

Biosorption of Cd (II), Cr (VI) & Pb (II) from Aqueous Solution Using *Mirabilis jalapa* as Adsorbent

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Abstract

Mirabilis jalapa (chandrakantha) leaves were used as a biosorbent for the removal of toxic metals ions cadmium (II), chromium (VI) and lead (II) from water. The physiochemical properties of the developed biosorbent were studied using FTIR. The efficiency of this developed biosorbent was tested using batch experiments under controlled conditions such as a function of pH, contact time, initial metal concentration and the optimization amount of biosorbent. The residual metallic ion concentrations of cadmium (II), chromium (VI) and lead (II) were determined using AAS. The biosorption capacity of *Mirabilis jalapa* was found to be pH dependant and the percentage removal of cadmium (II), chromium (VI) and lead (II) was increased with increasing adsorbate solution pH and a maximum value was reached at an equilibrium pH = 6 for cadmium (II), pH = 5.5 for chromium (VI) and pH 4.5 for lead (II) respectively. The equilibrium time required for the saturation loading of cadmium (II), chromium (VI) and lead (II) in the biosorbent was found to be about 120 min. The obtained equilibrium biosorption data was fitted to the linear forms of Freundlich isotherms. The results proved the efficiency of *Mirabilis jalapa* leaves powder as biosorbent for the removal of metal ions and it can be used for the development of an efficient, clean and novel technology for waste water treatment.

Keywords

Mirabilis jalapa, Biosorption, Toxic Metal Ions, Isotherm Models

1. Introduction

Toxic metal ions mainly cadmium (II), chromium (VI), mercury (II) and lead (II) have a lethal effects on all

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forms of life. They will enter the food chain through the discharge of waste from industries, mining and anthropogenic activities [1]. The presence of toxic heavy metals in the environment is of major concern because of their high toxicity, bio-accumulating tendency, which threatens human life and the environment [2]. Cadmium (II) has been recognized as one of the most toxic environmental and industrial contaminant due to its ability to induce severe alterations in various organs and tissues following either acute or chronic exposure [3] [4]. The symptoms of cadmium poisoning are instantaneous hypertension, shortening of life-span; kidney damage, bronchitis, retardation of growth, gross abnormalities of the vital organs and the risk of prostatic cancer [5]. The most serious situation being the disease called "Itai-Itai" which causes gradual weakening of the bone structure, diminution of stature and ultimately the total collapse of the entire skeletal system [6]. Chromium has long been used in electroplating, leather tanning, metal finishing and chromate manufacturing industries. Effluents from these industries contain both trivalent chromium (III), and hexavalent chromium (VI), with concentrations ranging from tens to hundreds of mg/L [7]. Hexavalent chromium occurs as highly soluble and toxic chromate anions (HCrO₄⁻ or Cr₂O₇²⁻), which are suspected to be carcinogens and mutagens [8]. Lead is one of the major heavy metal and often found in industrial wastewater and its discharge into the environment poses serious threat due to its toxicity to aquatic and terrestrial lives [9] [10]. Enhanced industrialization such as manufacturing of storage batteries, television tube, printing, paints, pigments, photographic materials, gasoline additives, matches and explosives brings about lead bearing wastewater [11]-[14]. Other problems associated with toxic levels of lead exposure are encephalopathy, seizures and mental retardation, anaemia and nephropathy [15]. Various traditional methods of removing heavy metals from wastewaters have been reported including the use of precipitation and coagulation, chemical oxidation, sedimentation, filtration, osmosis, ion exchange etc. [16]. Biosorption may offer an attractive alternative for the remediation of heavy metals in contaminated water samples, and is a process where biological materials are used to remove (adsorb/absorb) contaminants from waste streams. Biosorption has been used as an alternative technology for removing toxic heavy metals from waste effluents [17].

In addition to scientific preference, economic considerations also play crucial role in the selection of appropriate biomass for pollution abatement. Thus, intense research attention is now focused on cost effective, ecofriendly and easily available adsorbent particularly of biological origin [18]. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. However, the performance of a biosorbent depends on the characteristic properties of the biomass as well as the microenvironment of the target toxicant. The search for an appropriate and inexpensive biomass is a continuing process. The most effective and optimized utilization of a biomass demanded a detailed understanding of the binding mechanism. In the present study, removal of heavy metals cadmium, chromium and lead from water has been taken up by batch adsorption techniques using *Mirabilis jalapa* leaves powder as the adsorbent material.

