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Original Research Article

THE ANOVA AND ADSORPTION ISOTHERM STUDY OF ARSENIC REMOVAL USING A COAGULANT OF PLANT ORIGIN WITH FERRIC CHLORIDE

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Abstract:
This work has studied the adsorption isotherm of arsenic on ferric chloride with a coagulant of plant origin. The adsorption of arsenic by iron oxides is a very important natural process that is largely responsible for preventing widespread arsenic toxicity problems in nature. The ANOVA results are in good agreement with the addition of CPO to ferric chloride for arsenic removal. The amount of adsorption is described by the adsorption isotherm. The removal or transport of arsenic is closely related to the adsorption isotherm. The results of adsorption isotherm study shows that the adsorption of arsenic follows both the Freundlich and Langmuir adsorption isotherm and the addition of CPO plays a supportive action. The use of CPO extract with ferric chloride increased the non-linearity of both the isotherm which is indicated by the decrease in the R^2 value in case of arsenite adsorption isotherm using ferric chloride with CPO this increased non linearity favours the multi-layered adsorption process.

Keywords: Adsorption Isotherm, coagulant of plant origin, Ferric Chloride, Langmuir, Freundlich, Arsenic.

Introduction:

A *coagulant of plant origin* (CPO) is known to remove turbidity and arsenic present in natural water sample (Yadav, 2003).This natural coagulant has several advantages in comparison to alum. A crude water extraction procedure produces an extract that retains its activity throughout a wide range of pH values. The sludge produced with CPO coagulation has a much lower sludge volume than conventionally produced sludge, and the sludge is comprised of organic solids free of heavy metals, assuming heavy metals are not present in the raw water. The natural alkalinity of the water is not consumed during the treatment process. In addition, because CPO can be locally grown, harvested, and processed, it will be very cost effective when compared to the chemicals (Yadav, 2003).

The biochemistry of arsenic (As) has been reviewed by (Ferguson and Gavis. 1972; Korte and Fernando. 1990). The different forms of

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arsenic have different toxic effects to human and availability of these forms depends mainly on environmental conditions.

In oxidized water, arsenate is the predominant species while in reduced environment arsenite predominates because of the relatively slow redox transformations (Masscheleyn et al., 1991) both arsenate and arsenite are often found in either redox environment. Arsenite is 25-60 times more toxic than arsenate and has been reported to be more mobile in the environment (Korte and Fernando.1990).

Adsorption is one of the reactions that controls the mobility and bioavailability of arsenic. Arsenic adsorption has been studied using a variety of adsorbents like phyllosilicates, silica and hydrous oxides of Fe and Al. Arsenic adsorption is more highly dependent on the nature of ionic species than on the pH in the range of 5.5-7.5 (Ferguson. 1974).

The adsorption of arsenic by iron oxide is a very important natural process that is largely responsible for preventing widespread arsenic toxicity problems in nature. Arsenic is strongly adsorbed by the oxide, especially under oxidising and slightly acidic conditions. This is often the basis for the removal of arsenic during water treatment. The amount of adsorption is described by the adsorption isotherm, which relates the concentration of arsenic adsorbed to its concentration in solution. Once this is known for a wide range of conditions then many properties can be calculated, including the percentage of arsenic adsorbed as a function of pH, the likely efficiency of arsenic removal plants and the extent of retardation of arsenic during movement through soils and aquifers.

Adsorption isotherms are either linear or non-linear. A linear isotherm means that the amount of a species adsorbed is directly proportional to its concentration in solution. The isotherms for the two forms of arsenic, arsenite and arsenate, are very different including their pH dependence. An important consequence of the highly non-linear adsorption for arsenate is that even at the microgram/L level of arsenic in solution, the arsenic loading on the oxide can be appreciable corresponding to thousands of mg As/kg in the case of hydrous ferric oxide. The loading on more crystalline iron oxide such as goethite and hematite is somewhat lower because of their lower surface area, but is still appreciable (UN Synthesis report on arsenic in drinking water 2002).

Hingson et al., 1971 studied the adsorption of arsenate and other negatively charged legends on goethite and gibbsite as a function of pH and observed that adsorption was dependent on the nature of the anion and surface area of the adsorbent. Singh et al., 1988 studied the adsorption of arsenite on hematite and observed that the rate of adsorption was diffusion controlled and maximum adsorption occurred at pH 7.0 Hsia et al., 1992 studied the adsorption of arsenate on amorphous iron oxide in the pH range of 4 to 10 and suggested that arsenate is strongly adsorbed on the iron oxide surface by the formation of inner sphere complexes. Fuller et al., 1993 reported the kinetics of adsorption of arsenate with ferrihydride in the pH range of 6.6-8.0 and reported a slow approach to equilibrium due to the diffusion controlled rate-determining step.

