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Pb(II) removal from wastewater using Pomegranate waste biomass

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Abstract

The present work evaluates the sequestration of Pb(II) from aqueous solution by chemically pre-treated pomegranate (*Punica granatum*) biomass. The obtained results showed that initial metal ion concentration, kinetics affected the adsorption capacity of the pre-treated biosorbent. Maximum adsorption capacity for Pb(II) was observed at pH 4.5. Increase in biosorbent dose decreased Pb(II) uptake capacity. Metal uptake capacity of Pb(II) increased with increase in initial metal concentration. Metal uptake capacity decreased with time. Phosphoric acid pretreatment increased Pb(II) uptake capacity more than other acids. Equilibrium data was best represented by Langmuir adsorption isotherm and pseudo second order kinetic model.

Key words: Pb(II), pomegranate, biosorption, wastewater, isotherms

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1. Introduction

Heavy metal pollution in the aquatic system has become a serious threat today and has great environmental cancer, as they are non biodegradable and thus persistent. Metals are mobilized and carried into food web as a result of leaching from waste dumps, polluted soils and water. The metal increase in concentration at every level of food chain and are passed onto the next higher level a phenomenon called bio magnification [1]. The contamination of water with substances which have adverse effect on human beings animal and plant is called water pollution. Water pollution is a worldwide problem and its control has become increasingly important in recent years [2]. Municipal or industrial effluents treated by waste water treatment plants contain large amounts of organic matter and pollutants including metals such as Cu, Zn, Cd and Pb etc. The uptake of metals by sludge flocks is of great significance in pollution control [3]. Lead is very toxic heavy metal, its target organs are bones, brain, blood, kidneys, and thyroid glands [4]. Presence of lead in discharge and toxic nature cause other adverse effects on receiving waters in aquatic system. Even a very low concentration of heavy metals in water is very toxic to aquatic life. The main source of lead and cadmium in water are the effluents of processing industries i.e. electroplating, paint, pigment, basic steel work, textile industries, metal finishing and electric accumulators' batteries [5].

Conventional methods for removing metals from aqueous solutions include chemical precipitation, chemical oxidation and reduction, ion exchange filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation. The major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its disposal/treatment becomes costly affair and is not eco-friendly. Therefore removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance [6-8]. In recently years considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials. Natural materials that are available in large quantities or certain wastes from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources which are widely available and are environmentally friendly. Some previous investigations on the removal of heavy metal ions with many agricultural byproducts has been reported [9]. Biosorption is defined as the ability of biological materials to accommodate heavy metals from wastewaters through metabolically mediated physico-chemical pathways of uptake. Algae, fungi, bacteria, parts of some higher plants and yeasts have been proved to be potential metal bisorbents. When heavy metals concentration exceeds the tolerance level it show harmful effects on human physiological and other biological systems [10]. Traditionally the removal of heavy metals is made by chemical precipitation, ion exchange, and reverse osmosis. However, all these methods are not completely feasible to reduce the concentrations of heavy metals to low scale levels and are much costly. Pomegranate belongs to the genus *Punica*, order Myrtales and family *lythraceae*, which is a tropical family species with 73 genera and 850 species.

The genus *Punica* contains several that bears edible fruit. Most of the fruit trees that are commonly known as pomegranate belong to the species *P. granatum*. The other edible *Lythraceae* species generally have lower quality fruit and are commonly referred to as wild pomegranate [11].

In this study, the locally available pomegranate biomass was aused to study the adsorption performance from single metal ion aqueous solution. The effects of solution contact time and adsorbent concentration, on Pb(II) was investigated in detail.

2. Materials and methods

2.1. Biosorbent collection and preparation

Waste pomegranate biomass was collected from Faisalabad, Pakistan. It was washed with distilled water for three times. Washed Pomegranate biomass dried in open air then in oven at 65 ± 1˚C. Dried biomass was grinded into airtight plastic jars. After grinding the biosrobent was sieved by octagon siever for obtaining different particle sizes. The sieved biosorbent was stored separately and sealed in bottles to prevent readosrption of moisture [12]. The selected mesh size was 0.255mm. Powdered biosorbent (250g) was treated with 500ml of 0.1 N solutions of HCl**,** H_2SO_4**,** H_3PO_4 for 24h at 120 rpm and 30˚C. Afterwards each sample was neutralized by constant flow of distilled water, filtration and measuring the pH of filtrate. Then dried properly, grounded with mortar and pestle and kept in airtight jars.

