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Potential of the waste leaves of *Rhododendron arboretum* (Burans) for the removal Pb (II) and Cd (II) ions from waste water

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Abstract
In the present study, we have used the waste leaves of *Rhododendron arboreum* as adsorbent for the removal of Pb^{2+} and Cd^{2+} ions from waste water. The adsorbent was characterized by means of FTIR and FESEM methods. The percentage adsorption has been achieved as 67.9 %, 58.9% and 98.8% for Pb^{2+} and 41%, 22.4% and 86.2% for Cd^{2+} ions at contact time 60 minutes, dosage 1g and pH 6, respectively. The equilibrium data of adsorption were tested with Langmuir,Freundlich isotherm models, Pseudo-first order and Pseudo-second order kinetic models.
Keywords: Adsorption, Batch system, Optimized conditions, Isotherms, Kinetics

Introduction
The presence of heavy metals in the water bodies is due to discharge of untreated metal contaminated effluent into water bodies. Heavy metals are non-biodegradable and harmful to all living organisms. In human, these metals are deposited in tissues of different organs through different food chains and contaminated waters [1,2].The adsorption based removal of heavy metal ions from waste waters is a promising technique over the other conventional methods. The mechanisms of adsorption onto a selected biomaterial are based onchemisorptions, complexation, diffusion and ion exchange.Heavy metals such as chromium (Cr), lead (Pb), cadmium (Cd), nickel (Ni) and copper (Cu) may toxic among the other inorganic pollutants and cause a harmful effect to living forms and some of them are very toxic event at low concentrations [1-3]. Cadmium (Cd) and lead (Pb) are generally present in the wastewaters that released from different industries and cause a variety of diseases to human health.

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Lead (Pb) is introduced in fresh, saline and waste waters from different sources such as batteries, petrol, cable wires, alloys, steel, plastic, and glass and paint industries. Lead is metabolic poison and reduces the enzymatic activities in the human body. It is also a carcinogenic agent and its organic forms are more poisonous. The main sources of cadmium (Cd) in the aquatic bodies are ceramics, metal finishing, alloying, mining and other industries. It may cause hypertension, renal dysfunction, hepatic injury, lung damage etc [2-7].The plant Burans (Rhododendron arboreum) is an evergreen angiospermic plant and found as a small tree. The waste leaves of the plant were collected from the Kumaun hills of India and found highly efficient sorbents for the effective removal of Cd2+ and Pb2+ions from the waste waters.

Material and methods
The collected waste leaves of Rhododendron arboreum were washed with tap water and then 2-3 times with distilled water. After that, the leaves have been dried in tray dryer for 3.5 hours between the temperatures 65-70 0C. Now, the leaves grinded and sieved into particle size 0.075 mm and characterized by using FTIR and FESEM methods. Two different stock solutions containing 1000 mgl-1 of Pb2+ and Cd2+ ions were prepared by dissolving an adequate amount of Pb(CH3COOO)2 and Cd(CH3COOO)2in double distilled water and acidified. The stock solution containing 1000 mgl-1 of lead and cadmium ions has

been diluted in required working solutions.The pH of working solutions was adjusted 1-6 by using 0.1 M NaOH and 0.1 M HCl. A requisite amount of biomass was then treated with a necessary working solutions and pH at a constant rpm 150 and temperature. After a certain contact time, the contents of the reacting flask were filtered through a filter paper and the filtrate was analyzed by Atomic Absorption Spectroscopy (Thermo Scientific: iCE 3000 Series). The percentage adsorption of metal ions was calculated by following formula:

$$\% \text{ Adsorption or adsorption efficiency} = \frac{C_1 - C_2}{C_1} \times 100$$

(C_1 and C_2 are the metal ion concentrations in waste water before and after adsorption)

Fig: 1 Collected waste leaves of *Rhododendron arboreum*

Results and discussion

Characterizations of adsorbent

The FTIR spectrophotometer is used to scan the FTIR spectra in the range 4000-500 cm^{-1} (Fig: 2). Broad peaks have been obtained at 3400 cm^{-1}, 2927 cm^{-1}, 1723 cm^{-1}, 1623 cm^{-1}, 1449 cm^{-1}, 1376 cm^{-1}, 1249 cm^{-1}, 766 cm^{-1} and 611 cm^{-1}. Such peaks indicated that the organic groups like –OH, –NH, –C-H (Aliphatic), C=O, C=C,–CH_3, C–N etcbonds on leaf powder[1].The FESEM image of leaf powder before adsorption is shown in figure 3.