The objective of this research work was to study the adsorption isotherm of arsenite and arsenate on ferric chloride with and without CPO (coagulant of plant origin). The significance of adding CPO with ferric chloride in As removal is tested with ANOVA calculations. In this paper in order to determine a reliable adsorption isotherm that would be useful for studying the effect of CPO on adsorption efficiency of ferric chloride in removal of arsenic and then for adoption of the technology in municipal water treatment process targeted at arsenic removal.

The transport of chemicals and adsorption are closely related in that adsorption slows down the transport of a chemical compared with the water flow (Appelo and Postma, 1992). In a simplest case of linear adsorption isotherm, the relationship is straightforward and the partition cofficient, Kd, defines a constant retardation factor. With non-linear adsorption, which is most likely to be the case for arsenic adsorption, the value of Kd varies with concentration and is related to the slope of the isotherm. Normally the Kd decreases with increasing concentration, leading to less retardation at high concentrations and ultimately to self-sharpening and diffuse fronts. For example greater the non-linearity, the longer it will take to flush completely all of the arsenic from an aquifers- the last bit is removed reluctantly because the binding is so strong at low concentrations.

Since the transport is so closely related to the adsorption isotherm, it follows that arsenate and arsenite should travel through an aquifer with different velocities leading to their increased separation along a floe path. This paper describes the scientific assessment of the physiochemical behaviours affecting the arsenic removal.

Methods and Materials

This experiment was carried out with an optimised dose of 16 mg/L (0.4 mL of 4% solution) of ferric chloride to achieve maximum removal at the lowest dose of ferric chloride. The CPO dosing was 2.0mL.of 5% w/v extract solution is used for both arsenite and arsenate with ferric chloride.

Adsorption experiments were carried out by equilibrating ferric chloride solution with and without CPO having the arsenic concentration of 0.2, 0.4 0.6 0.8, 1.0 mg/L. Adsorption experiments were conducted with laboratory six paddles multiple stirrers with a variable speed of 10-100 rpm. Co-agulation experiments involved filling of six beakers with 1000 mL of raw water at room temperature of 25-30^{o}C. The coagulant dosages were added simultaneously to all beakers by pipette. All samples were mixed for 45 minutes at 40 rpm and finally allowed to settle for 60 minutes1-50 mL of supernatant from each samples was carefully decanted using a 50 mL pipette and As was analysed. The fit of the adsorption data to the Freundlich and simple Langmuir was tested graphically. The extracted solution were analysed by HGAAS (Hydride generator Atomic Absorption Spectrophotometer).

Result and Discussion

Edwards (1994) had indicated that, at all dosages greater than 20 mg/L as ferric chloride or 40 mg/L as alum, greater than 90 percent removal of As(V) was achieved. It is also established that at lower coagulant dosages there was considerable scatter in the data attributed to poor particle removal, high initial As(V) concentrations, and possible interferences from other anions in the different waters tested.

Nevertheless, the use of $FeCl_3$ (lest its high dose) is not desirable in municipal water treatment, due to the following reasons:

1. High running cost
2. Large quantity of sludge formation and the problem its volume reduction i. e. dewatering
3. Incomplete precipitation/removal of reduced iron species and flocks of hydrated ferric oxide leading to the aesthetic quality deterioration in water.
4. Propensity of resuspension of flocks and probable remobilisation of toxic elements (if present).
5. For arsenic removal also the use of ferric chloride is severely handicapped as it cannot achieve a satisfactory removal of As (III) (Herring *et al*., 1996).
6. The removal efficiencies achieved by iron removal are not as high or as consistent as those achieved by activated alumina or ion exchange.

Hence, there clearly exists an urgent need to improve upon the performance of iron-assisted removal of arsenic. To obviate the problems as enumerated above a plant extract was tried in conjugation with ferric chloride to seek a complete removal of both As (III) and As (V) at a lower coagulant dose.

First the parameters for complete removal of arsenic are set. In our experiments the complete removal of As(V) in varying ppm (from <0.05-0.6 ppm) was achieved on dosing 16 mg/L $FeCl_3$, 2.0 mL of 5% extract of CPO at a pH of 4.5 at the temperature of 30°C. The method can be further optimised to remove As concentration as high as 1 ppm with a marginal increase in ferric chloride dose. Now the role of CPO in As removal with ferric chloride is tested with ANOVA (Analysis of Variance) calculations.