2.2. Preparation of Pb(II) solution

The synthetic solution of lead was prepared by dissolving 1.59g of lead nitrate in deionized distilled water (DDW).

2.3. Batch experiments

After preparation of solution different parameters like pH, concentration of metal and kinetics were studied in batch setup [7]. In all the experiment 100ml of metal solution of known concentration was taken in each 250ml conical flask along with the control and blank (having no biosorbent). Weighed amount of biosorbent was added to each conical flask, it was approximately 0.1g. Conical flasks were over sealed with aluminum foil. The solutions were agitated on orbital shaking incubator at 120 rpm at 30˚C for 24 hours. The experiments were conducted in triplicate for concordant readings. After 24 hours samples were filtered through filter papers and stored in plastic sample bottles. The concentration of lead and cadmium was determined after 15 times diluting the solution with by Perkin Elmer Atomic Absorption Spectrophotometer (A.Analyst 300).

2.4. Statistical analysis

The data obtained was analyzed using Standard deviation and by linear regression analysis.

3. Results and Discussion

3.1. Effect of pH

pH is an important parameter, which influences the biosorption process. With increase in pH to certain limit, the adsorption capacity increases (Fig. 1). The adsorption capacity (q) of biosorbent for Pb (II) from aqueous solution was highly dependent on pH of the solution. Maximum Pb(II) uptake capacity of pomegranate after treatment with HCl, H_2SO_4 and H_3PO_4 was 67.44, 65.80 and 68.74 mg/g, respectively at 4.5 pH. Pb(II) uptake capacity of native biomass was 67.50 mg/g. The other important reason is that at lower pH values, the cell wall ligands would be closely associated with the hydronium ions (H_3O^+) that restrict access to legends by metallic ions as a result of repulsive forces. This repulsion is stronger at lower pH. On increasing, pH more ligands (carrying negative charges) would be exposed with the subsequent attraction of positively charged metal ions. Similar results were reported by previous investigators. Some researchers stated that the increase in metal biosorption after pre-treating the biomass, could be due to the removal of surface impurities and exposure of latent binding sites for metal biosorption [12].

3.2. Effect of Biosorbent dose

Metal adsorption capacity of pomegranate biomass decreased with increase in biomass concentration (Fig. 2). It was suggested that an increase in adsorbent dose interferes between the binding sites and caused electrostatic interaction between cells. Adsorbent dose added into the solution determines the number of binding site available. An increase in adsorbent quantities strongly affects the quantities of metals removed from aqueous solutions to a certain limit. This effect was also reported in literature for biosorption phenomenon of heavy metals. Similar type of results was noted by Hanif et al. [7].

3.3. Effect of initial Pb(II) concentration

Equilibrium adsorption capacity of biomass increased with the increase in the initial Pb (II) concentration (Fig. 3). The difference between bulk and surface metal ions concentration is one of the driving forces to overcome the resistance to adsorption process in the absence of mass transfer resistance surface and bulk concentrations [7].

To examine the relationship between adsorbed (q_e) and equilibrium concentrations (Ce), sorption isotherm models are widely employed for fitting the data is which the Langmuir and Freundlich equations are widely used. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with correlation coefficients. The Langmuir model better represented the sorption process in comparison to model of Freundlich. The Langmuir parameters can be determined from a linearized form of equation (1), represented by:

$$C_e/q_e=1/X_mK_1+ C_e/X_m \text{----------(1)}$$

Where X_m and K_1 are the Langmuir constants. The Freundlich parameters can be determined from a linerized form of equation (2) represented by:

$$\text{Log } q_e = 1/n \log C_e + \log K \text{----------(2)}$$

Where q_e is metal ion adsorbed (mg/g). C_e is the equilibrium concentration of metal ion solution mg/L, K and 1/n are constant. The constant K and 1/n were determined by linear regression form the plot of log q against log Ce. Best fit model was Langmuir adsorption isotherm (Table 1).