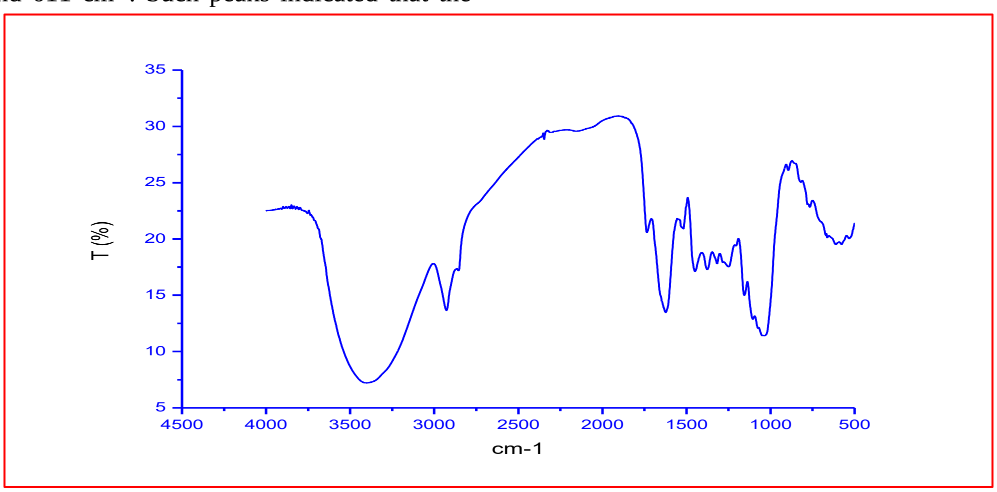

Fig: 2 FTIR Characterizations of adsorbent

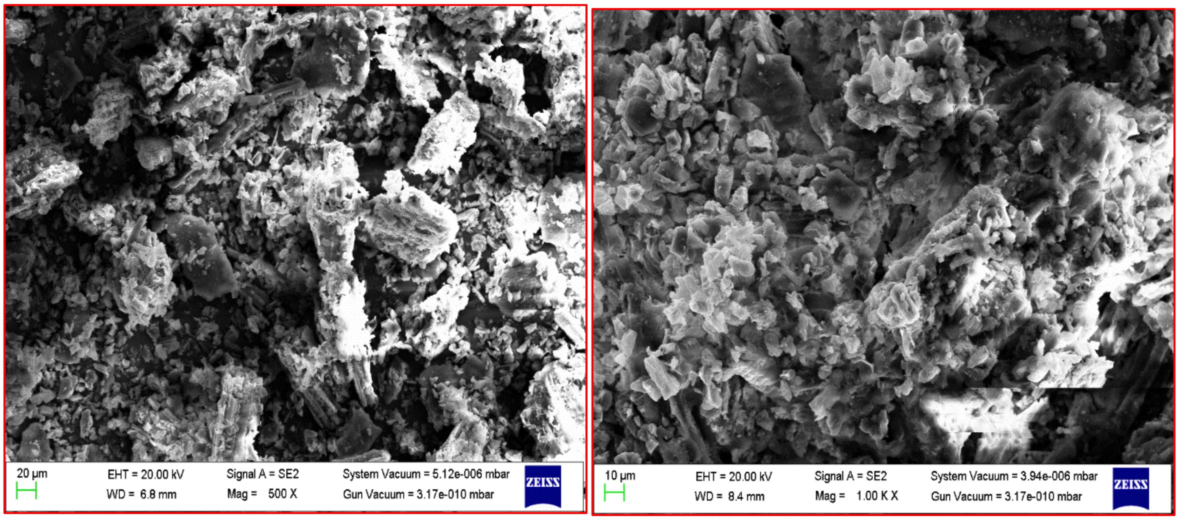

Fig: 3 FESEM images of adsorbent

Effect of pH and contact time:

