Adsorption and Equilibrium Studies of Cadmium (II), Chromium (VI) and Lead (II) Ions using Ecofriendly Biosorbent

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Abstract - Datura inoxia, a medicinal plant leaves was used as biosorbent to remove cadmium (II), chromium (VI) and lead (II) ions from aqueous solutions. Physical and chemical characterization of biosorbent was studied by FTIR. Experiments were carried out in a batch studies and various parameters such as effect of pH, contact time, initial metal concentration and the optimization amount of biosorbent was studied. The developed biosorbent allowed multilayer adsorption to take place on the surface of the adsorbent. Freundlich isotherm model provided a better fit with the experimental data than Langmuir model by high correlation coefficients \( R^2 \), 0.995, 0.996 and 0.998 for cadmium (II), chromium (VI) and lead (II) at pH 5.0, 5.5 and 4.5 respectively. The present adsorption process involves ion exchange and surface complexation was found to be the main mechanisms. The developed biosorbent found to be more efficient in removal of cadmium (II), chromium (VI) and lead (II) from water solution.

Keywords-Datura inoxia, batch studies, biosorbent, correlation coefficient, FTIR

I. INTRODUCTION

Rapid industrialization and urbanization generates large amount of heavy metals in to the environment and contaminate the water resources. Water is one of the precious and important for the well being of humans. Heavy metals are non degradable and discharge from many sources like paper and pulp industries, leather and tanneries, fertilizers and also due to agricultural activities [1]. Heavy metals are not hazardous at lower concentrations however, at higher concentrations they can bioaccumulate and enter in to human beings through the food chain and can cause several health problems [2]. Among these heavy metals cadmium (II), chromium (VI) and lead (II) found to be most toxic in the environment. Cadmium can damage to kidneys, lungs and many hazardous effects on human health. It has been reported that hexavalent chromium is most toxic than trivalent chromium) and widely recognized as carcinogen [3]. Lead can cause anemia and brain disorders and finally lead to death of human beings [4-5]. The maximum permissible limits of cadmium (II), chromium (VI) and lead (II) have been recommended in drinking water are 0.005mg/l (WHO) [6], 0.1mg/L (EPA) [7] and 3-10µg/L (WHO) [8].

Therefore, removal of toxic metals from waste water is essential to avoid contamination [9] several researches have reported many conventional physical and chemical processes which have many drawbacks like partial metal removal and costly 10-13]. Attention was given to adsorption using various agro based byproducts as adsorbents and can be considered as cost effective, novel technique for the removal of heavy metals [14]. Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. Several studies have been reported on various low cost adsorbents like prosopis cineraria leaf powder [15], custard apple leaf powder [16], acacia seeds [17], sesame leaf [18] banana, lemon, and orange peel [19] Saraca indica leaf powder [20]. However, many factors like dosage of adsorbent, pH, contact time, temperature and metal concentration influence the sorption of metal ions [21-22].

Present study aims to identify the potential of Datura inoxia leaf powder as an inexpensive and abundantly available adsorbent for the removal of cadmium (II), chromium (VI) and lead (II) from aquatic samples. The effects of various parameters are also studied. The Freundlich and Langmuir isotherms models were used to study the adsorption process.

II. MATERIALS AND METHODS

2.1 Preparation and characterization of biosorbent

In the present study Datura inoxia leaves were used as adsorbent. Leaf material was collected from uncontaminated sites. The collected leaf material thoroughly washed with distilled water repeatedly to remove dust and solid particles and allow dry in room
temperature for 3 days. The dried leaf material was grinded to and sieved to get 20-50 mesh size. To identify the functional groups of the adsorbent FTIR used (Nicolet IR-200, USA) in the range of spectra from 4000-400 cm⁻¹.

2.2. Preparation of stock and standard solutions of cadmium (II), chromium (VI) and lead (II)
Stock solutions of cadmium (II), chromium (VI) and lead (II) were prepared by using required amount of CdCl₂, K₂Cr₂O₇ and Pb(NO₃)₂ using double distilled water. Standard solutions were prepared for experiment by diluting the stock solutions of cadmium (II), chromium (VI) and lead (II) with double distilled water. All the chemicals and reagents used were obtained from merk.