3.4. Effect of contact time

Effect of contact time (15 to 1440 min) on Pb (II) uptake is presented in Fig. 4. Contact time study revealed the biosorption took placed in two steps, a rapid surface adsorption within 30 min and slow intercellular adsorption

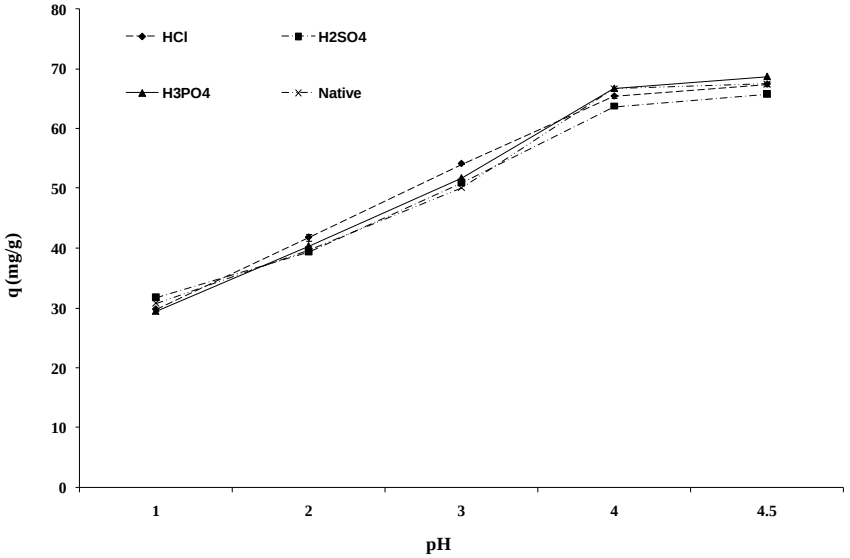

Fig. 1. Effect of pH on Pb(II) uptake using pomegranate waste biomass.

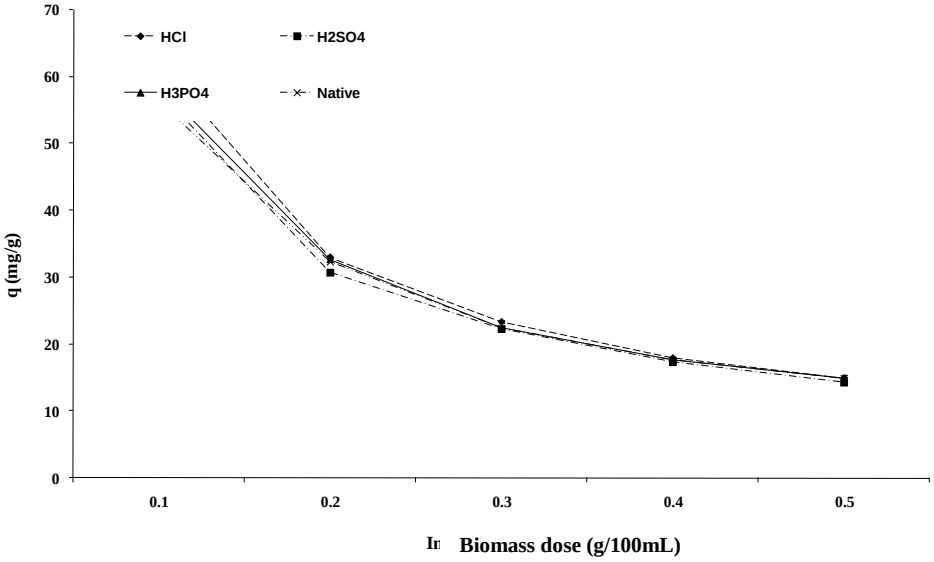

Fig. 2. Effect of biosorbent dose on Pb(II) uptake using pomegranate waste biomass