For ANOVA calculations we assume the Null hypothesis as

$$A1 = A2 = 0.$$

Where A1 represent effect of Ferric Chloride and A2 represents effect of Ferric chloride with CPO.

In this model we assume that there is no effect of adding CPO in the arsenic removal and to test this hypothesis the following data were considered for ANOVA calculation. Assuming there is no effect of CPO added on the removal of As III and As V and the increased percentage removal is occurred by chance. For this study the ANOVA table is constructed for As III and As V and F value is calculated for both the species and compared with the F table value.

For the treatment A1 and A2 the five different samples were analysed for their percentage arsenic removal. The removal percentage data using ferric chloride with and without CPO five different concentration solutions of As III and As V are presented in table 1 and 2.

For the above results the anova table was constructed and the following F value is obtained for As III (table 3) and As V (table 4).

The statistical significance of the ratio of the mean square variation due to the regression and mean square residual error is tested using analysis of variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of ariation for the purpose of testing hypothesis on the parameters of the model [Segurola etal. 1999]. According to the ANOVA (Table 3, 4), the F statistic values for all regressions are higher. The large value of F indicates that the most of the variation in the response can be explained by the regression equation. The ANOVA table also shows a term for the residual error, which measures the amount of ariation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct and has very good agreement with the experimental value.

The F table value for (1,8) degree of freedom is 5.32 and F calculated value for As III is 11.6 and for As V is 5.93. In both the cases the F value calculated is higher than the F table value. This signifies that we can reject the Null hypothesis and accept the alternative hypothesis. So the result present that there is a significant effect of CPO addition on the percentage removal of As III and AS V and this increased removal is not by chance or by error.

There is a 99.5 % probability that this increase is due to the addition of CPO to ferric chloride. Hence ANOVA calculation signifies the addition of CPO to ferric chloride for better arsenic removal.

The ANOVA table also shows a term for the residual error, which measures the amount of ariation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct and has very good agreement with the experimental value.

Smedley and Kinniburgh (2002) had carried out a review on Source and behaviour of arsenic in natural waters. Based on the review it is clear that the adsorption of arsenic by iron oxides is a very important natural process that is largely responsible for preventing widespread arsenic toxicity problems in nature. Arsenic is very strongly adsorbed by iron oxides, especially under oxidising and slightly acidic conditions. This is often the basis for the removal of arsenic during water treatment. The amount of adsorption is described by the adsorption isotherm, which relates the concentration of arsenic adsorbed to its concentration in solution. The freundlich and Langmuir adsorption isotherms were studied for As III and As V and the results are shown in Figs. 1 to 8.

Fig. 9 shows the effect of various initial concentration of arsenic on fraction adsorbed. It is clear that adsorbed fraction is higher with CPO than ferric chloride alone. The adsorption isotherms are plotted for both the As III and As V for ferric chloride alone and ferric chloride with CPO. The Freundlich isotherm favours the multilayered physical adsorption while the Langmuir supports the monolayer chemisorptions by which the concentration of an ion chemisorbed on the surface of the mineral may be described (Stumm, 1992).

Both the isotherms have been frequently used to fit the experimental data (Holan et al., 1993; Holan and Volesky, 1994; Leusch et al., 1995; Costa and Franca, 1996) in studies with different metals and biomass.

The Freundlich isotherm form is:

$$\boxed{S = K_F C^{1/N}}$$

The linear form of the Freundlich isotherm is

$$\boxed{\log S = \log K_F + (1/N) \log C}$$

Where:

S = moles sorbed at equilibrium per mass of sorbent

K_F = Freundlich isotherm constant (L/g)

N = Freundlich isotherm constant; N >=1

C = Sorbate concentration in solution at equilibrium (mol/L)

The constant K_F is the measure of adsorption capacity and 1/n is the measure of adsorption intensity. The value of K and n for both arsenate and arsenite with and without CPO is given in Table 5.

The Freundlich isotherm form is:

$$\boxed{S = K_F C^{1/N}}$$

The linear form of Langmuir isotherm is:

$$\boxed{S = (K_L * A_M * C)/(1 + K_L C)}$$

Where S = Moles sorbed at equilibrium per mass of sorbent (mol/g)

A_m = maximum sorption capacity of the sorbent (mol/g)

K_L = Langmuir sorption constant, related to binding energy of the sorbate (L/mol)

C = sorbate concentration in solution at equilibrium (mol/L)

A_m is the maximum sorption capacity of the sorbent and K is the Langmuir adsorption constant. The values of constant Am and K is given in table 6.

