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Thermodynamic and isothermal study on the sorption of heavy metals from aquous solution by water hyazinth (E.crassipes) biomass "

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Abstract
Present paper signifies the effect of temperature on the removal of heavy metal Cd^{2+}, Cr^{2+} Pb^{2+} and Zn^{2+}ion from aqueous solution using E.crassipes biomass in a batch sorption process. From the results it is concluded that the most suitable sorption temperature for the sorption process through the biomass is 30^{0}C with maximum sorption capacities of 4.2, 3.34, 5.28 and 3.2 mg/g respectively for Cd^{2+} , Cr^{2+} Pb^{2+} and Zn^{2+} metal ions. In thermodynamical study various parameters, such as ΔG^o, ΔH^o, ΔS^o have been calculated. The data showed that the sorption process is spontaneous and exothermic in nature and that lower solution temperatures favors metal ion removal by the biomass. The findings of this investigation suggest that physical sorption plays a role in controlling the sorption rate.

*Keywords:*Adsorption, E.crassipes, Dry biomass, Heavy metals, thermodynamics, eco-friendly.

Introduction
In the adsorption reactions temperature plays a crucial role. According to the adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface tend to desorb from the surface at elevated temperatures. However, temperature has not been studied as relevant variable in biosorption experiments. The tests are usually performed at approximately 25-30ºC. However, it is also reported that there is a slight increase in cation uptake in case of seaweed in the range of 4 to 55ºC [1],[2] and [3].

Increasing heavy metals in the environment have now become a major threat to plants, animals and human life due to their bio accumulation tendency and toxicity and therefore must be removed from municipal and industrial effluents before discharge into water bodies or openly.The conventional technologies, which have been used for controlling the concentrations of these metals in aqueous discharges/effluents, ranged from granular activated carbon to reverse osmosis [4]. However, these processes are not economically feasible for small-scale industries prevalent in developing countries due to huge capital investment. It is therefore necessary to search for alternative adsorbents, which are low-cost, often naturally occurring biodegradable products that have good adsorbent properties; low value to the inhabitants and most importantly should be eco-friendly, for which a range of products has been examined including pillared clay[5] sago waste [6] , cassava waste [7], banana pith [8], peanut skins),*Medicago sativa* (Alfalfa) [9] and spagnum moss peat [10].

The characteristics of the dry biomass of E.crassipes , its proximate composition also some surface characteristics essential in assessing the ability of *E.crassipes*as an adsorbent, for the sorption of heavy metals using *E.crassipes* (water hyazinth) biomass has rarely been reported.Though there is very large data which show that E. *Crassipes as living macrophyte*is an excellent adsorbent for metal and nutrient ions. In this paper, we report the effect of temperature on the sorption of Cd^{2+} , Cr^{2+} Pb^{2+} and Zn^{2+} from single metal ion solution using the dry biomass of E. *crassipes* (Waterhyazinth) in a temperature range of 30-60ºC.

2. Materials and Methods

Biomass preparation

The plants of E.crassipes are taken from sahapura lake drainage basin. Macrophytes were washed with Milli-Q water to eliminate the remains of lake sediments and particulate matter, and then the plants are cut into pieces and sun dried. After being completely dried / dehydrated they are grinded into powder. The powder was grounded to pass through 2 mm sieve.

Sorption as a function of temperature

The samples for analyzing various parameters were prepared by standard method [11] of 10, 50 and 100 mg/l concentration. In 100 ml of each of the samples of Heavy metal i.e. Cadmium ,chromium, lead and zinc,1gm of the E.crassipes powder was added and then put into shaker at 65 rpm for 30 min. and for varied temperatures ranging from 30^0C to 60^0C and a control sample for all the test was also taken. And then the samples were filtered with whatman no. 40 filter paper after attaining the reaction period. All the experiments were set up in duplicate, for all parameters a control set was also studied i.e. without adding dry biomass. Heavy metals were analysed with atomic absorption spectrophotometer [11].

Data evaluation

The mean metal ion sorbed by the biomass at each temperature was determined using a mass balance equation expressed as

$qe = (C_0\text{-}Ce)v /m$ (1)

where *qe* = metal ion adsorption per unit weight of biomass (mg/g biomass) at equilibrium, *Ce* = metal ion concentration in solution (mg/L) at equilibrium, *Co* = initial metal ion concentration in solution (mg/L), *v* = volume of initial metal ion solution used (L), *m* = mass of biomass used (g).