2.3. Experimental procedure
The adsorption process was carried out through batch experiments [23] using Datura inoxia leaf powder as adsorbent. The experiment was conducted with a fixed volume of 50 ml of cadmium (II), chromium (VI) and lead (II) solutions re stirred with different dosages of biosorbents (50-125mg) for 2 hours at different pH range (3-8), initial concentration (1-6µg/mL) and contact time (30-150 minutes) were studied. The stirring glass flasks stopped after attaining equilibrium period and the solutions were filtered through whatman40 filter paper. In order to regulate pH of the medium, 0.1 N of HCl and NaOH was used in the study. All the experiments were carried out in triplicate. The initial and final concentration of metal ions in the solutions were measured using Flame Atomic Absorption Spectroscopy. The amount of metal ion adsorbed in mg g⁻¹ at time was computed by using the following equation.

\[ Q_e = \frac{(C_0 - C_e)V}{m} \] ... (1)

where \( C_0 \) (mg L⁻¹) and \( C_e \) (mg L⁻¹) are concentrations of cadmium (II), chromium (VI) and lead (II) before and after adsorption respectively, \( m \) (g) is the weight of the biosorbent used and \( V \) (L) is the final volume of the aqueous solution containing Cd(II) or Pb(II). The percentage uptake of the biosorbent or removal percentage of cadmium (II), chromium (VI) and lead (II) was calculated by the following equation.

\[ R_{em} (%) = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \] ... (2)

Where \( C_0 \) and \( C_e \) are the initial and equilibrium concentration of metal ion (mg/L).

The adsorption isotherms play an important role in the predictive modeling procedures for analysis and design of adsorption systems. The Langmuir and Freundlich isotherms, which assume a monolayer adsorption on a homogenous surface and a multilayer adsorption on a heterogeneous surface respectively, are the most frequently used models to represent the data of adsorption from the solution. To estimate the removal efficiency of metal ions cadmium (II), chromium (VI) and lead (II).

III. RESULTS AND DISCUSSION
FTIR spectra of powdered biosorbent Datura inoxia was shown in Figure 1. As shown in the Figure 1 various bands observed between wave numbers 4000-400 cm⁻¹ shows that the spectrum of the biosorbent was different in shape and intensity displayed many peaks which indicates the presence of many functional groups. The peak at 3262.73 cm⁻¹ is due the stretching of hydroxyl groups and this may be due to acid or alcohol structures. The peak at 2920.21 cm⁻¹ is due to the stretching of C=O bonds, The peak at 1626.21 cm⁻¹ is due to the presence of vinyl stretch C-H, C-N stretching vibrations.
pH is most important factor which influence the adsorption process[25]. To study the effect of pH, several experiments were carried out in the range of 3.0-8.0. Figure 2 shows the maximum removal found to be 92% for cadmium (II) at pH 6.0, 90% for chromium (VI) at pH 5.5 and 93% for lead (II) at pH 4.5 respectively. Results indicate the removal of metal ions increased with increase of pH. There is a decline in the removal of cadmium (II), chromium (VI) and lead (II) when the pH exceeds 6.0. This is probably due to the precipitation of metal ions at higher pH [26].

The effect of contact time on biosorption of cadmium (II), chromium (VI) and lead (II) on Datura inoxia was studied over a period of (30-150 minutes). Results indicate that the adsorption of metal ions in solution increased with increase in time. Figure 2 shows that equilibrium time for adsorption of metal ions was attained within 150 minutes. The optimum contact time was set as 150 minutes for the all experiments. Result indicate that in the beginning the adsorption rate was high due to having abundant free space probably on the surface of adsorbent and thereafter slowly reaching maximum adsorption after 120 minutes [27].
To study the effect of dosage on adsorption of cadmium (II), chromium (VI) and lead (II) on Datura inoxia, several experiments were conducted with the varied dosage (25mg -125mg). As shown in the Figure 3 the maximum removal found to be 92% for cadmium (II), 90% for chromium (VI) and 93% for lead (II). Results indicate the removal percentage of metal ions increased with the increase amount of adsorbent. Thus the optimum dosage for the removal of cadmium (II), chromium (VI) and lead (II) from the solution was found to be 100mg. This may be probably due to the greater availability of active sites on the adsorbent at higher concentrations which makes easier penetration and having more possibilities of the metal ions in to the sorption sites [28].
In the Present study Langmuir and Freundlich models were used to describe the adsorption equilibrium for cadmium (II), chromium (VI) and lead (II) ions. The Langmuir isotherm model based on sorption of metal ions on a uniform surface with monolayer adsorption [29] and described by the following equation.

\[
\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}} \quad \ldots (3)
\]

The values of Langmuir constant \(Q_{\text{max}}\) and \(K_L\) were calculated from the slope and intercept of the linear plot \(C_e/Q_e\) versus \(C_e\).