It is clear from this table that the value of Am i.e. the maximum sorption capacity is higher in case of CPO indicating that the sorption capacity of ferric chloride increases when used with CPO. This observation indicates the adsorption of arsenic on ferric chloride with and without CPO can be fit to Langmuir adsorption isotherm.

A study on the effects of varying initial arsenic concentrations on the removal efficiencies was carried out. The results obtained are shown in Fig. 9. At lower initial concentration of arsenic 2.67-13.35 micromole /L, the removal efficiency was higher.

Based on the results presented above it can be concluded that adsorption of arsenic species (III and V) can be explained both by Freundlich and Langmuir equations. A comparison of experimental and predicted values were also carried out and medium differences were noticed between the two values. Such a difference is acceptable and explainable if the complex mechanisms of adsorption modified by the presence of a plant extract are considered. This plant extract has been found to contain variety of low molecular weight proteins and thus many chemical groups are expected to play a role in the bio-sorption process which none of the two models take into account.

To put it simply the adsorption equilibrium isotherm (Fig. 1 to 8) represents the equilibrium distribution of arsenic ions between the aqueous and solid phases with respect to the increasing concentrations. The results shows that arsenic accumulation by hydrated ferric oxide (HFO) in the presence of CPO is a chemical equilibrated and saturable mechanism as is expected by Langmuir adsorption pattern. However, the adsorption sites available don't exhaust by saturation, as may be the case if only Langmuir adsorption isotherm is followed. Rather at this time the Freundlich model comes into being where there is no surface saturation and hence arsenic species may continue to be adsorbed in the form of multi-layered structure.

If we consider the individual differences and the adsorption capacity for arsenic III and V then it is clear that As(III) adsorption is properly explained by Langmuir adsorption isotherm because beyond a certain concentration the adsorption sites gets saturated whereas As V is not burdened by any such limitations and can well be extrapolated to Freundlich model also.

The above observations are further corroborated if the correlation coefficient values (R^2) obtained for the linear plot of the both isotherms is studied for the As (V) and (lll) Table 7.

The results obtained clearly show that the graphs obtained are becoming increasingly non-linear when the ferric chloride was used in conjunction with CPO. This non linearity which is more pronounced in case of As (III) which is clearly indicated by more effective removal of As (III) which can never be achieved by HFO alone.

This experiment confirms that the arsenic adsorption is favourably altered in the presence of CPO extract. The data for ferric chloride alone are in good agreement with Langmuir adsorption and applicable to Freundlich isotherms. The addition of CPO extract along with ferric chloride confirms the sorption supportive nature of CPO extract.

Based on the results of this experiment it can be concluded that the CPO extract exerts a palliative effect on adsorption of arsenic. This conclusion has been drawn on the fact that the Freundlich and Langmuir adsorption isotherms obtained in case of both arsenate and arsenite show an increased non-linearity. The values of coefficient of determination (r^2) for the fit of arsenite and arsenate adsorption data shows a decrease in the value in case of the use of CPO extract with HFO. This decrease means a greater scattering of the data points and an increased non-linearity in case of both arsenate and arsenite. Further, the non-linearity is more pronounced in case of arsenite, which is reflected, in near total removal of arsenite, which is non-achievable with HFO alone.

These observations also mean that the adsorption mechanism is also changing from the normal Langmuir adsorption where the formation of an adsorbed solute monolayer takes place with no side interactions between the adsorbed ions.

The mechanism, which governs the process, may be the adsorption and inter-particle bridging of the adsorbed arsenic on HFO. This inter-particle bridging of CPO increases the removal of arsenic with ferric chloride. Hence, ferric chloride in smaller amount with CPO gives better results in better removal of both arsenite and arsenate. It also appears that the adsorption of arsenite and arsenate is a case of formation of an inner sphere complex rather than simple adsorptions, which are further enhanced by the addition of CPO extract by the mechanism of inter-particle bridging.

Conclusion

Adsorption is the process where a solute in the liquid phase becomes bonded to the surface of a solid. Metal adsorption to sediments is considered analogous to the formation of soluble complexes. The difference is that the 'ligand' in the reaction is a surface site. There are three pathways by which adsorption can occur. These are:

- Physical Adsorption; due to non-specific forces of attraction (e.g. Van der Waals forces).
- Electrostatic Adsorption; due to coulombic forces of attraction between charged solute species and the adsorbing phase. Ion

exchange is an example where the simultaneous adsorption and desorption of two species bonded by electrostatic attraction occurs.

