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"Study of adsorption isotherms and thermodynamics for heavy metal removal from aqueous solutions using *Canna indica* biomass"

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Abstract- Surface water bodies like lakes, ponds, and streams anchorage the survival of aquatic life flora and fauna and maintain ecological balance. Due to urbanization population explosion, and industrialization, the water sources are getting polluted, present paper is an attempt to evaluate the adsorption of heavy metals like cadmium (Cd), chromium (Cr), zinc (Zn), and lead (Pb) by the dry biomass of *Canna indica* commonly called keli. Very less literature is available on the adsorption capacity of this plant though is found in excess in Indian climate. Living *C.indica* plants have minor capacity to absorb heavy metals from waste water. The present experimental study was conducted to assess the adsorption capacity of dry biomass of *C.indica* to compare and identify their potential to improve the water quality by removing the impurities. The paper critically evaluates the water – purifying capacity of dry – biomass of *C.indica*. It also evaluates the extent up to which heavy metals can be removed by the dry biomass of this terrestrial plant in a given period of time.

Keywords - Plants, Dry biomass, *C.indica*, heavy metals, adsorption, isotherm, thermodynamics.

1 INTRODUCTION

Waste water is generated from residential and industrial day today activities but it must be treated before it is released into surface water bodies or to environment. So that it does not cause further pollution of water sources. Waste water comes from variety of sources. Everything that you flush down your toilet or rinse down the drain is waste water. Waste water can also come from agricultural and industrial sources.

Surface water bodies are the major sources of water to human beings which satisfies many day today purposes. Water Quality of surface water bodies is subjected to the natural degradation, the process of eutrophication and the impact of human activities, [1]. Natural sources of water are depleting fast and are polluted due to industrialization and urbanization in haphazard manner.

Pollution of the aquatic bodies by (synthetics and organic) pollutants like pesticides, polyaromatic hydrocarbons, heavy metals, etc, have caused imbalance in the natural functioning of the ecosystem. All of these pollutants and heavy metals cause severe damage to the living system at various levels. The World Health Organization [2] have prescribed standards for heavy metals and other parameter in both aquatic life and drinking water as shown in (Table1)

The Potential toxic metal elements such as cadmium, chromium, lead, Copper, Zinc etc. are identified to cause health hazards in animals [3] , [4] these heavy metals are reported to be toxic and found associated with the occurrence of several health effects. Considering its effect on human being and aquatic life, appropriate treatment of heavy metals from waste water is of utmost importance. Increasing awareness of ecological hazard of toxic metals from urban and industrial sources has involved considerable interest in the study of levels and fate of heavy metals in the aquatic environment [5].

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Table 1 Maximum permissible limit for the studied parameters (WHO standards)

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S.No.	Heavy metal`	Aquatic life`(ppb)	Drinking Water (mg/l)
1	pH	-	6.5-8.5
2	Total Hardness	-	300
3	Fluoride	-	1.0
4	Chloride	-	250
5	Chromium	100.0	0.05
6	Cadmium	0.017	0.003
7	Lead	20.00	0.10
8	Zinc	30.00	5.00

Various techniques are being used to purify the water, like the installation of ozonizer, aerator, filtration units, sedimentation tanks, electro dialysis, reverse osmosis, addition of chemicals etc. All of these methodologies used are quite costly and energy intensive, none of them could claim to treat all the heavy metals in economically feasible manner [6]. Various waste biomaterials such as grape stalk waste [7], green coconut shell powder [8], chaff [9], and crab shell particles [10] have been studied for the removal of heavy metal ions [11] from the effluents.

Water can be purified by natural means such as phytoremediation technique i.e. using plant for purification but in present study dry biomass of plant (*C.indica*) is used to overcome many inconvenience cased due to living plants. Plants have the ability to assist the breakdown of human and animal derived waste water and remove disease causing microorganisms and pollutants [12]. Their ability to absorb pollutants has been recognized worldwide in the treatment of water [13]. Vietmeyer [14] suggested that *Eichhornia crassipes* could be used for removal of nutrients and heavy metals from sewage and sludge ponds [15] studied on *Hydrilla verticillata* and observe the Bio- absorption of copper from wastewater.

Manuscript will be helpful in showing the water purifying capacity of dry biomass this terrestrial or semi aquatic plant (*C.indica*) and also will evaluate the best results of adsorption shown in varied time period.