2. Experimental

2.1. Apparatus

Measurements were performed with a model 6300 Flame atomic absorption spectrometer, Shimadzu (Japan), with flame of air-acetylene and the instrument settings were according to the manufacturer's recommendations. A LI-120 digital pH meter (Elico, India) was used for the pH measurement, weighing of the reagents and chemicals were carried with Shimadzu AUX 320 digital electronic balance. IR spectrometer (Thermo-Nicolet FT-IR, Nicolet IR-200, USA) was used for functional group analysis of the biomass.

2.2. Reagents and Standards

Standards of cadmium (II), chromium (VI) and lead (II) solutions (1000 μ g/ml), were prepared by weighing 1.7911 g of CdCl₂ (Merck), 2.8288 g of K₂Cr₂O₇ (Merck) and 1.60 g of Pb(NO₃)₂ (Merck) dissolving in double distilled water to give a volume of 1000 ml.

2.3. Preparation of Bio-Sorbent Material

Leaves of *Mirabilis jalapa* were collected and washed several times and dried in shadow. Dried leaves were grinded and sieved to 50μ cm size mesh. Sieved leaves powder was washed with deionised double distilled wa-

ter and then dried. To avoid the release of colour from the leaves powder in to the aqueous solution during adsorption, it was treated with formaldehyde. To this solution, 5 mL of aqueous formaldehyde was added to 100 mL 0.1 M H_2SO_4 and then 10 g of washed leaves powder was added. The final mixture was stirred and heated at 50°C for 24 - 48 hours till the mixture became thick slurry. The slurry was washed with deionised distilled water and then dried. The prepared biomass was then stored in air tight glass bottles to protect from the moisture. The prepared biosorbent was used for further studies [19].

2.4. Fourier Transformed Infrared Spectroscopic (FTIR) Analysis of Biosorbent

FTIR spectra of powdered *Mirabilis jalapa* biomass adsorption was recorded on IR spectrophotometer (Thermo-Nicolet FT-IR, Nicolet IR-200, USA). Pressed pellets were prepared by grinding the samples with KBr in a mortar and immediately analyzed in the region of $4000 - 400 \text{ cm}^{-1}$.

2.5. Batch Adsorption Studies

The affinity of biomass to adsorb heavy metals like cadmium (II), chromium (VI) & lead (II) were studied in batch experiments. In all sets of experiments, fixed volume of metal solution in 50 mL was stirred with desired biosorbent dose (50 - 125 mg) for the period of two hours. Different conditions of pH (3 - 8), initial concentrations (1 - $6 \mu g/mL$) and contact time (30 - 150 minutes) were evaluated during the study. In order to regulate pH of the medium, 0.1 N of HCl and NaOH were used. The solutions were separated from the biomass by filtration through whatmann 40 filter paper. The initial and final concentrations of the metal ions in the solution were measured using Flame Atomic Absorption Spectroscopy.

The amount of metal ion adsorbed in $mg \cdot g^{-1}$ at time was computed by using the following equation.

$$Q_e = \frac{\left(C_i - C_e\right)V}{m} \tag{1}$$

where

Qe is the metal ion concentration adsorbed (mg metal ion concentration/g biosorbent) at equilibrium,

V is the volume of the solution (L),

 C_i and C_e are the initial and equilibrium concentrations of metal ion (mg/L) and m is the dry weight of the biosorbent (g).

The percentage of the removal of metal ion concentration (R_{em} %) in solution was calculated using equation:

$$\mathbf{R}_{\rm em}\left(\%\right) = \frac{\left(\mathbf{C}_{\rm i} - \mathbf{C}_{\rm e}\right)}{\mathbf{C}_{\rm i}} \times 100 \tag{2}$$

where C_i and C_e are the initial and equilibrium concentration of metal ion (mg/L).

2.6. Adsorption Isotherm Models

An adsorption is a quantitative relationship describing the equilibrium between the concentrations of absorbate in solution (mass/volume) and its concentration (mass adsorbate/mass adsorbate).

An adsorption isotherm relates the concentration of solute on the surface of the adsorbent to the concentration of the solute in the fluid with the adsorbent in contact. These values are usually determined experimentally. In order to describe the equilibrium isotherm of biosorption process, Langmuir and Freundlich isotherm models are discussed in the present study.

