Removal of Cadmium(II) and Lead(II) from Water by Chemically Treated Citrullus lanatus Peels as Biosorbent in Cost Effective Way

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Abstract. This study presents the use of Citrullus lanatus peels for the removal of Cd(II) and Pb(II) using batch mode. Their chemically modified acid and base treated forms were utilized for biosorption studies by optimizing all parameters. Results indicated that base modified Citrullus lanatus peels were more effective for removal of these metal ions. Removal efficiency for cadmium and lead was found to be 92.32-94.1 % and 91.94-92.58 %, respectively. Isothermal and thermodynamic investigations were carried out to find sorption mechanism and their suitability to use on bulk scale. Promising sorption capacity values for Cd(II) 19.310 mg/g and Pb(II) 25.775 mg/g, along with pseudo-second order mode and exothermic thermodynamic nature; all these favour their use for industrial scale water treatment.

Keywords: Cd(II), Pb(II), Sorption, Citrullus lanatus peels, Base treatment

1. Introduction

Environment is a serious victim of human activities since ancient times. A continuous degradation of surroundings and the whole environment is caused by man due to burning of domestic waste including human waste, sludge and different types of smokes from automobiles, etc. Also in past few decades a huge population expansion led to the increased demand of basic necessities of life. Natural resources being unable to meet these demands including food, shelter clothing, etc., resulted into a proportionally rapid development of industry. This industry includes the production of different chemicals, catalysts, intermediates and other products of human use. The waste and the discharged chemicals from these industries caused a serious damage to the soil and water bodies like rivers, canals and streams etc., the water from these water bodies is being used for irrigation and through the plant and animal sources these harmful chemicals are being transferred to the human body and cause serious danger to the quality of life.

One of the chief classes of chemicals used in industry include different metal salts, metal salts are ionic in nature are easily dissociated into constituent ions, supplying different heavy metal ions into the water bodies. Several are non-biodegradable as well as carcinogenic in nature [1]. There is a need of some sustainable and instant research technique for the quantitative removal of such toxic metal ions up to safe limit approved by WHO and EPA for different metals [2, 3]. Dome of the toxicities of these metal include physical sufferings and diseases leading to mortality. A number of methods are in practice for the removal of these toxic metals like electro-dialysis, cementation, ion-exchange, coagulation, adsorption reverse osmosis, and precipitation [4].

Out of all these methods adsorption especially biosorption is recognized as a green technique also being economical and result oriented. Design flexibility, operational convenience and reversibility for regeneration of adsorbents are its main characteristics [5, 6]. The physical binding is explained by electrostatic attraction or London-Van der Waals forces, while chemical binding is covalent or ionic. This technique is less expensive and less hazardous in comparison to other methods [2]. The traditional methods are found to be expensive, less efficient nonspecific [7].

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Pakistan economy is mostly agricultural based, so various agro-waste materials were exploited to be used for curing environmental issues, like water treatment, road carpeting, biogas generation, fuel alternatives, etc. *Citrullus lanatus* (Water melon) was widely used during summer season for off setting heat effects. Due to its greater production and cheap rates, it is extensively used for both human beings and animals as food. That’s why its peels were selected due to their ease in availability and less cost.

2. Materials and methods

**Sorbent preparation**

*Citrullus lanatus* peels were collected from home town markets, washed and dried in sunlight. Then it was ground to fine powder and sieved through 60 mesh. It was labeled as (WMP) and stored in plastic jars. For base treatment, it (1.0 g) was treated with 100 mL of 0.1N NaOH by shaking for 2 h. Then it was washed with distilled water to remove extra chemicals. After that, it was dried again and stored with label (B-WMP). It was also reported by us to be used for removal of acidic dyes from water in efficient way, where its characterization was explained in detail [8]. Here its brief glimpses were mentioned in result sections.

**Preparation of synthetic waste water samples**

Stock solution of 1000 ppm having Cd(II) and Pb(II) were prepared using Cd(NO$_3$)$_2$ and Pb(NO$_3$)$_2$, separately. Successive dilutions were made to prepare standards in the range of 10–50 ppm [9]. The concentration of Cd(II) and Pb(II) ions in remaining solution after biosorption was determined through AAS (Perkin Elmer AA analyst 100).

**Optimization study of batch sorption**

The sorption of cadmium and lead ions onto biomass depends upon chemical composition and binding interactions of peels and metal ions. The binding interactions further depend upon surface area, pore size, morphology of the sorbent surface, pore volume of sorbent, pore area and properties of the metal ions in solution and chemical nature of metal ion. All these factors were optimized and then optimized conditions were used for isothermal, kinetic and thermodynamic studies [10, 11].