The pH of aqueous solution is very important parameter in the removal of heavy metals and adsorption of Pb^{2+} and Cd^{2+} ions increases with the increase in pH of working solutions [8,9]. At lower pH, the active sites on surface of adsorbent undergo protolysis and become positively charged. It results the repulsions between Pb^{2+} and Cd^{2+} ions and active sites but at higher acidic pH, all the active sites are available for the interactions with Pb^{2+} and Cd^{2+} ions. At initial pH 1, the removal efficiencies of Pb^{2+} and Cd^{2+} ions have recorded 8.4 and 1.009% that rapidly increases to 93.2 and 67.6 %, respectively at pH 5. The maximum percentage adsorption is found for Pb^{2+} and Cd^{2+} ions as 98.8 and 86.2% at pH 6 (Fig: 4A). The uptake of metal ions during sorption increases with the increase of applied contact time periods. It is due to the availability of more active sites for the metal ions but after certain time, the removal efficiency of metal ions become constant due to the coverage of about all active groups by metal ions [1]. Initially, 49.4 and 12.7 % adsorption of Pb^{2+} and Cd^{2+} ions was found at contact time 10 minutes and that increases to 58.4 and 25.7 % for Pb^{2+} and Cd^{2+} ions. The maximum adsorption of Pb^{2+} and Cd^{2+} ions have been found 67.9 and 41% at contact time 60 minutes, pH 4 and concentration 10 mgl^{-1}, respectively(Fig: 4B).

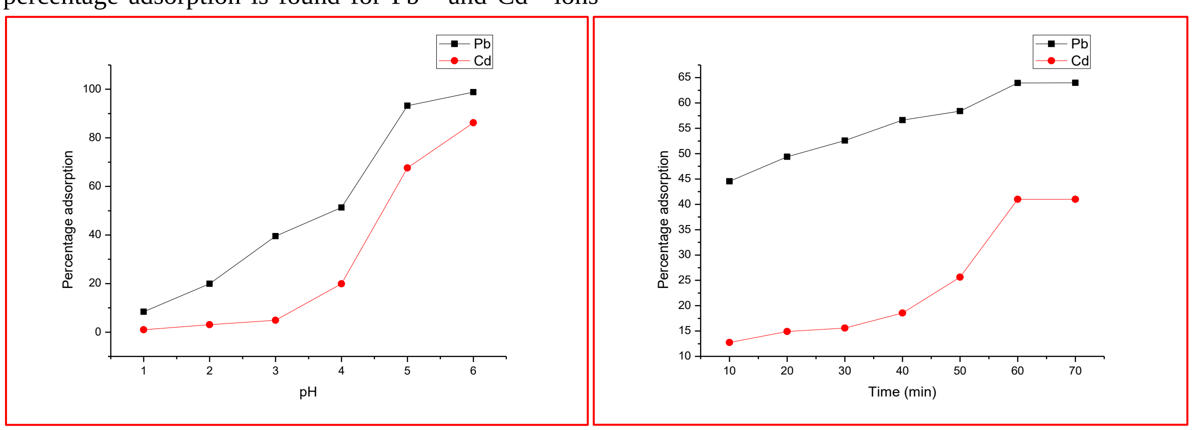

Fig: 4(A) Effect of pH and (B) Effect of contact time on the removal of Pb^{2+} and Cd^{2+}ions

Effects of dosage and concentration

The adsorption of metal ions was found at the higher dosage of adsorbent.This can be explained by the fact that the active sites on adsorbent remain unsaturated during the sorption process and the number of sites available for adsorption by increasing the amount of sorbent [6]. The percentage removal 19.1 and 1.9% for lead and cadmium are observed at the initial dose of adsorbent 0.1 g and increased to 37.2 and 12.3 % at 0.5g. The removals of lead and cadmium have been recorded 56.3 and 20.3 % at the dose 0.8g. The maximum removal of Pband Cd is found 58.9 and 22.3% at the highest dosage 1g (Fig: 5A).The adsorption of lead and cadmium ion decreases with the increase of concentration of solutions (Fig: 5B). It may due to the saturation of active sites at higher concentrations [3].