Two models were used to fit the experimental data: Langmuir model and the Freundlich model. The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to biomass surface saturation. The linealised form of the above equation after rearrangement is given below:

$Ce/qe =1/q_{max}b+ C_e/q_{max}$ (2)

where *b*(dm3 g-1) is a constant related to the adsorption/desorption energy, and *q*max is the maximum sorption upon complete saturation of the biomass surface.

The experimental data were fitted into equation (2) for linearization by plotting C_e/q_eagainst C_e .

The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the biomass and the linear form is represented by equation 3:

$Lnq_e = lnK_F+1/n\ lnC_e$ (3)

where; *qe* = the metal ion uptake per unit weight of biomass (mg of metal ion adsorbed/g biomass); *Ce* = Conc. of metal ion in solution at equilibrium (mg dm-3); *Kf* and *n* are the Freundlich constants. The value of *n* indicates the affinity of the sorbent towards the biomass. A plot of ln *Ce* against ln *qe* in equation (3) yielding a straight line indicates the confirmation of the Freundlich adsorption isotherm. The constants 1/n and ln *Kf* can be determined from the slope and intercept respectively.

In these systems, the Gibbs free energy change is the driving force and the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if Δ*Go* is a negative quantity. The free energy of the sorption reaction, considering the sorption equilibrium constant, *Ko*, is given by the following equation:

$\Delta G^{0}= -RT \ln K_0$ (4)

Where Δ*Go* is standard free energy of change, J/gmol; *R* is universal gas constant, 8.314 J/(gmol K); *Ko* is the thermodynamic equilibrium constant and *T* is absolute temperature. Values of *Ko* for the sorption process may be determined by plotting ln q_e/C_e against q_e at different temperatures and extrapolating to zero *qe* [12]. The other thermal parameters such as enthalpy change (Δ*Ho*), and entropy change (Δ*So*), may be determined using the relationships:

$\ln K_0 = \Delta So /R- \Delta Ho/RT$ (5)

3. Results and Discussion

The main purpose of the research is to ascertain the effect of temperature on the sorption capacity of metal ion by an invasive weed, *E. crassipes* biomass plant. The effect of temperature on the removal of Cd^{2+} , Cr^{2+} Pb^{2+} and Zn^{2+} in aqueous solution by the biomass was studied by varying the temperature between 30 and 60ºC. The data presented in Figure 3 showed that adsorption of metal ion by the biomass increased with increase in temperature, which is typical for the biosorption of most metal ions from their solution [13], [14], [15].However, the magnitude of such increase continues to decline as temperatures are increased from 30 to 80ºC. This is because with increasing temperature, the attractive forces between biomass surface and metal ions are weakened and the sorption decreases. Careful examination of the figures revealed that most of the metal ions were removed between the temperatures of 30 to 50ºC. It was seen that for lower temperatures, equilibrium sorption occurs rapidly at lower metal ion concentration and becomes relatively constant at higher concentration. The percent adsorption observed at 30^0C was 76%, 80%, 95%, and 75% respectively for cadmium, chromium, lead and zinc at 50 mg/l concentration. As temperature increased above 50ºC, an initial low sorption was observed. The equilibrium concentrations for higher temperatures (60- 80ºC) were not significantly different for those of lower temperatures. This indicates that increasing the initial metal ion concentrations above the equilibrium concentrations of 50 – 70 mg/L may not have any significant increase in the sorption of metal ions by *E. crassipes* biomass. At high temperature, the thickness of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase, which results in a decrease in adsorption as temperature increases [3]. The decrease in adsorption with increasing temperature, suggest weak adsorption interaction between biomass surface and the metal ion, which supports physisorption. In this investigation temperatures of 30 and 45ºC is the optimal temperature of adsorption for selected heavy metal.