3. Results and discussions

For monitoring, adsorption and removal of Pb(II) and Cd(II) ions, over water melon peel is studied. Abundant supply of water melon peels as agro-waste material, played role in its selection as sorbent, which is just discarded after extracting the juice. We also used them for removing acidic dyes from water on lab scale [8] and their promising results encourage us to use them for removal of toxic metals in efficient way.

**Adsorbent characterization**

Proximate analysis of selected sorbent material i.e. (WMP) was made by reported method [12] and shown in (Figure 1); (B-WMP) was found to be rich in cellulose, lignin, hemicellulose and fiber. Ligno-cellulosic materials are known to vary in chemical structure and carbon content.

Elemental analysis was done to get the % age of C, H and N in (B-WMP) and found that it contains: 26.13–29.09 % carbon, 7.11–7.92 % nitrogen and 2.56–4.32 % hydrogen. Auspiciously, the opted sorbent material displayed the considerable carbon content, shows their noteworthy capacity as sorbent.
FT-IR results were given in (Figure 2). It shows alcohol, carboxylic groups, amines, phenol, alkanes, alkyl halide, amino acids, hydroxyl and aromatic functional groups in water melon peel. At 3100 cm⁻¹, a deep band of strong absorbance was appeared that can be responsible for the existence of hydroxyl or amine groups. This spectrum turned out to be deeper i.e. indicating more absorbance, (on treating with 0.1 N NaOH), that may be due to increased concentration of -OH groups; 1400-900 cm⁻¹ region was found abundant in peaks, which appeared to be merged in the form of complex matrix. The peaks of phenol/tertiary alcohol, C–O stretch, and primary amine and C–N stretch were at 1230.82 cm⁻¹, 1049.71 cm⁻¹ and 795.97 cm⁻¹ represent, respectively [14, 15].

SEM analysis of (B-WMP) was shown in (Figure 3). Apparently, pores (irregular shaped) are found in SEM graphs, yet seem evenly distributed on the whole surface. It may be assumed, (B-WMP) have more binding ability due to presence of uneven shaped pores.

To observe the configuration of chemical changes in the ligno-cellulosic pattern, thermogravimetric analysis is found as one of the effective techniques. Thermogravimetric analysis of (WMP) was carried out, over a wide range of temperature (25-1000°C) (Figure 4). As shown in this figure, initial decline in weight was observed below 200°C and may be assigned to loss of light volatiles, mainly water while the weight loss between 200-400°C may be due to degradation of ligno-cellulosic material. Above 500°C, a continual weight loss was seen, which may be assigned to sluggish decay of metal oxide like components [13, 16].
Figure 2. FT-IR spectrum of A) raw (WMP) B) acid treated-(WMP) C) B-(WMP)

Figure 3. SEM micrograph of (B-WMP)
Optimization of parameters

To improve the efficiency of (WMP) for removing metal ions, they were treated with acid and base, separately and labeled as (A-WMP) and (B-WMP), respectively. Then a comparison was made between their removal proficiency for the removal of metal ions.

(a) Sorbent dose

A certain sorbent dose makes equilibrium between sorbent surface & aqueous solution and shows maximum adsorption (an equilibrium process). More amount of adsorbent adsorbs more amount these toxic ions, but at a point, adsorption decreased due to coagulation of adsorbent particles, Cd(II) & Pb(II) was carried out with (WMP) as sorbent at different sorbent dose over the range of 0.2g to 2.0g, in its raw, acid-treated&base-treated form (Figure 5). Among the three forms of sorbent, maximum sorption was witnessed for base treated sorbent (B-WMP). For the removal of Cd(II) and Pb(II), highest removal efficacy was exhibited by (B-WMP) at sorbent dose of 1 g/50 mL (93.41 %) and 0.8 g/50 mL (92.58 %), respectively [17].

Figure 4. TGA curve of (B-WMP)

Figure 5. Effect of different sorbent doses on the sorption of Cd(II) and Pb(II)
(b) Contact time

One of the important parameters, affecting the efficacy of sorption process is contact time of (B-WMP) and metal ion solution as given in (Figure 6). Whenever metal ions dissolved in aqueous solutions, is made in contact with solid sorbent material, it starts migrating, establishing a state of equilibrium, from aqueous phase onto the surface of solid sorbent.

Maximum amount of cadmium and lead ions was removed over contact time of 20 minutes and 30 minutes, which is 84.23 % and 83.86 %, respectively. Base-treated form of the sorbent exhibited the highest removal efficacy for Cd(II) & Pb(II), followed by acid-treated and raw forms, respectively [18].