Freundlich isotherm is based on multilayer adsorption with heterogeneous surfaces with the interaction between adsorbed molecules [30] The linear form of Freundlich isotherm equation can be as;

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \ldots (4)
\]

The Freundlich isotherm constants \(1/n\) and \(K_f\) are calculated from the slopes and intercepts of the linear plot of \(\log Q_e\) versus \(\log C_e\).

| Table 1 Aqueous concentration (\(C_i\)) and sorbed quantity (\(Q_e\)) at equilibrium for metal ions cadmium (II), chromium (VI) & lead (II) by Datura inoxia |
|---|---|---|---|---|---|
| Metal ions | \(C_i\) | \(C_e\) | \(Q_e\) | \(C_e/Q_e\) | \(\log C_e\) | \(\log Q_e\) |
| Cadmium(II) | 1 | 0.09 | 0.455 | 0.198 | -1.046 | -0.342 |
|  | 2 | 0.17 | 0.915 | 0.186 | -0.770 | -0.039 |
|  | 3 | 0.23 | 1.385 | 0.166 | -0.638 | 0.141 |
|  | 4 | 0.31 | 1.845 | 0.168 | -0.509 | 0.266 |
|  | 5 | 0.41 | 2.295 | 0.179 | -0.387 | 0.361 |
|  | 6 | 0.47 | 2.765 | 0.170 | -0.328 | 0.442 |
| Chromium(VI) | 1 | 0.11 | 0.445 | 0.247 | -0.959 | -0.352 |
|  | 2 | 0.19 | 0.905 | 0.210 | -0.721 | -0.043 |
|  | 3 | 0.31 | 1.345 | 0.230 | -0.509 | 0.129 |
|  | 4 | 0.41 | 1.795 | 0.228 | -0.387 | 0.254 |
|  | 5 | 0.49 | 2.255 | 0.217 | -0.310 | 0.353 |
|  | 6 | 0.51 | 2.745 | 0.186 | -0.292 | 0.439 |
| Lead(II) | 1 | 0.08 | 0.46 | 0.174 | -1.097 | -0.337 |
|  | 2 | 0.13 | 0.935 | 0.139 | -0.886 | -0.029 |
|  | 3 | 0.22 | 1.39 | 0.158 | -0.658 | 0.143 |
|  | 4 | 0.27 | 1.865 | 0.145 | -0.569 | 0.271 |
|  | 5 | 0.34 | 2.33 | 0.146 | -0.469 | 0.367 |
|  | 6 | 0.43 | 2.785 | 0.154 | -0.367 | 0.445 |
Table 2 Linear regression data for Langmuir and Freundlich isotherms for metal ions cadmium (II), chromium (VI) & lead (II) by and Datura inoxia

| Biosorbent | Metal ions | Langmuir parameters | Freundlich parameters |
|------------|------------|---------------------|-----------------------|
|            |            | $Q_{max}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $N$ | $K_f$ | $R^2$ |
| Datura inoxia | Cadmium(II) | 12.5 | 0.323 | 0.392 | 0.954 | 0.802 | 0.995 |
|            | Chromium(VI) | 18.18 | 0.285 | 0.148 | 0.911 | 0.711 | 0.996 |
|            | Lead (II) | 33.33 | 0.187 | 0.101 | 0.949 | 0.853 | 0.988 |

Figure 4 Langmuir isotherm model for adsorption of metal ions cadmium (II), chromium (VI) and lead (II) by Datura inoxia as biosorbent.

Figure 5 Freundlich isotherm model for adsorption of metal ions cadmium (II), chromium (VI) and lead (II) by Datura inoxia as biosorbent.
The results indicate the adsorption was better described by the Freundlich isotherm than the Langmuir isotherm model. As shown in the Figure the regression coefficient ($R^2$) for cadmium (II), chromium (VI) and lead (II) was 0.995, 0.996 and 0.998 respectively. Langmuir isotherm was less accurate with a lower $R^2$ value. Table 1 indicates the values of $N$, $K_{F}$ and $R^2$ and the values of $q_{max}$ and $K_{L}$ (l/mg). Results of the present adsorption study revealed that Freundlich isotherm fits the data probably due to heterogeneous distribution of active sites with interaction between adsorbed molecules and also due to the Freundlich model can also apply in the low to intermediate concentration range. The Langmuir isotherm failed to apply in this instance. The correlation coefficient ($R^2$) values indicate that the data is fitted to the Freundlich isotherm in the present studies.

IV. CONCLUSION

In the present investigation, the biosorbent obtained from *Datura inoxia* was used to remove cadmium (II), chromium (VI) and lead (II) from aqueous solutions. The developed biosorbent allowed multilayer adsorption to take place on the surface of the adsorbent and this could be well described by Freundlich model with $R^2$ 0.995 at pH 5 for cadmium (II), 0.996 at pH 5.5 for chromium (VI) and 0.988 at pH 4.5 for lead (II) respectively. In the present adsorption process involves ion exchange and surface complexation was found to be the main mechanisms. The developed biosorbent found to be more efficient in removal of cadmium (II), chromium (VI) and lead (II). The study can be concluded that *Datura inoxia* is a locally available medicinal plant with high adsorption potential and considered as alternative ecofriendly adsorbent for the removal of cadmium (II), chromium (VI) and lead (II) from water solution and also can be apply for real water samples.

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