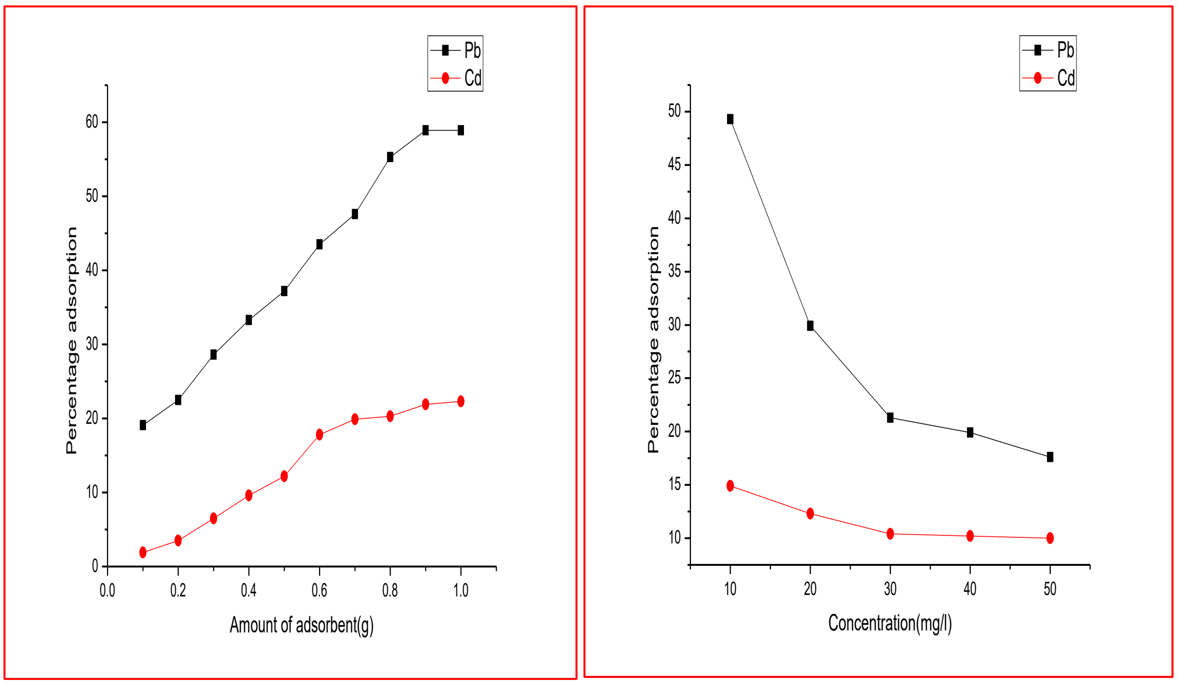

Fig: 5(A) Effect of dosage and (B) Effect of concentration on the removal of Pb^{2+} and Cd^{2+}ions

Isotherm modeling

Langmuir isotherm assumes that the formation of a single layer of metal ions on surface of adsorbents that containing an adequate number of binding sites which are arranged very regularly [10]. The Langmuir isotherm model is represented as below:

$$\frac{C_2}{Q_e} = \frac{1}{K_1 A} + \frac{C_2}{K_1}$$

Where, C_2 and Q_e are the equilibrium concentrations (mgl^{-1}) of ions and their amount adsorbed (mgg^{-1}) on the surface of leaf powder. The constant K_l and A are the adsorption capacity (mgg^{-1}) and adsorption equilibrium constant (Lmg^{-1}), respectively. When a graph is plotted between C_2 / $Q_e$vs C_2 (Fig: 7A); the values of K_l and A have been evaluated for Pb^{2+} ions as 10.101 mgg^{-1} and 1.001 Lmg^{-1} and for Cd^{2+} ions 11.235 mgg^{-1} and 1.008 Lmg^{-1}, respectively. The values of regression (R^2) are indicating that the Langmuir isotherm model is best fitted to the removal of Pb^{2+} ions from contaminated waste waters (Table: 1).