![Figure 6. Effect of contact time of sorbent on the sorption of Cd(II) and Pb(II)](image)

(c) Effect of p\(H\)

Change in \(pH\), highly affects the degree of precipitation, chelation, and solubility of metal ions. Solutions of cadmium and lead ions were made in aqueous buffers, having \(pH\) range of 1-7. Basic \(pH\) conditions were not used due to metal hydroxides precipitation phenomenon. Trend of sorption among the sorbent materials remained the same, as discussed above. On the whole, (B-WMP) exhibited the better removal efficiency. For Cd(II), maximum removal was at \(pH\) 5 and in case of Pb(II) maximum removal was at \(pH\) 4, as shown in (Figure 7).

![Figure 7. Effect of \(pH\) on the sorption of Cd(II) and Pb(II) on sorbent](image)
Base treatment of (WMP) causes protonation of oxygenated functional groups or their ionization as proposed in (Figure 8). Both of them facilitates Pb(II) and Cd(II) ion removal due to chelation or hydrogen bonding. Further this effect was enhanced in acidic conditions of metal ion solution, which stabilize ionic strength of metal ions, by inhibiting their precipitation [19].

**Figure 8.** Proposed effect of base treatment of (WMP) and its effect on biosorption of Pb(II) and Cd(II)

**(d) Effect of agitation speed**

Sorption of different sorbates is also affected by the agitation speed. Sorbate materials require particular agitation speed, for maximum sorption. As agitation speed increases, the availability of surface area and effective distribution of the sorbate ions in solution. A scale of 75-200 rpm was picked to achieve the optimum agitation. Maximum removal (84.63 % and 80.2 %) for Pb(II) and Cd(II) was achieved at agitation speed of 125-150 rpm, respectively as shown in (Figure 9).
Figure 9. Effect of agitation speed on the sorption of Cd(II) and Pb(II) on sorbent

(e) Effect of temperature

Magnitude and adsorption rate is strongly affected by temperature. For both, Cd(II) and Pb(II), base treated sorbents shows maximum sorption. In this study, Cd(II) showed maximum sorption at 313 K (84.38 %) while maximum Pb(II) is adsorbed at 303 K (85.01 %) as shown in (Figure 10) [18]. At higher temperature, removal efficiency decreased due to higher agitation and less contact between metal ions and sorbent surface. It also indicated its exothermic nature.

Figure 10. Effect of temperature on the sorption of Cd(II) and Pb(II) on sorbent

Mathematical modeling

(a) Isothermal studies

As (B-WMP) give best results in above factors studies, so Langmuir and Freundlich model were used for its equilibrium modeling of data using equations (1) and (2) [20].

\[
\frac{1}{q_e} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (1)
\]

\[
\log q = \log K_F + \frac{1}{n} \log C_e \quad (2)
\]

In case of Langmuir model, on the basis of $R^2$ values given in (table 1), it was presumed that Langmuir isotherm could explain the sorption process in good way. Maximum sorption capacity ‘\(q_m\)’ for Cd(II) and Pb(II) was 19.310 mg and 25.775 mg, respectively [21]. It was compared with other adsorbents as reported [22, 23] in (table 2) and found that they have comparable sorption capacity with
various agro-waste materials. Separation factor “R_L” was computed through equation (3) using 50 ppm value for “C_0”; its values less than unity also support this fact.

\[
R_L = \frac{1}{1 + bC_0}
\]  

(3)

Table 1. Langmuir isotherm for Cd(ii) and Pb(ii) Removal by base-treated sorbents

| Sorbent       | Slope | Intercept | R^2  | q_m (mg) | b (L/g) | Specific surface area (m^2/g) | Separation Factor (R_L) |
|---------------|-------|-----------|------|----------|---------|--------------------------------|------------------------|
| Cd(II)        | 4.140 | 0.054     | 0.998| 19.310   | 0.013   | 3.901                          | 0.649                  |
| Pb(II)        | 3.105 | 0.041     | 0.988| 25.775   | 0.015   | 4.182                          | 0.701                  |

Table 2. Comparative maximum sorption capacity of other reported adsorbents

| Biosorbent for Pb(II) | q_m (mg/g) | Biosorbent for Cd(II) | q_m (mg/g) |
|-----------------------|------------|-----------------------|------------|
| Olive tree pruning waste (raw) | 26.4       | Microwaved olive stone activated carbon | 11.72      |
| Olive mill solid residues (raw) | 55.94      | Olive cake (raw)       | 10.56      |
| Olive stone waste activated carbon (KOH) | 22.37      | Rice straw             | 13.9       |
| Banana peel (raw)      | 2.18       | Banana peel (raw)      | 5.71       |
| Agave bagasse (raw)    | 35.60      | Agave bagasse (raw)    | 13.27      |
| Orange peel (KCl)      | 141.84     | Orange peel (KCl)      | 125.63     |
| Wheat straw            | 0.38       | Olive stones           | 17.66      |
| Cornsobs               | 8.29       | Cornsobs               | 8.89       |
| P. glaucum             | 15.24      | P. glaucum             | 5.55       |

 Freundlich model explained heterogeneous surface sorption and multilayered physio-sorption process; its results in (Table 3) had shown that the ‘n’ value under this study is less than 8 showing physisorption. Base treated water melon peel (B-WMP) showed maximum values of “K_F” for Cd(II) and Pb(II) was 0.535 and 1.580, respectively.