2. MATERIALS AND METHODS

The present study is concentrated on the adsorption of four heavy metals viz. chromium, Cadmium, lead and zinc by dry biomass of *C.indica* for which the experiments are conducted. The plants of *C.indica* were taken from sahapura lake drainage basin and 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. The samples for analyzing various parameters were prepared by standard method [16] of 10, 50 and 100 mg/l concentration. In 100 ml of each of the samples of Heavy metal i.e. chromium, Cadmium, lead and zinc,1gm of the *C.indica* powder was added and then put into shaker at 60 rpm and at temperature of 28^0C, for varied time periods viz. 15 to 120 min and a control sample for all the test was also taken. And then the samples were filtered with whatmann no 40 filter paper after attaining their reaction period. All the experiments were set up in duplicate for all parameters a control set was also studied and there was no powder (dry biomass) added. All the parameter were analyzed by the method as mentioned in APHA i.e. Heavy metals with atomic absorption spectrophotometer.

3. Result and Discussion

Results presented in Table -1- (I), (II) indicate the effect of various dosage of adsorbent (powdered *C.indica*) at two different contact duration's on equilibrium concentration, reaction rate constant and percent removal of Cd. Cr, Zn and Pb ions content when dosage vary from 0.5 gm/l to 4.0 gm/l. It also represents the data for the model of Freundlich and Langmuir adsorption isotherm for removal of Cd. Cr, Zn and Pb ions. For Freundlich adsorption isotherm the logarithmic values of equilibrium concentration (Ceq) and per gram removal (x/m) of Cd. Cr, Zn and Pb are given. For Langmuir isotherm model, the inverse values of equilibrium concentration i.e. 1/Ceq and removal per gram liter, i.e. 1/qe are considered.

Table 2 represents the Langmuire and Freundlich isotherm parameters for Cd. Cr, Zn and Pb ion . Here the Θ_0 value (adsorption capacity) is the slope of the straight line and 'b' is the intercept on X-axis is the energy of adsorption. The freundlich isotherm parameter K is the intercept on X- axis and 1/n is the slop of straight line.

Fig.-1 represents adsorption of Cd, Cr, Pb, and Zn ion on dry biomass of *C.indica* at various contact time from 15 to 120 minutes.

Fig. 2 - indicates Freundlich adsorption isotherm model i.e. the logarithemic values of equilibrium concentration and x/m (where x= removal of Cd. Cr, Zn and Pb ions amd m= weight of adsorbent) is plotted, which gives straight line.

Fig. 3- represents the data for Langmuir isotherm model for the removal Cd. Cr, Zn and Pb using powdered *C.indica* as an adsorbent. The inverse values of equilibrium concentration (Ceq) Vs removal/ gm/1(qe) for heavy metals (Cd. Cr, Zn and Pb) is plotted for that.

Adsorption of Heavy metals

Cadmium - Results after treating cadmium standard solution of 10 ppm concentration at different time are very encouraging. Adsorption % of 10 ppm 'Cd' solution in 15 – 120 min. it was found in the range of 60 to 96.5 % (Fig.1) it shows that the dry biomass adsorbed almost whole of the Cd metal ion. Here in this case also the adsorption concentration was directly proportional to increasing time. Cadmium has been recognized as a toxic metal for a long time but it attracted attention due to the spread of the disease 'itai-itai' in Japan. The exposure to cadmium for extended periods results in respiratory distress and uncontrolled cough and gastrointestinal pain. Its permissibility is 0.017 ppb for aquatic life and 0.003 mgL-1 for drinking water as per WHO.

Chromium- Dry biomass of *C.indica* efficiently adsorbed Cr from 10, 50, 100 mg/l concentration of Chromium solution at varied time period. The adsorption percent increased with increasing time (Fig 1-a). i.e. the adsorption shown by the material at normal condition of temperature and pressure at various time period starting from 15 min. to 120 min. the average percentage adsorption of chromium is 73.25 % . The results show that initially the adsorption rate was high and after duration of 2 hr. it slowly got reduced but overall the adsorption was remarkably satisfying. Cr is very much toxic and carcinogenic for living beings.