The Freundlich isotherm model is based on the presence of different functional groups with varying energies on the heterogeneous surface of the sorbents [3]. The Freundlich model is mathematically given as:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_2$$

Where Q_e and C_2 represent the amount of lead and cadmium adsorbed on the surface of adsorbent (mgg^{-1}) and equilibrium concentration (mgl^{-1}). The Freundlich constant K_f and 1/n represents adsorption capacity and intensity of adsorption and their values are calculated from the graph log $Q_e$vs log C_2 (Fig: 7B).The values of K_f for Pb and Cd have been found 1.840 and 3.672 mgg^{-1}, respectively; values of 1/n for Pb and Cd found to less than one and itexplains favorable adsorption (Table:2). The value of correlation (R^2= 0.978) for Cd indicates that the suitability of Freundlich model for Cd is more than Pb.

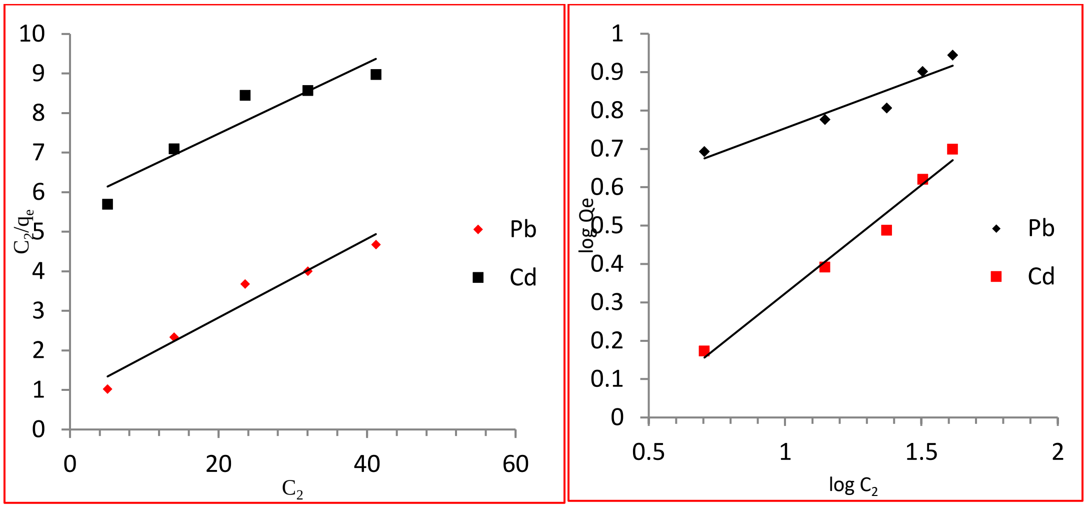

Fig: 7 (A) Langmuir and (B) Freundlich isotherm model

Table: 1 Isotherm parameters for lead and cadmium

Isotherm models	Metal	Parameters	Values
Langmuir	**Pb**	K_l (mgg^{-1})	10.101
		A (Lmg^{-1})	1.001
		R^2	0.950
	Cd	K_l (mgg^{-1})	11.235
		A (Lmg^{-1})	1.008
		R^2	0.891
Freundlich	**Pb**	K_f (mgg^{-1})	1.840
		1/n	0.488
		R^2	0.908
	Cd	K_f (mgg^{-1})	3.672
		1/n	0.241
		R^2	0.978

Kinetics of adsorption

The pseudo-first kinetic equation is generally represented by following equation:

$$\ln (Q - Q_t) = \ln Q - k_1 t$$

Where Q and Q_t represents the adsorption capacity at equilibrium and at time t, respectively, in mgg^{-1} and k_1 is rate constant (min^{-1}). The pseudo-first-order kinetics explains that the rate of adsorption is based on the availability of binding groups for the interactions with metal ions [11]. The value of regression (R^2= 0.996) for Pb^{2+} ions indicate that this kinetic model is more favorable for the adsorption of Pb^{2+} ions as compared with Cd^{2+} ions (R^2= 0.9111).