Table 3. Freundlich isotherm for Cd(ii) and Pb(ii) removal by base-treated sorbents

| Sorbent       | Slope | Intercept | R^2  | K_F  (mg^1.10^L^-1.10^-g^1) | n     |
|---------------|-------|-----------|------|-----------------------------|-------|
| Cd(II)        | 0.759 | 0.281     | 0.997| 0.535                       | 2.119 |
| Pb(II)        | 0.276 | 0.203     | 0.994| 1.580                       | 3.639 |

(b) Kinetic studies

As evident from (Table 4) that coefficient values of pseudo second-order model values are more for the sorption data, near to unity, ranging 0.957 to 0.962. The initial sorption rate (h) was determined from k_2 and q_e values which are more for (B-WMP), indicating sufficient adsorption sites were vacant for Cd(II) and Pb(II) ions, thus favoring good adsorption [19].

Table 4. Kinetic parameters for the sorption of base-treated sorbent for Cd(II) and Pb(II)

| Sorbent       | Slope | Intercept | R^2  | K_F  (mg^1.10^L^-1.10^-g^1) | q_e (mg/g) | H   | T_e2 |
|---------------|-------|-----------|------|-----------------------------|------------|-----|------|
| Cd(II)        | 0.799 | 7.901     | 0.972| 0.111                       | 1.103      | 0.160| 11.213|
| Pb(II)        | 0.570 | 6.243     | 0.953| 0.093                       | 2.134      | 0.565| 19.425|
(c) Thermodynamic studies

Thermodynamic properties of the process were evaluated by calculating the Gibbs free energy change ($\Delta G^o$), entropy change ($\Delta S^o$) and enthalpy change ($\Delta H^o$) by equations 4 to 6 and results were tabulated in (table 5) [24, 25];

$$\Delta G^o = -RT \ln K_d$$  \hspace{1cm} \text{(4)}

$$K_d = \frac{q_d}{C_d}$$  \hspace{1cm} \text{(5)}

$$\ln K_d = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$  \hspace{1cm} \text{(6)}

Comparing the value with literature it is found that sorption process under this study is physisorption. Negative value of enthalpy change supports values in nature (of process) and positive ($\Delta S^o$) values confirmed the increased randomness during sorption process.

| Sorbate | Slope | Intercept | $R^2$ | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol.K) | $\Delta G^o$ (kJ/mol) |
|---------|-------|-----------|-------|------------------------|------------------------|------------------------|
| Cd(II)  | 0.003 | 0.003     | 0.911 | -0.040                 | 0.051                  | -15.461                |
| Pb(II)  | 0.003 | 0.003     | 0.923 | -0.041                 | 0.060                  | -18.212                |

Applications of Developed Method to industrial waste water samples

Optimized conditions were used for surface and ground water samples of Lahore and results were given in (Table 6). For estimation of the removal efficacy of (B-WMP) in waste water samples, 100 mL portions of water samples and 0.2 g of (B-WMP) was sonicated for 60 min at optimized conditions and then recovered using ethanol washing. The percent sorption and percent recoveries are mentioned in (Table 6) which was quite good to be using them on larger scale.

| Sorbate | Surface water | Ground water |
|---------|---------------|--------------|
|         | Removal (%)   | Recovery (%)  |
|         | with 5 mL ethanol | with 5 mL ethanol |
| Cd(II)  | 96.7 ± 0.4    | 96.8 ± 0.4    |
| Pb(II)  | 92.3 ± 0.2    | 91.2 ± 0.4    |

4. Conclusions

It is concluded from the study that water melon peel (Citrullus lanatus) can be efficiently utilized for removal of Cd(II) and Pb(II) from waste water jets of textile industry. The adsorption capability of this agro-waste peel also has potential to improve adsorption capacity by chemical modifications. Base treated (B-WMP) found to show good results for removing toxic metal ions. Scavenging efficiency of these peels decreases slightly due to the presence of sodium chloride and sodium sulphate, but from these adsorbents Cd(II) and Pb(II) ions can easily be recovered with ethanol washing. So they can be applied on larger scale for waste water treatment using indigenous agro-waste sources.

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