Lead - The lead metal concentration was remarkably reduced by the dry biomass from the sample from 10 ppm to 1.5 ppm. There was the adsorption of about 89.58 % on an average. With the increasing time period the original concentration in the solution decreased with slow rate and this concentration increased with very slow rate with increasing time and remained almost stationary after 60 min attaining adsorption of 97 %. Lead is very much toxic and carcinogenic for living beings. Its permissible limit is 25.00 ppb aquatic life and 0.10 mg/l for drinking water as per WHO.

Zinc- Results obtained by treating 10 mg/l of zinc soln. for varied time period showed marked decrease in its concentration (Fig.1) with the contact period of only 1/2 hr. and then the values showed linear trend after 1 hr. The % adsorption of Zn metal ion of 10 mg/l concentration calculated for period of ½ hr., 1hr., and 2 hr., were 42 %, 58 % and 60% respectively. As we know, zinc is not very much toxic up to permissible limit (30.0 ppb for aquatic life and 5.0 mg L-1 for drinking water as per WHO). It is one of trace element for regulating plant metabolism.

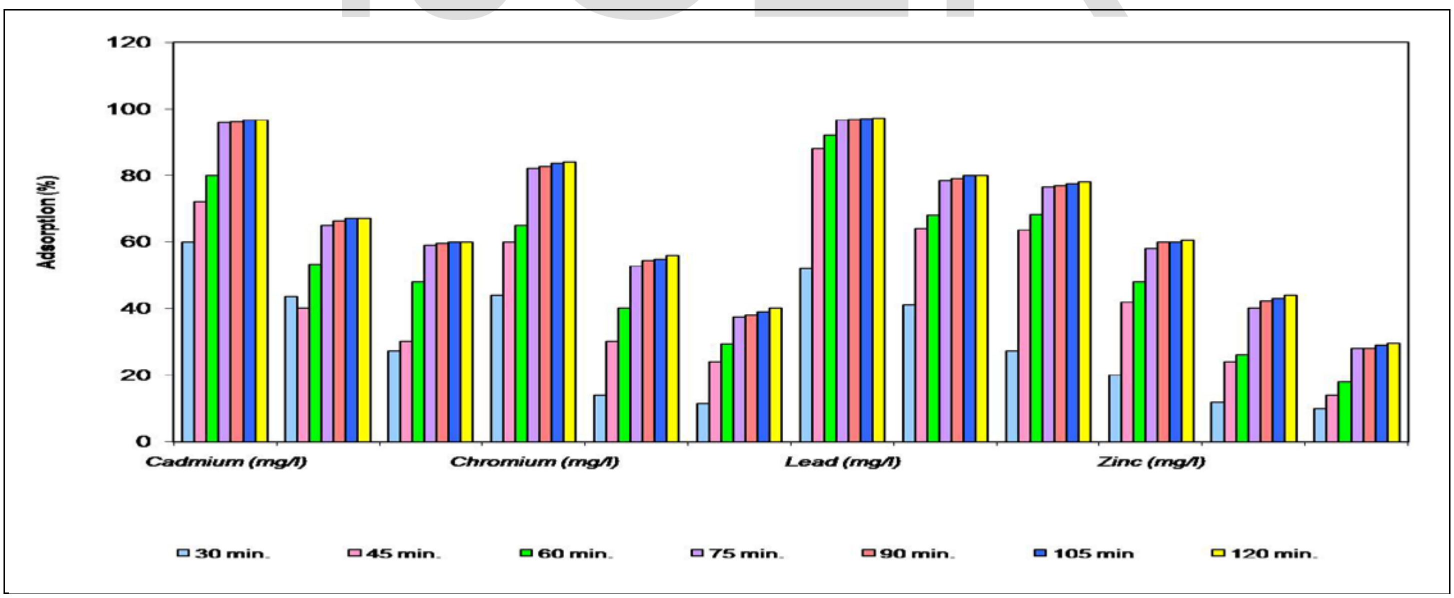

Fig. 1 Percent adsorption of heavy metals by dry biomass of C.indica

Adsorbent : Powdered C.indica Temperature : 28±1 ^{0}C

Size : 200 μ Contact time : **30 Minutes**

	Initial Conc.	Final Conc.	Removal	Log Ceq	Log qe	1/Ceq	1/qe
	mg/l	Ceq (mg/l)	x/m =qe (mg/g)				
Cd	5	0.21	2.395	-0.678	0.379	4.7619	0.418
	10	2	4	0.301	0.602	0.5	0.250
	50	20	15	1.301	1.176	0.05	0.067
	100	60	20	1.778	1.301	0.0166	0.050