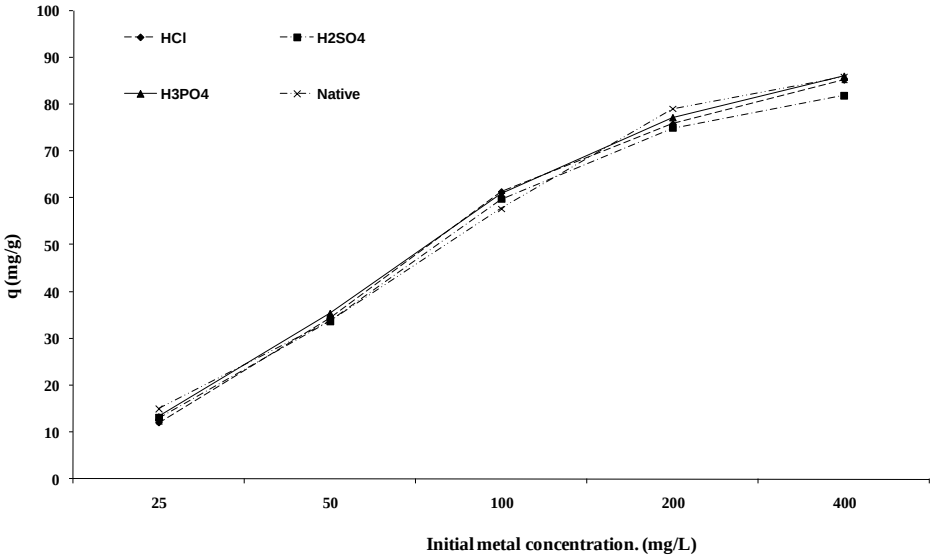

Fig. 3. Effect of initial concentrations on Pb(II) uptake using pomegranate waste biomass

Table 1: Comparison between Langmuir and Freundlieh isotherm parameters for Pb(II) uptake using pomegranate waste biomass

Pretreatment	Langmuir isotherm parameters			Freundich isotherm parameters		
	Xm (mg/g)	KL (L/mg)	R^2	K (mg/g)	1/n	R^2
HCl	113.25	0.023	0.974	6.01	0.503	0.691
H_2SO_4	121.23	0.0416	0.992	16.71	0.310	0.700
H_3PO_4	105.26	0.0416	0.993	14.85	0.341	0.704
Native	111.52	0.0040	0.963	25.29	0.243	0.142

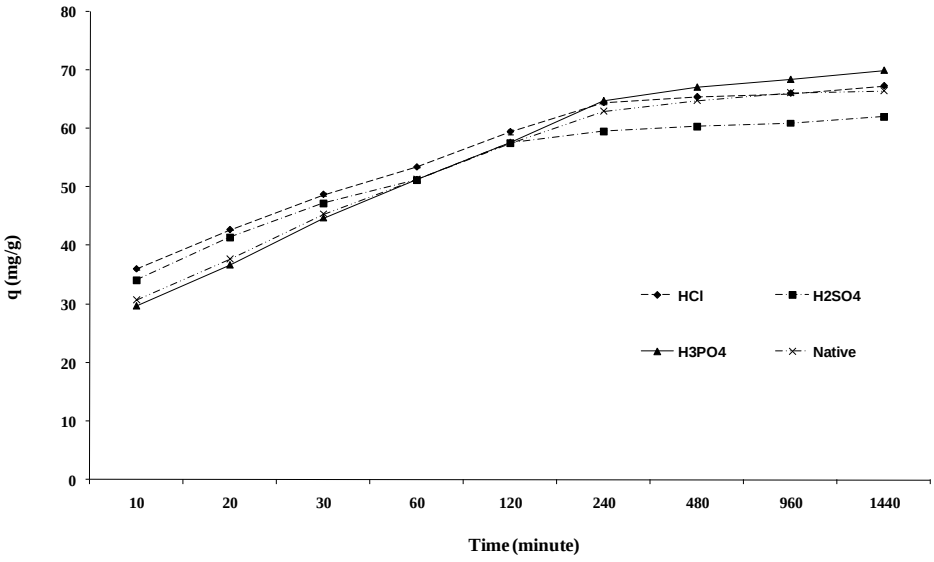

Fig. 4. Effect of Time on Pb(II) uptake using pomegranate waste biomass

Table 2: Comparison between pseudo-first order and pseudo-second order kinetic models for Pb(II) uptake using pomegranate waste biomass

Pretreatment	Pseudo first order kinetic model			Pseudo second order kinetic model		
	q_e (mg/g)	$k_{1,\ ads}$ (min^{-1})	R^2	q_e (mg/g)	$k_{2,\ ads}$ (g/mg min)	R^2
HCl	44.66	2.7174	0.565	71.42	0.00098	0.999
H_2SO_4	52.84	6.8199	0.487	62.5	0.00014	0.999
H_3PO_4	52.23	5.3328	0.626	71.42	0.00065	0.999
Native	52.60	5.592	0.593	71.42	0.00081	1.00

up to equilibrium [13-14]. The obtained results are in agreement to earlier reported results of Nadeem *et al*., 2009 [12]. Two different kinetic models were used to test the experimental data of Pb (II) and Cd (II) biosorption on acid pretreated *Pomegranate* (*Punica granatum*) biomass. The pseudo first order is generally expressed as (eq. 3):

$$\text{Log}(q_e - q) = [\log q_e - (K_{adst})/2.303\} \text{ ----------(3)}$$

Where q_e (mg/g) and q are the amount of absorbed metal ions on the biosorbent at the equilibrium at any time t, $K_{1,}$ adsorption is the rate constant of first kinetic model.