The Pseudo second order model is generally used in the explanation of physicochemical interactions of metal ions between two phases [12]. Mathematically, the pseudo second order kinetic model is given as below:

$$\frac{t}{Q} = \frac{1}{k_2} * Q_t - Q$$

Where k_2 is second order rate constant in g $mol^{-1}min^{-1}$ and Q and Q_t are the amount of metal ion adsorbate at equilibrium and at time t in mgg^{-1}, respectively. A higher regression value (R^2= 0.994) for Pb^{2+} ions proves that the pseudo second order kinetics is more favorable for Pb^{2+} ions and the rate limiting step is not a physical interaction.

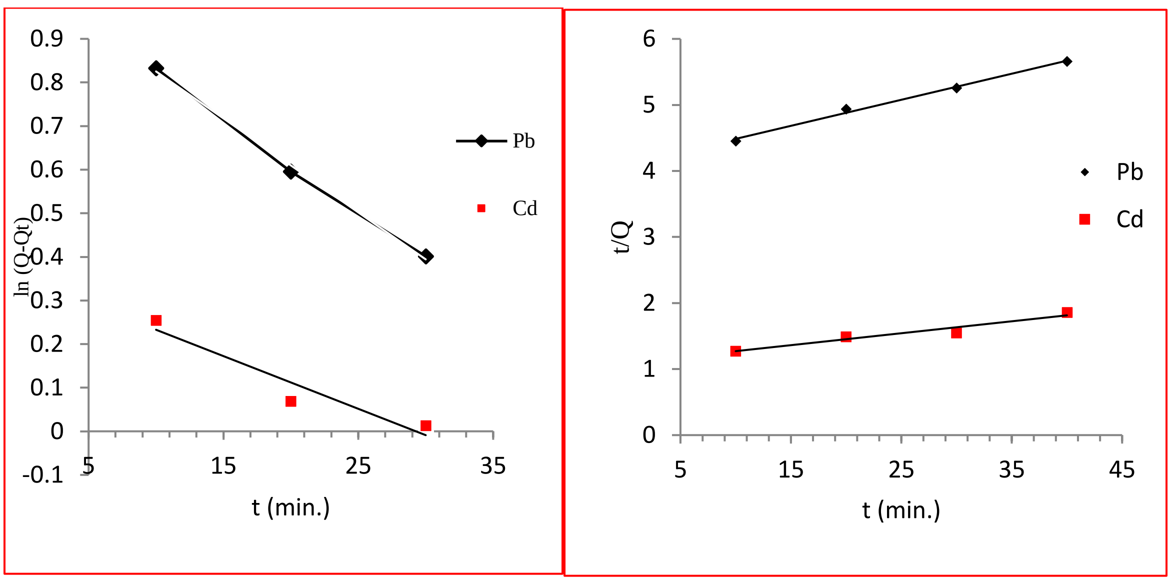

Fig: 9 (A) Pseudo first and (B) second order kinetic models

Table: 2 Kinetic parameters for lead and cadmium

Kinetic model	Metal	Parameters	Values
Pseudo first order	**Pb**	k_1 (min^{-1})	-0.021
		R^2	0.996
	Cd	k_1 (min^{-1})	-0.012
		R^2	0.911

Pseudo second order	**Pb**	k_2 ($gmol^{-1}min^{-1}$)	25.555
		R^2	0.994
	Cd	k_2 ($gmol^{-1}min^{-1}$)	55.555
		R^2	0.940

Conclusion

The waste leaves of *Rhododendron arboretum* have been found good adsorbent for the removal of lead and cadmium from waste water. The adsorbent was characterized by using FTIR and FESEM methods. The maximum adsorption capacity was observed at higher contact time, higher acidic pH and moderate temperature. The data of adsorption have been correlated with isotherm and kinetic models.

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