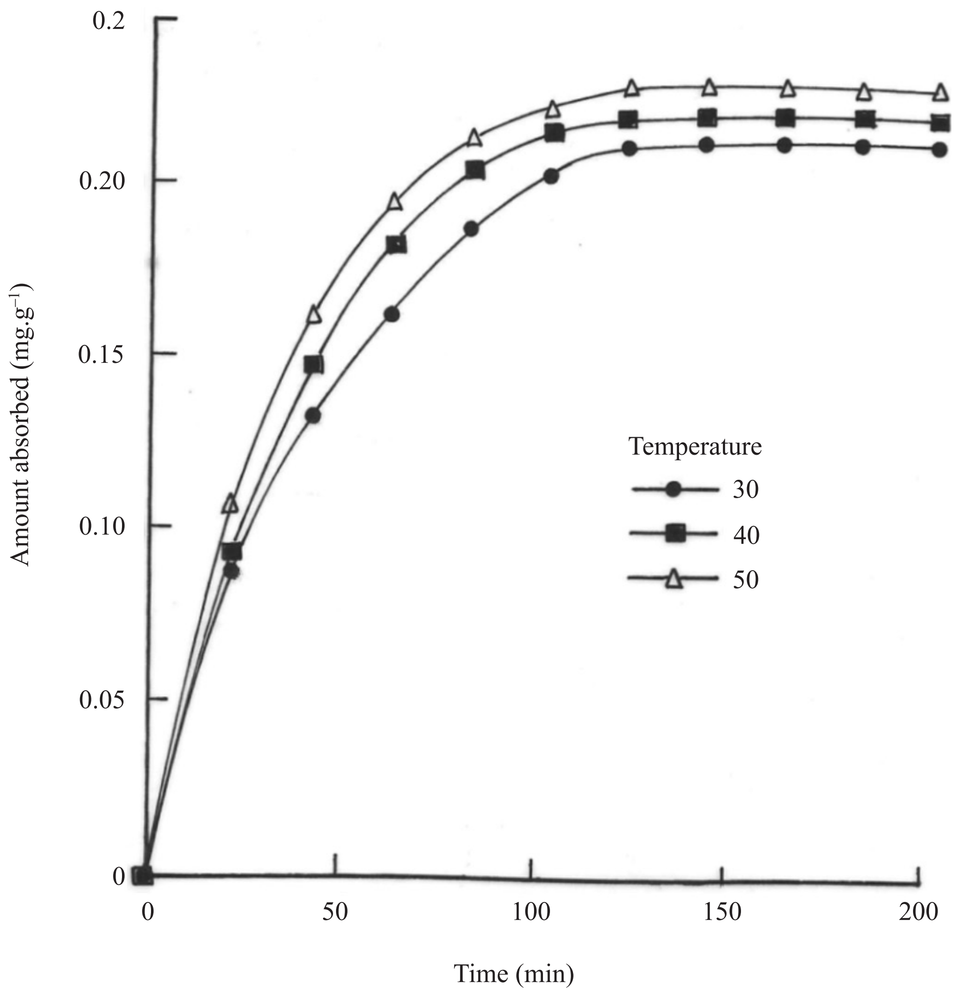

Figure 4. Time variation of adsorption of As(III) on red mud at different temperatures.

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