	500	350	75	2.544	1.875	0.0028	0.013
Cr	5	0.32	4.84	-0.495	0.685	3.125	0.207
	10	0.42	9.79	-0.377	0.991	2.3809	0.102
	50	24	38	1.380	1.580	0.0416	0.026
	100	70	65	1.845	1.813	0.0142	0.015
	500	362	319	2.559	2.504	0.0027	0.003
Pb	5	0.27	4.865	-0.569	0.687	3.7037	0.206
	10	2.2	8.9	0.342	0.949	0.4545	0.112
	50	20.8	39.6	1.318	1.598	0.0480	0.025
	100	62.6	68.7	1.797	1.837	0.0159	0.015
	500	352	324	2.547	2.511	0.00284	0.003
Zn	5	4	3	0.602	0.477	0.25	0.333
	10	6.6	6.7	0.820	0.826	0.1515	0.149
	50	35.8	32.1	1.554	1.507	0.0279	0.031
	100	77.5	61.25	1.889	1.787	0.0129	0.016
	500	446	277	2.649	2.442	0.0022	0.004

Adsorbent : Powdered C.indica Temperature : 28±1 ^{0}C

Size : 200 μ Contact time : **60 Minutes**

		Final Conc.	Removal	Log Ceq	Log qe	1/Ceq	1/qe
		Ceq (mg/l)	x/m =qe (mg/g)				
Cd	5	0.55	2.225	-0.2596	0.3473	1.818	0.4494
	10	5.6	2.2	0.7481	0.3424	0.1785	0.4545
	50	36.8	6.6	1.5658	0.8195	0.0271	0.1515
	100	75	12.5	1.8750	1.0969	0.0133	0.08
	500	460	20	2.6627	1.3010	0.0022	0.05
Cr	5	4.8	2.6	0.6812	0.41497	0.2083	0.3846
	10	4.2	7.9	0.6232	0.8976	0.2381	0.1265
	50	45.6	27.2	1.6589	1.4345	0.0219	0.0367
	100	91.5	54.25	1.9614	1.7344	0.0109	0.0184
	500	458	271	2.6608	2.4329	0.0022	0.0036
Pb	5	4.8	2.6	0.6812	0.4149	0.2083	0.3846
	10	6	7	0.7781	0.8450	0.1667	0.1428
	50	38.8	30.6	1.5888	1.4857	0.0258	0.0326
	100	78	61	1.8920	1.7853	0.0128	0.0163
	500	462.5	268.8	2.6651	2.4293	0.0024	0.0037
Zn	5	5	2.5	0.6989	0.3979	0.2	0.4
	10	9.5	5.25	0.9777	0.7201	0.1053	0.1904
	50	50	25	1.6989	1.3979	0.02	0.04
	100	98.5	50.75	1.9934	1.7054	0.0102	0.0197
	500	458	271	2.6608	2.4329	0.0022	0.0036