- Specific Adsorption; due to the action of chemical forces of attraction leading to surface bonds to a specific site on the solid phase.
- The increased organic discharge by domestic, agricultural and industrial sources may convert some of the area in a stream bed to reducing nature such a scenario may favour the reductive dissolution of arsenic and thus can mobilise arsenic to the peril of local flora and fauna and ultimately may become a environmental nuisance.

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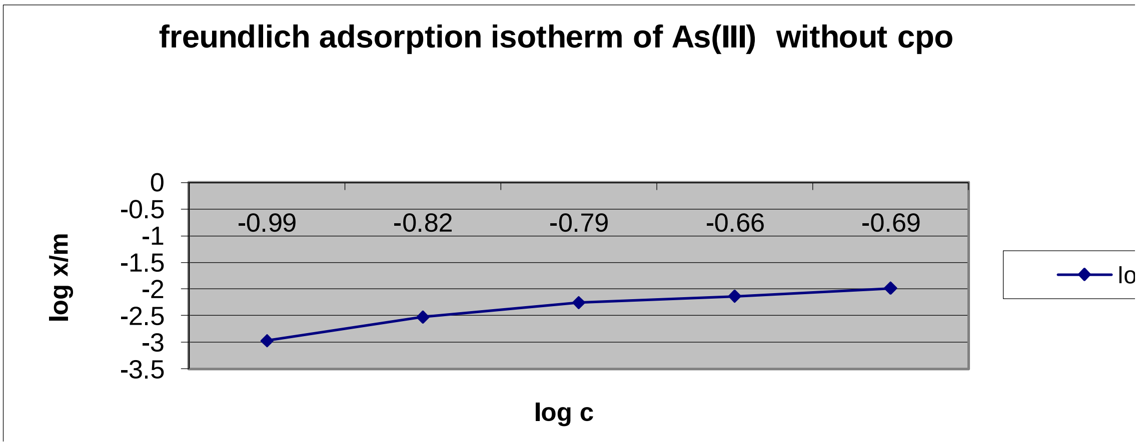