The pseudo second order model is based on assumption that biosorption follows a second order mechanism. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The pseudo second order equation is expressed as (eq. 4):

$$t/q = l/ k_{2,ads}q_e^2 + t/qt\text{----------(4)}$$

where k_2 is the rare constant of second order kinetic model. q_e and k_2 adsorption can be calculated from the slope and intercept of the plot t/q versus t. The pseudo second order better represented the adsorption process, in comparison to the pseudo first order due to high value of correlation coefficient. Best fit model was pseudo-second order kinetic (Table 2).

4. Conclusions

Following important conclusion can be withdrawn from present study:

- Pomegranate waste biomass is a useless material without any commercial importance. Obtained results clearly demonstrate pomegranate waste biomass can be effectively used for Pb(II) from wastewater.
- Optimized pH, biosorbent dose and contact time for Pb(II) uptake by pomegranate waste biomass were 4.5, 1g/L and 240 min.
- Equilibrium data is best represented by Langmuir adsorption isotherm and pseudo second order kinetic model.

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References

[1] P.K. Pandey, Y. Verma, S. Choubey, M. Pandey and K. Chandrasekhar. (2008). Biosorptive removal of cadmium from contaminated groundwater and industrial effluents. Bioresource Technology. 99 (10) 4420-4427.

[2] T. Robinson, B. Chandran and P. Nigam. (2001). Studies on the decolourisation of an artificial textile-effluent by white-rot fungi in N-rich and N-limited media. Applied Microbiology and Biotechnology. 57 (5-6) 810-814.

[3] G. Guibaud, E.V. Hullebusch and F. Bordas. (2006). Lead and cadmium biosorption by extracellular polymeric substances (EPS) extracted from activated sludges: pH-sorption edge tests and mathematical equilibrium modelling. Chemosphere. 4 (11) 1955-1962.

[4] T.M. Ansari., M.A. Hanif., A.Mahmood., U. Ijaz., M.A. Khan., R. Nadeem and M. Ali. (2011). Immobilization of rose waste biomass for uptake of Pb(II) from aqueous solutions. Biotechnology Research International. In press.

[5] J. Hering. (2002). A better method for evaluating heavy metal water pollution. Url: http://escholarship.org/uc/item/54d8z28g#page-1 Retrieved 29-Sep-2011.

[6] S.S. Ahluwalia and D. Goyal. (2007). Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresource Technology. 98(12):2243-2257.

[7] M.A. Hanif., R. Nadeem., M.N. Zafar, K. Akhtar and H.N. Bhatti. (2007). Kinetic studies for Ni^{2+} biosorption from industrial wastewater by *Cassia fistula* (Golden shower) biomass. Journal of Hazardous Materials. 139(2):345-355.

[8] M.A. Hanif., R. Nadeem., M. N. Zafar., K. Akhtar and H.N. Bhatti. (2007). Kinetic studies for Ni^{+2} biosorption from industrial wastewater by *Cassia*

fistula (Golden shower) biomass. Journal of Hazardous Materials. 139(2) 345-355.

[9] D. Mohan and K.P. Singh. (2002). Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse--an agricultural waste. Water Reserch. 36(9):2304-2318.

[10] M.H. Jnr and A.I. Spiff. (2004). Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wild cocoyam), African Journal of Biotechnology. 4:191–196.

[11] S.D. Doijode. (2001). Seed storage of horticultural crops. New York: Food Products Press. pp. 77.

[12] R. Nadeem., M.A. Hanif., V. Shaheen., S. Perveen., M. N. Zafar and I. Iqbal. (2008). Physical and chemical modification of distillery sludge for Pb (II) biosorption. Journal of Hazardous Materials. 150: 335-342.

[13] G. Yan and T. Viraraghavan. Effect of pretreatment on the bioadsorption of heavy metals on *Mucor rouxii.*, Water SA 26 (1) 119–124.

[14] B. Benguella and H. Benaissa. (2002). Cadmium removal from aqueous solution by chitin: kinetic and equilibrium studies. Water Research. 36 (10) 2463–2474.

[15] H.N. Bhatti, B. Mumtaz, M.A. Hanif, and R. Nadeem. (2007). Removal of Zn(II) ions from aqueous solution using *Moringa oleifera* Lam. (horseradish tree) biomass. Process Biochemistry. 42 (2007) 547–553.