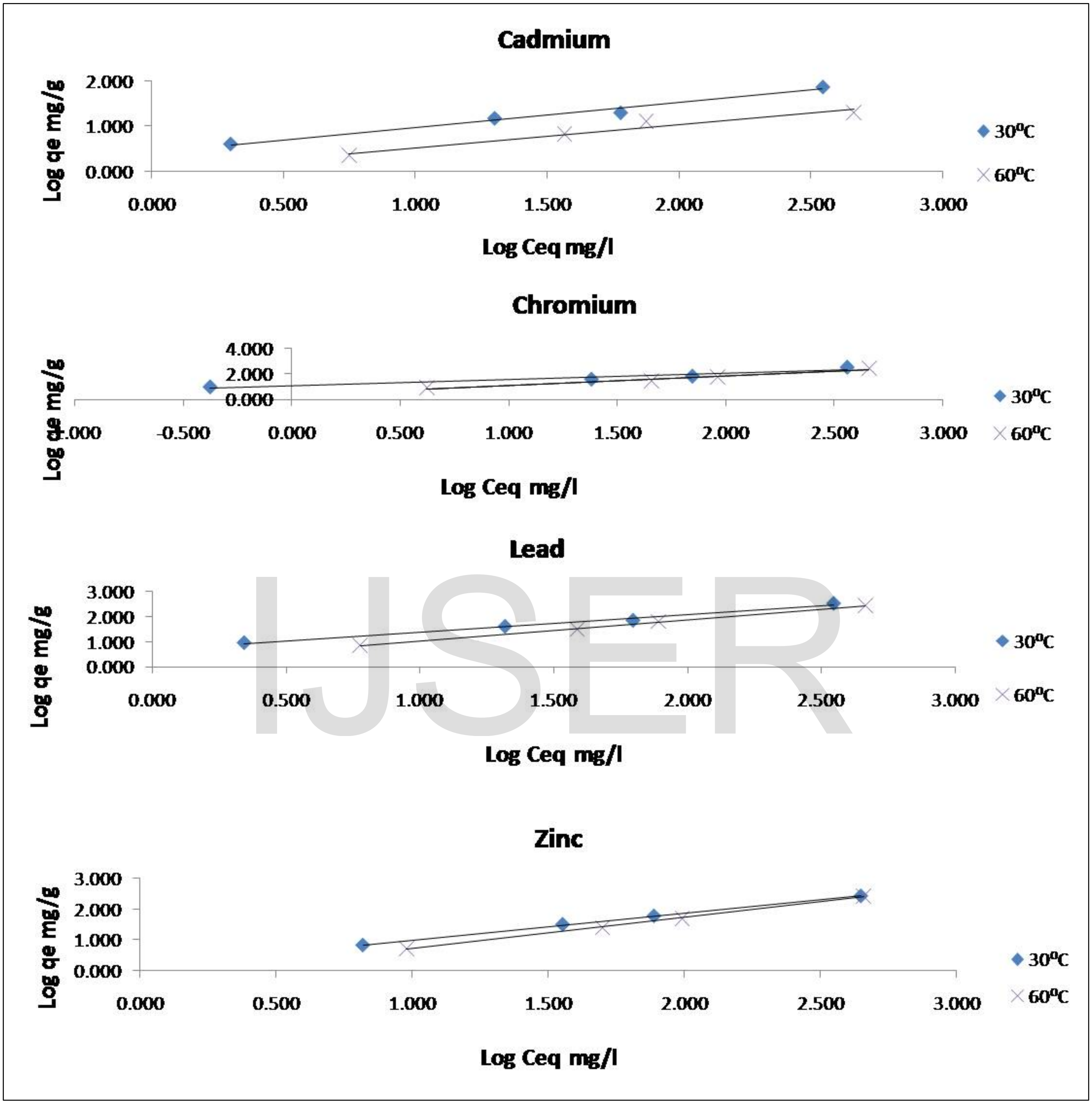

Fig. 2 Freundlich adsorption isotherm

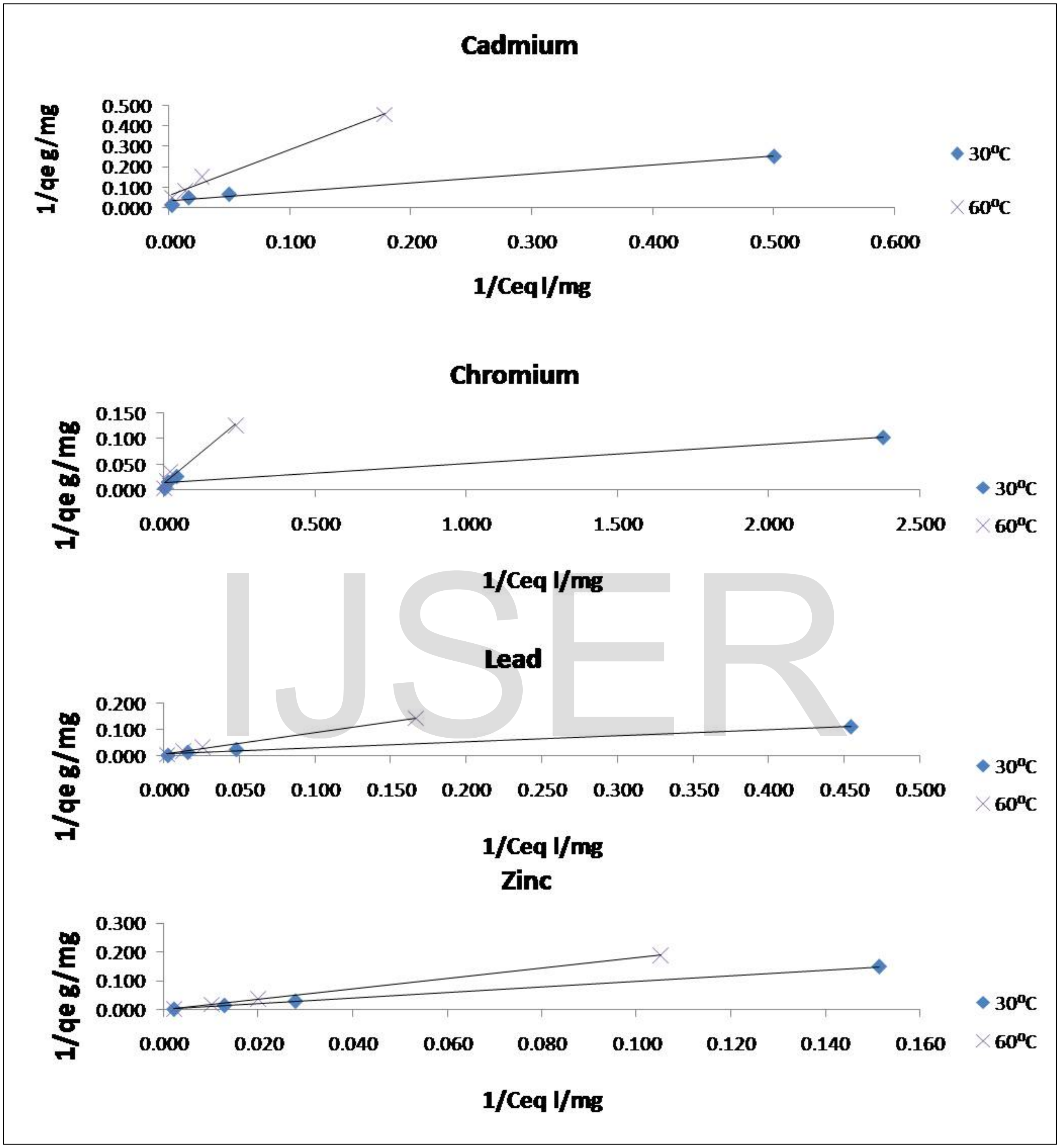

Fig. 3 Langmuir adsorption isotherm

Table 2 Freundlich & Langmuir isotherm parameters for Cd, Cr, Pb, and Zn

Metal	Temperature^0 C	Langmuir isotherm			Freundlich isotherm		
		Q° (mg/g)	bX10^3 (dm^3/mg)	R^2	1/n	K	R^2
Cadmium	30	31.25	71.51	0.979	0.632	0.421	0.982
	60	16.39	7.37	0.987	0.511	0.013	0.953
Chromium	30	71.43	1930.50	0.963	0.742	1.073	0.931
	60	76.92	160.93	0.944	0.479	0.343	0.926
Lead	30	111.11	487.33	0.99	0.694	0.680	0.989
	60	166.67	400.64	0.996	0.843	0.176	0.999
Zinc	30	322.58	333.80	0.999	0.881	0.117	0.999
	60	1000.00	556.17	0.999	1.017	0.300	0.998

It is evident from the results presented in table 1 that increase temperature leads to gradual reduction in Cd. Cr, Zn and Pb content, this can be contributed to considerable increase in dissociation of adsorbent particles. Increase in temperature restricts adsorption of heavy metal ions to adsorbent molecule.

Increase in percent removal of Cd. Cr, Zn and Pb with increase in contact time of adsorbent suggest more adsorption of these ions, supporting considerable increase in reaction rate. The equilibrium study has been conducted based on the commonly used monolayer and multi layer adsorption isotherm models of Langmuir and Freundlich. The adsorption data were fitted in two models viz., Freundlich and Langmuir isotherms.

The significance of adsorption isotherms is that they show how the adsorbate molecules (metal ion in aqueous solution) are distributed between the solution and the adsorbent solids at equilibrium concentration at different temperatures. The purpose is to understand the strength of the solute-surface bond, during the study of adsorption form the solution. The nature of isotherm clearly indicates the dependence of the solvent on the level of adsorption.