To facilitate the estimation of the adsorption capacities at various temperatures, experimental data were fitted into equilibrium adsorption isotherm models of Freundlich and Langmuir.Sorption data were fitted by Freundlich adsorption isotherm at all temperatures (r^2 were greater than 0.72). The Freundlich adsorption isotherm parameter, 1/n and KF, were then plotted against temperature .The values of 1/n were found to be less than unity at all temperatures where the values are found to be closer to zero which means the adsorption surface is more heterogenous, indicating that desorption occurs at above 40ºC. The significant adsorption took place at low temperatures, which becomes less significant at higher temperatures. The ultimate adsorption capacity of the biomass at the different temperatures can be calculated from the isothermal data by substituting the required equilibrium concentration in the Freundlich equation. The value of KF, which is a measure of the degree of adsorption, decreases with increase in temperature (Figure 2). The higher KF values at lower temperatures indicate that more sorption would be expected at these temperatures. The most probable temperature of adsorption was further evaluated by the Langmuir isotherm. The Langmuir maximum adsorption, q_{max}, for a monomolecular surface coverage and the adsorption equilibrium constant, b, at the temperatures investigated were obtained from the plot (Figure.3) for the prediction of the probable temperature of adsorption. Relevant parameters values as shown in Table 1 indicate that optimal temperature of adsorption in utilizing *Echornia crassipes* biomass for the removal of metals in aqueous solutions is about 30ºC. The Langmuir fits at all temperatures show slight curvatures (Figure 3), which suggest that the surface adsorption is not a single monolayer with single sites. Two or more sites with different affinities and maximum may be involved in metal ion sorption. After 30ºC, the values of q_{max} and b decreased with increase in temperature, showing that adsorption capacity and intensity of adsorption are enhanced at lower temperatures.

Thermodynamic study

The study of sorption data by thermodynamic treatment indicates that ΔGo values were negative at all the studied temperatures. The negative values of ΔGo (Table 3) indicate the spontaneous nature of adsorption of metal ion by the biomass. The ΔGo values obtained in this study for the studied metal ions are <-10 KJ $gmol^{-1}$, indicate that physical adsorption is the predominant mechanism in the sorption process. The values of Δ*Ho* and Δ*So* were obtained from the slope and intercept of plots of ln *Ko* vs 1/T . The negative values of Δ*Ho* for Cd2+ , Cr2+ , Pb2+ and Zn2+ on to the biomass further confirm the exothermic nature of the adsorption process. The negative values of Δ*So* (Table 3) show that the process reaction proceeds spontaneously in the forward direction.

Table 1 Langmuir adsorption isotherm parameter

Temp (^{0}C)	**Cd**			**Cr**			**Pb**			**Zn**		
	q_{max}	**b (L/mol)**	**R^2**	**q_{max}**	**b (L/mol)**	**R^2**	**q_{max}**	**b (L/mol)**	**R^2**	**q_{max}**	**b (L/mol)**	**R^2**
30	28.01	0.956	0.917	23.81	1.17	0.938	32.26	1.81	0.962	20.83	1.14	0.900
40	23.47	0.916	0.866	21.74	1.03	0.913	28.74	1.38	0.943	17.54	1.10	0.869
50	18.15	0.808	0.775	17.79	1.004	0.836	24.10	1.01	0.921	16.13	1.07	0.827
60	13.35	0.679	0.740	9.43	1.005	0.512	17.39	1.09	0.831	9.10	2.24	0.423

Table 2 Freundlich adsorption isotherm parameter

Temp (^{0}C)	**Cd**			Cr			Pb			Zn		
	1/ n	K_f	R^2	1/n	K_f	R^2	1/n	K_f	R^2	1/n	K_f	R^2
30	0.360	0.901	0.917	0.342	0.845	0.899	0.356	0.994	0.968	0.336	0.787	0.855
40	0.355	0.842	0.866	0.350	0.792	0.871	0.365	0.920	0.936	0.314	0.738	0.836
50	0.340	0.772	0.775	0.333	0.727	0.844	0.369	0.820	0.895	0.314	0.706	0.813
60	0.270	0.720	0.740	0.274	0.545	0.668	0.329	0.730	0.825	0.245	0.624	0.543

Table 3 Thermodyanamic parameters for the adsorption of heavy metal on the biomass E.crassipes

Temp. (^{0}C)	**Cd**			**Cr**			**Pb**			**Zn**		
	$-\Delta^0G$ (kJ/mol)	**$-\Delta^0H$ (kJ/mol)**	**$-\Delta^0S$ (J/mol-K)**	**$-\Delta^0G$ (kJ/mol)**	**$-\Delta^0H$ (kJ/mol)**	**$-\Delta^0S$ (J/mol-K)**	**$-\Delta^0G$ (kJ/mol)**	**$-\Delta^0H$ (kJ/mol)**	**$-\Delta^0S$ (J/mol-K)**	**$-\Delta^0G$ (kJ/mol)**	**$-\Delta^0H$ (kJ/mol)**	**$-\Delta^0S$ (J/mol-K)**
30	0.41	133.20	133.20	0.17	13.53	13.53	0.65	42.30	42.29	0.15	54.26	54.26
40	0.72	116.16	116.16	0.03	10.64	10.64	0.36	3.0	3.0	0.10	57.33	57.33
50	1.03	149.87	149.86	0.01	104.67	104.67	0.01	579.96	579.96	0.08	1054.09	1054.09
60	1.77	109.20	109.19	0.01	2.42	2.42	0.11	11.82	11.82	1.07	526.46	526.45