Fig. 1. Freundlich adsorption isotherm of As (III) without CPO

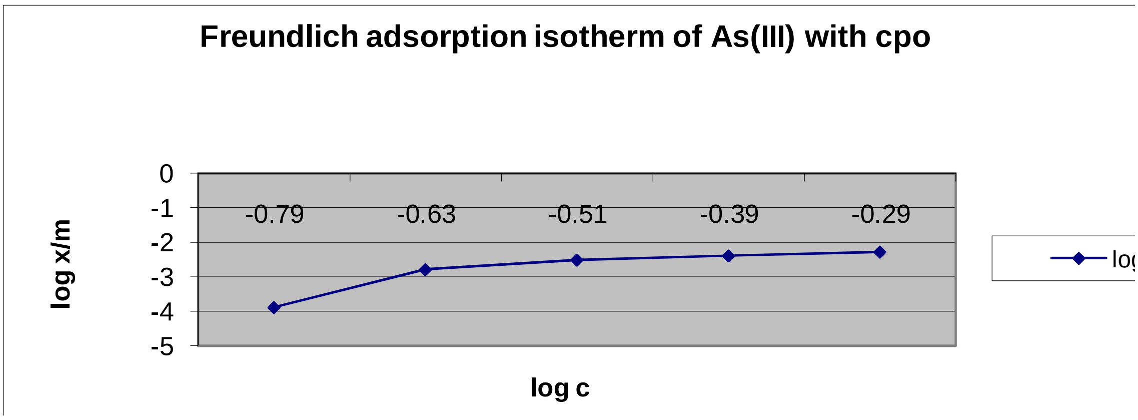

Fig. 2. Freundlich adsorption isotherm of As (III) with CPO

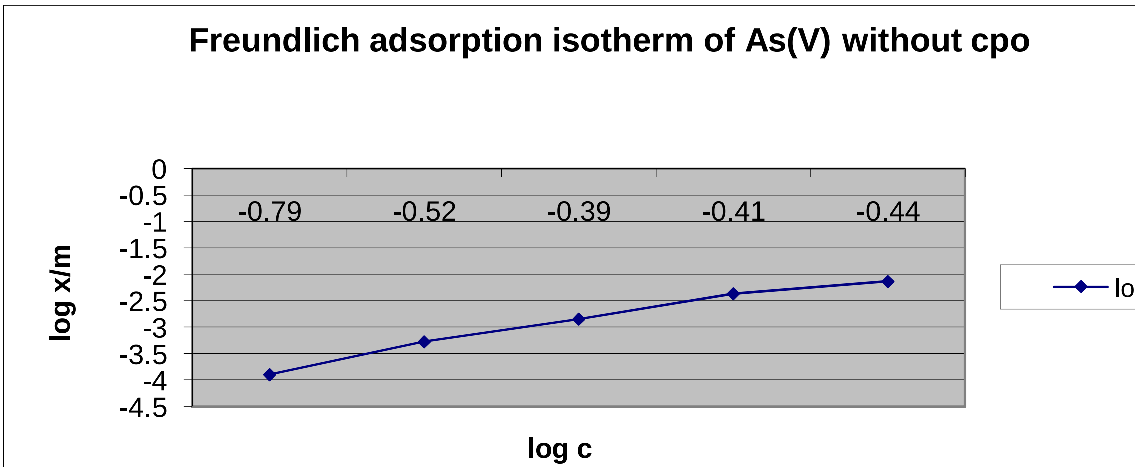

Fig. 3. Freundlich adsorption isotherm of As (V) without CPO

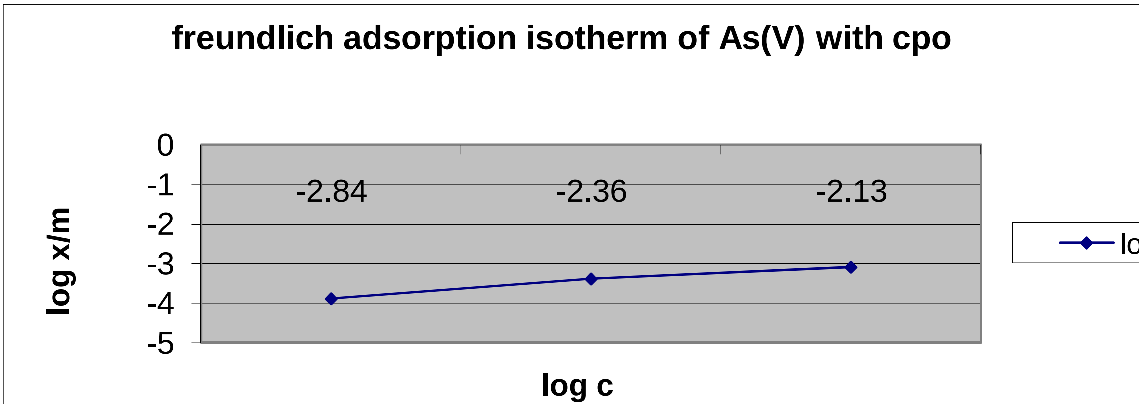

Fig. 4. Freundlich adsorption isotherm of As (V) with CPO

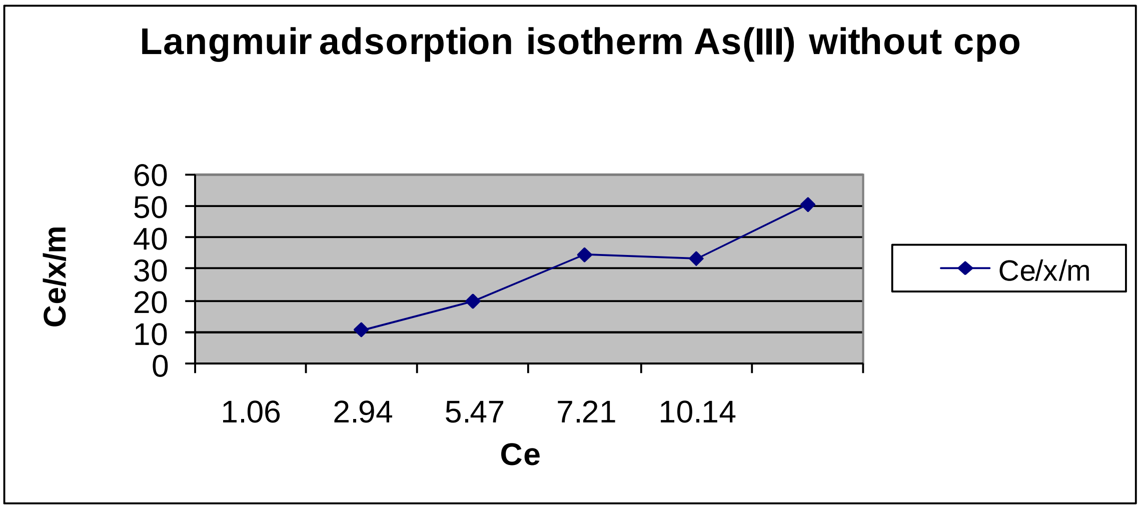

Fig. 5. Langmuir adsorption isotherm of As (III) without CPO

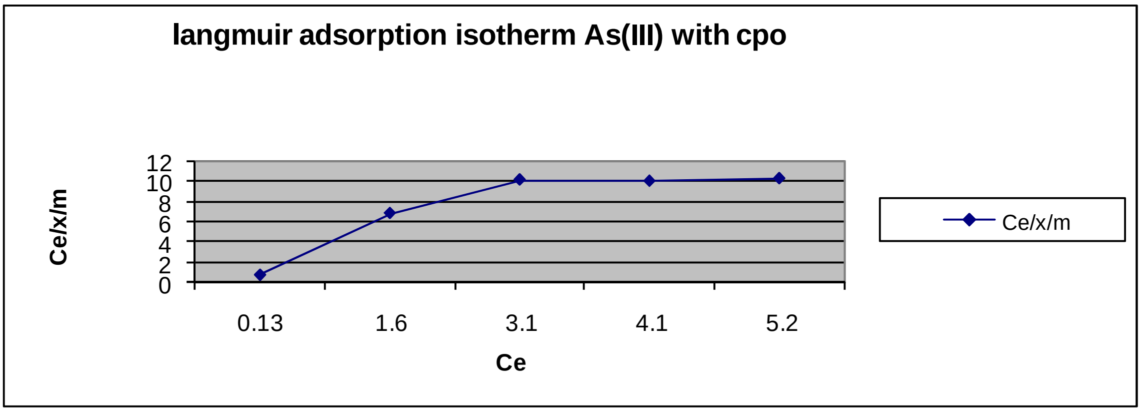

Fig. 6. Langmuir adsorption isotherm of As (III) with CPO

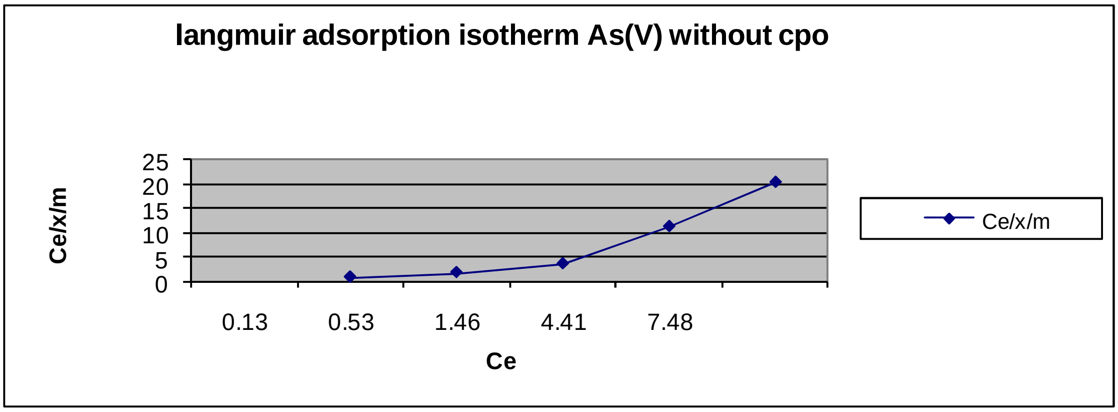

Fig. 7. Langmuir adsorption isotherm of As (V) without CPO

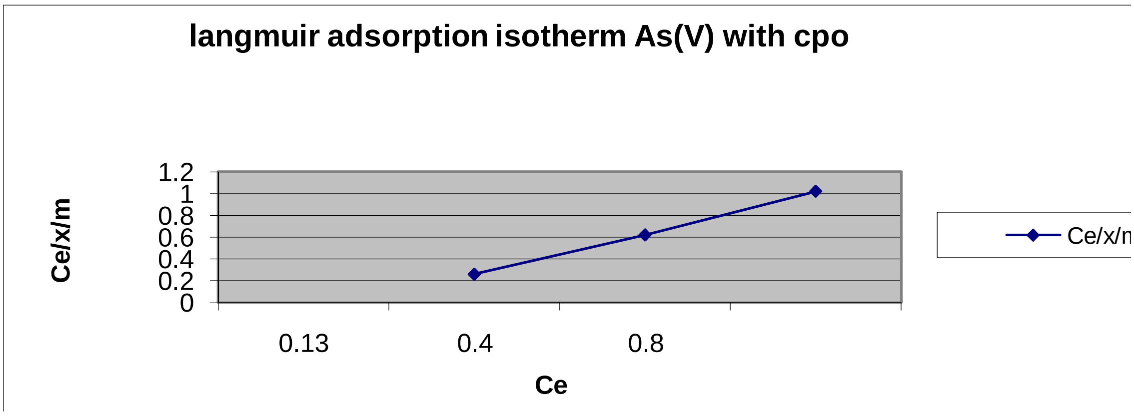

Fig. 8. Langmuir adsorption isotherm of As (V) with CPO