Results of Table 1 representing Freundlich isotherm for Cd. Cr, Zn and Pb removal indicate that when contact period is increased from 30 to 60 min. lesser amount of adsorbent is required to attain equivalence concentration, while the same equivalence concentration is attained with more adsorbent at contact period of 30 minutes. This can be interpreted as more removal of Cd. Cr, Zn and Pb contents with less amount of adsorbent, when longer contact period is permitted. In other words, increase in contact period which affects economics of the adsorption process and enhances the removal Cd. Cr, Zn and Pb contributing components of the waste water.

The linear plots at different temperatures indicate the applicability of the Freundlich equation the values K_f and n are calculated from the intercept and slope respectively of the linear plots of log q_e versus log C_{eq}. The constant K_f, which is a measure of sorption capacity, decreases with increase of temperature the decrease in the values of K_f with increase in temperatures shows the decrease in adsorption. It validates the experimental observation about the decrease in percent adsorption with gradual increase in temperature.

The values of *l/n* are less than unity [17] , [18] for all the four metal ions, showing the favorable adsorption of Pb^{2+} ,Cd^{2+} ,Cr^{6+} and Zn^{2+} on *C.indica.*

This equation is empirical expression that covers the heterogeneity of the surface and the exponential distribution of sites and their energy value of n and K_f is presented in table 1.

The data presented in table 1 give linear natures of the plots presented in Fig.3; confirm applicability of Langmuire model also. Which is governed by the expression.

$$1/qe = 1/ Q° b \times 1/Ceq + 1/ Q°$$

(Where, qe = amount of Cd. Cr, Zn and Pb adsorb per unit weight of absorbent (mg/g), Ceq = equilibrium concentration of

Cd. Cr, Zn and Pb (mg/l), x = amount of Cd. Cr, Zn and Pb adsorbed (mg/l), m= weight of adsorbent (gm/l), Q° = Langmuir constant ; related to the capacity of adsorption (mg/g), b = Langmuir constant ; related to the energy of adsorption (dm^3/mg).)

The Langmuir constant (b) represents the degree of adsorption affinity of the adsorbate. The maximum adsorption capacity (Q) associated with complete monolayer cover is typically expressed in (mg/g). High value of b indicates for much stronger affinity of metal ion adsorption. The Langmuir equation is tested by plotting 1/qe versus l/Cqe for different metal ions present as single species in solution at different temperatures. The straight-line plots indicate the applicability of the model for the present systems. The values of Q^0 and b for the metal and nutrient ions were calculated from the slopes and intercepts of the plots through regression analysis and the value of Q° and b decreases with increasing temperature indicating the exothermic nature of adsorption. The applicability of the four linear forms of Langmuir model to the adsorbent was proved by the high correlation coefficients R^2>0.8.

The adsorption isotherm studies clearly indicated that the adsorptive behaviour of heavy metal ions on adsorbents satisfies not only the Langmuir assumptions but also the Freundlich assumptions, [19] i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy.

The regression analysis and experimental observations show that the experimental data fitted well in both the isotherms. As seen from results the Langmuir model exhibited a slightly better fit to the biosorption data than the Freundlich model as the values of correlation coefficient 'R^2, were marginally better for Langmuir isotherm than the values of 'R^2, for Freundlich isotherm [20].

Two types of observations were collected after treating the water with the dry- biomass.

1. Reduction concentration of heavy metals from aqueous sample.
2. Effect in the rate of adsorption with changing time.

4. CONCLUSION

Observations obtained from the above mentioned batch study concluded that not only living plants of *C.indica* but also dry biomass of the plant can also be used for reducing heavy metals present in waste water generated from industrial activities. The control samples merely showed any visible difference in the concentration to that of original concentration which signifies that the dry biomass of the plant has good potential for waste water treatment. It is well evaluated that the dry mass of the plant showed the required good results in case of heavy metals is astonishing as it has shown great reduction from its original concentration for all the studied heavy metals and the results obtained were comparatively better than that done with the living plants. It was also noticed that many of the studied heavy metals viz. Cadmium, Chromium, Zinc and Lead showed reduction in their concentration with increasing contact period but after 4 hr. they showed stability in reduction percentage. This concludes that the dry biomass powder of *C.indica* can be effectively utilized for reducing heavy metals and it gives the results in short span of time and so will prove to be a powerful tool among various waste water treatment technologies.

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