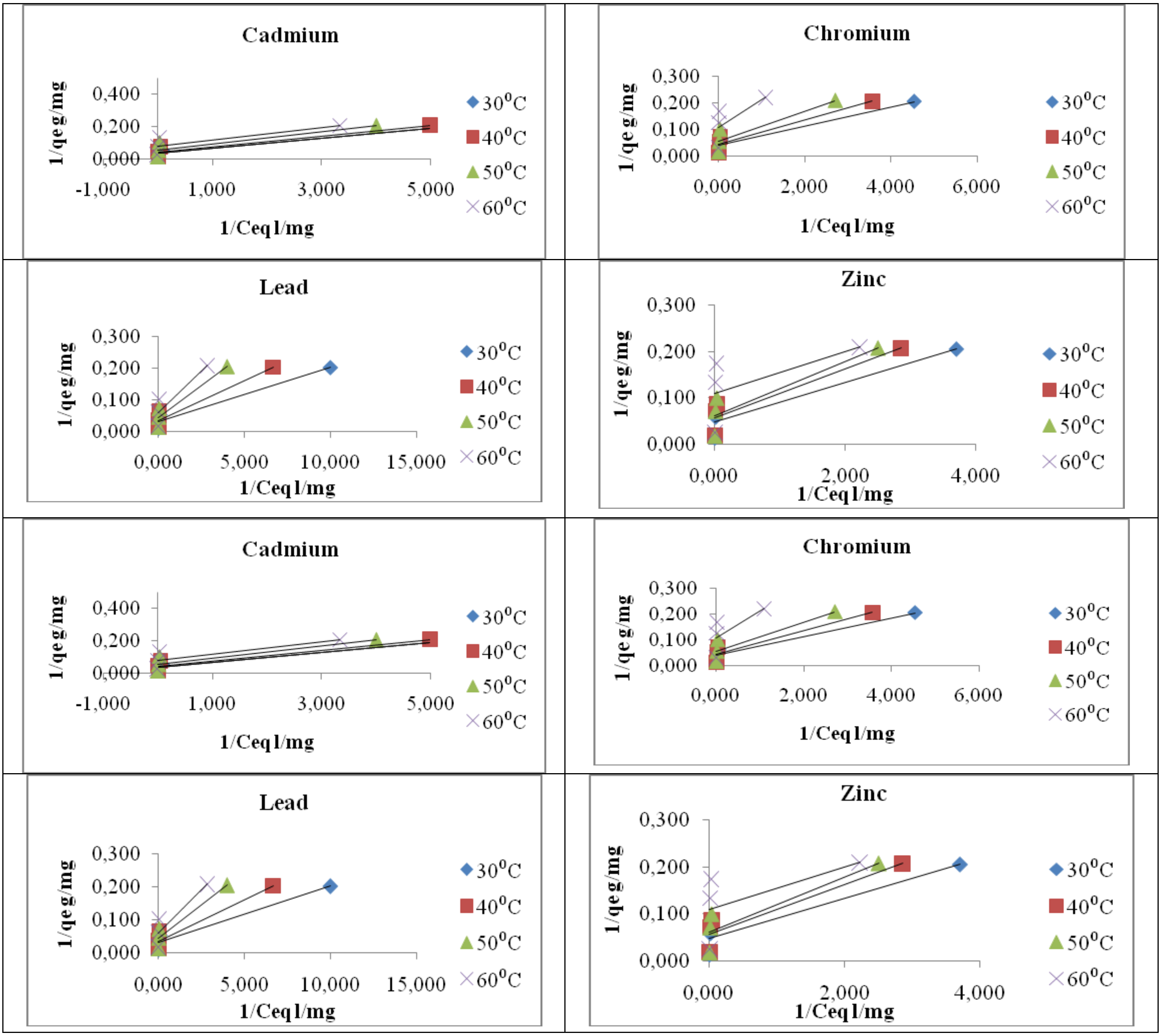

Figure 1 Langmuir isotherm plots for the adsorption of heavy metals onto E.crassipes biomass