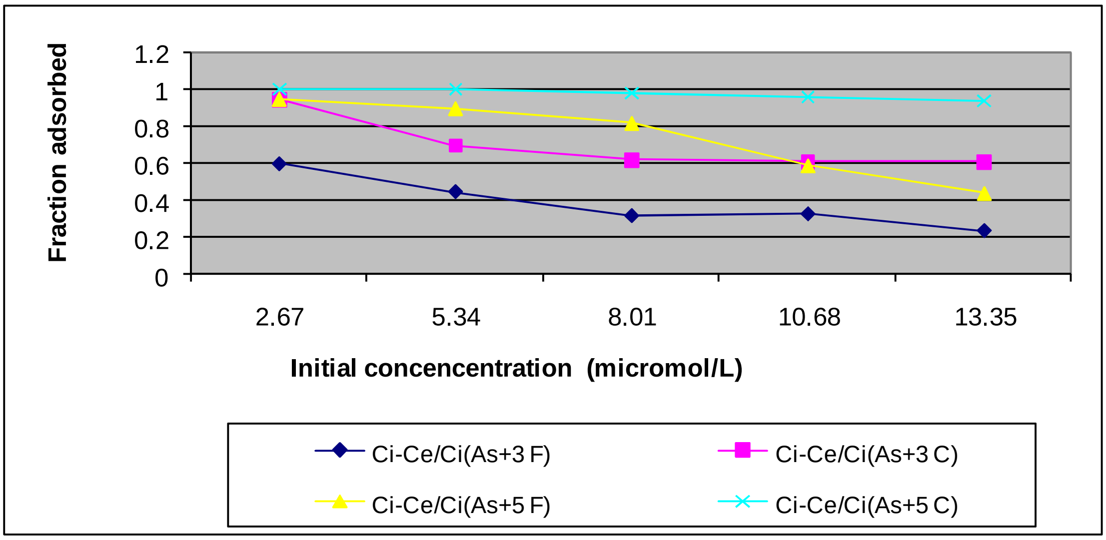

Fig. 9. Effects of various initial Arsenic (III and V) concentration on fraction adsorbed

Table 1. Percentage removal of As III using ferric chloride with and without CPO

Treatment	Percentage removal				
	S1	S2	S3	S4	S5
FeCl3	60	45	32	32	23.7
FeCl3+ CPO	95	70	62	61.3	60

Table 2. Percentage removal of As V using ferric chloride with and without CPO

	Percentage removal				
Treatment	S1	S2	S3	S4	S5
FeCl3	95	90	81.6	58.75	44
FeCl3+ CPO	100	100	98.6	96	94

Table 3. Anova table for As III removal

	df	SS	MS	F value
Treatment	1	2421.136	2421.136	11.6
Error	8	1672.144	209.018	
Total	9	4093.28	454.8089	

Table 4. Anova table for As V removal

	df	SS	MS	F value
Treatment	1	1422.056	1422.056	5.94
Error	8	1915.206	239.4008	
Total	9	3337.262	370.8069	

Table 5. Freundlich adsorption isotherm fit constants

With CPO and Ferric chloride			Ferric chloride without CPO	
	Log K_F	1/n	Log K_F	1/n
Arsenite	0.409	0.313	1.94	0.324
Arsenate	0.657	0.248	0.131	0.218

Table 6. Langmuir adsorption isotherm conastants

With CPO and Ferric chloride			Ferric chloride without CPO	
	Am	K_L	Am	K_L
Arsenite	0.553	1.36	0.237	1.67
Arsenate	0.79	3.14	0.377	0.039

Table 7. r2 value for Freundlich and Langmuir adsorption isotherm compared with reported results

	Ferric chloride (HFO) alone	Ferric chloride (HFO) with CPO	HFO Reported result (Raven et al., 1998)
Freundlich			
As(III) pH 9.2	0.9287	0.7677	0.966
As (V) pH 4.5	0.9788	0.9708	0.809
Langmuir			
As (III) pH 9.2	0.9345	0.7373	0.979
As (V) pH 4.5	0.8663	0.999	0.994