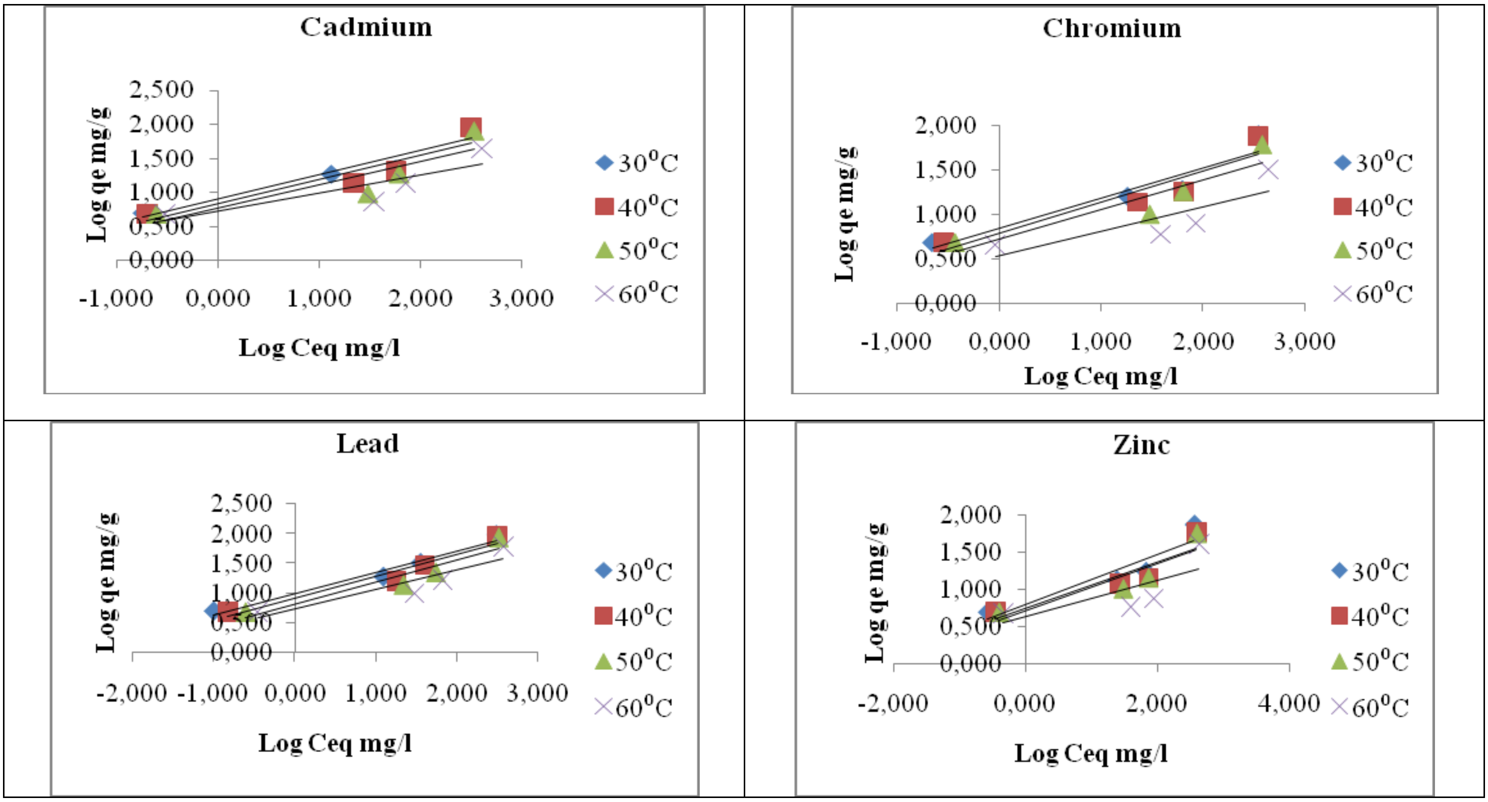

Figure 2 Plots of Freundlich isotherm parameters as a function of temperature

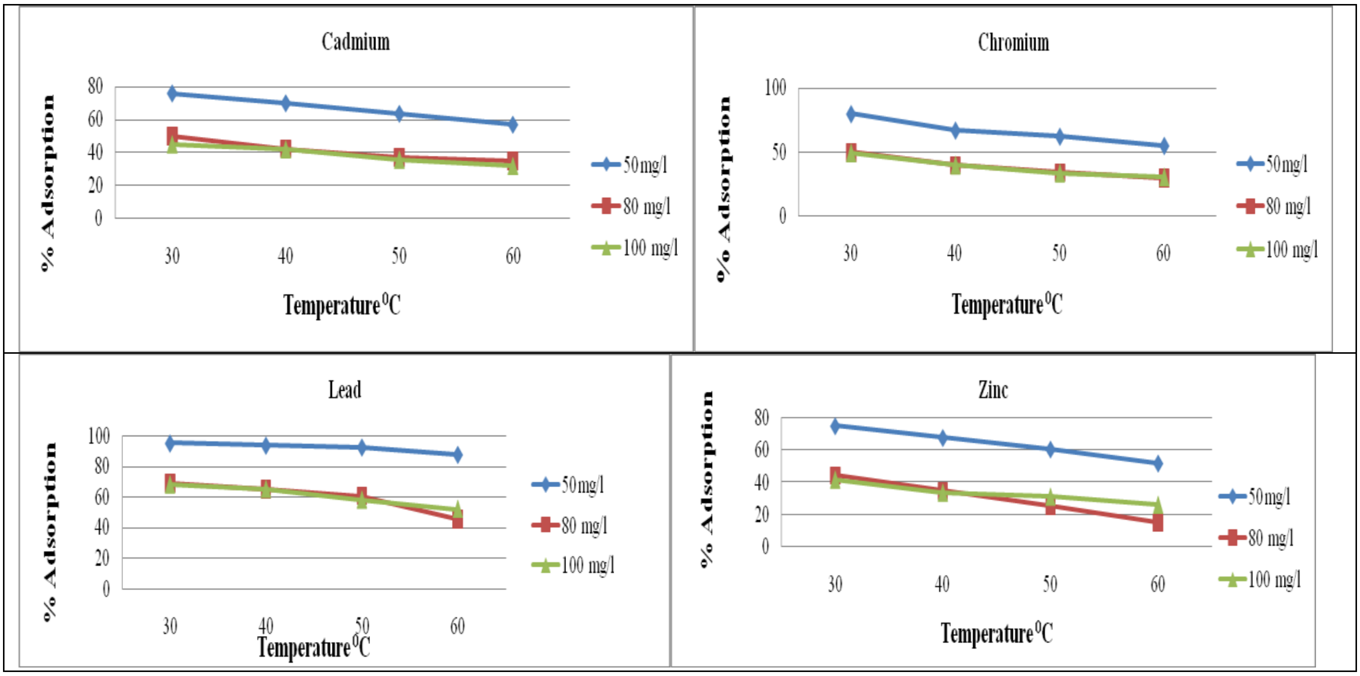

Figure 3 Effect of temperature on the adsorption on to E.crassipes biomass

Conclusion

The results clearly establish that the sorption of Cd^{2+}, Cr^{2+}, Pb^{2+} and Zn^{2+} onto *E.crassipes* is favoured at lower solution temperatures. The range of temperatures which favours the adsorption process was 10-45ºC with optimal temperature at 30ºC. This temperature range is favourable for solubility of chemicals in wastewater treatment systems and will also enhance the reaction rates. The activation energy further supports lower solution temperatures.The sorption process is spontaneous and exothermic and the mechanism is physisorption. The equilibrium data agrees with the Langmuir isotherm. The sorption capacity of $Pb^{2+}$is higher than Cd^{2+}which is higher than Cr^{2+} and comparatively less adsorption is observed for Zn^{2+}; however, there is no significant difference in the sorption potential of the biomass towards the four metal ions in aqueous solution. Echornia *crassipes* is a non-useful plant growing in the wild, its use as an adsorbent may eventually encourage cultivation of the plant and enhance the economies of local farmers and generate employment. The biomass from *E.crassipes* may be recycled and the recovered also the biomass is biodegradable and therefore environment friendly it also has the potential for metal removal and recovery of metal ions from contaminated waters.On the other hand *E.crassipes* is not only waste inexpensive and readily available in fact has become a great problem for water bodies due to its invading property. This process will be environment friendly and reduce the huge amount of indiscriminate effluent discharges all around the small industry concerns in India and also will control the invasion of this weed. It may also provide an affordable technology for small and medium-scale industry in India.

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