2.6.1. Langmuir Isotherm Model

The Langmuir isotherm model is based on the following assumptions:

- Each active site interacts with only one adsorbate molecule,
- Sorbate molecules are adsorbed on well localized sites,
- There is no interaction between adjacent adsorbed molecules and
- The adsorption sites are all energetically equivalent.

Langmuir isotherm is given by the following equation:Z

$$Q_{e} = \frac{K_{L}Q_{max}C_{e}}{1+K_{L}C_{e}}$$
(3)

where Q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/g), Q_{max} is the maximum biosorption capacity of adsorbent (mg/g) and K_L is the Langmuir biosorption constant (L/mg). The Equation (4) can be represented by the following linear form;

$$\frac{C_{e}}{Q_{e}} = \frac{1}{K_{L} \cdot Q_{max}} + \frac{C_{e}}{Q_{max}}$$
(4)

The values of Langmuir constant Q_{max} and K_L were calculated from the slope and intercept of the linear plot C_e/Q_e versus C_e . The essential features of Langmuir isotherm model can be expressed by means of a separation factor of equilibrium parameter (R_L), which is calculated according to the following equation;

$$R_{L} = \frac{1}{1 + K_{L}C_{i}}$$
(5)

The values of R_L indicate the type of biosorption isotherm to be:

- Linear $(\mathbf{R}_{\mathrm{L}}=1)$,
- Favorable $(0 < R_L < 1)$,
- Unfavourable $(R_L > 1)$ and
- Irreversible $(R_L = 0)$.

2.6.2. Freundlich Isotherm Model

The Freundlich isotherm model is derived from Gibbs adsorption combined with a mathematical description of the free energy of the surface. Freundlich proposed an empirical isotherm equation assuming a heterogeneous adsorption surface and active sites with different energy. The Freundlich equation is as follows:

$$Q_e = K_f C_e^{1/n} \tag{6}$$

The Freundlich isotherm can be derived from Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbents with each site behaving according to Langmuir isotherm. Here, K_f is a measure of the capacity of the adsorbent and n is a measure of how affinity for the adsorbate changes with changes in adsorption density.

When n = 1, the Freundlich isotherm becomes linear isotherm and indicates that all sites on the adsorbent have equal affinity for the adsorbates. Values of n > 1 indicate the affinities decreases with increasing adsorption density. The linear form of Freundlich isotherm equation can be as;

$$\log Q_{e} = \log K_{f} + \frac{1}{n} \log C_{e}$$
(8)

The Freundlich isotherm constants 1/n and K_f are calculated from the slopes and intercepts of the linear plot of $logQ_e$ versus $logC_e$.

2.7. Application to Real Water Samples

The developed procedure was used for the removal and determination of cadmium (II), chromium (VI) and lead (II) in the real water samples and industrial effluents. Water samples were collected in and around agricultural sites of Tirupati. To the volume of 50 mL of real samples (ground water/tap water), known amount of metal ions concentration were spiked, then the spiked samples were stirred with biosorbent by maintaining the pH at 6, 5.5 & 4.5 for cadmium (II), chromium (VI) and lead (II). Metal ions were determined by flame atomic absorption spectroscopy after completion of batch adsorption studies.

3. Results and Discussion

Results demonstrate the important role of selected biosorbent *Mirabilis jalapa* for the removal of metal ions cadmium (II), chromium (VI) and lead (II) from aqueous samples. The factors like pH, dosage of biosorbent, initial concentration of metal ion, time of stirring etc., were optimized by varying with different dosages.

3.1. Fourier Transformed Infrared Spectroscopic (FTIR) Analysis

FTIR spectra of powdered biosorbent *Mirabilis jalapa* shown in **Figure 1**. According to **Figure 1**, As shown in the **Figure 1** various bands observed between wave numbers 4000 - 400 cm⁻¹ shows that the spectrum of the bisorbent shows many peaks which indicates the presence of many functional groups. The peak at 3269 cm⁻¹ is due the stretching of hydroxyl groups and this may be due to acid or alcohol structures, The peak at 2920.28 cm⁻¹ is due to the stretching of C=O bonds, The peak at 1607.16 cm⁻¹ is due to the presence of presence of vinyl stretch C-H, C-N stretching vibrations

3.2. Effect of pH

pH is an important parameter that influences the adsorption process by the way of modifying the functional groups of biomass. The effect of pH on adsorption of metal ions was conducted in the pH range of 3.0 - 8.0. Adsorption of cadmium (II), chromium (VI) & lead (II) by *Mirabilis jalapa* was found to be maximum at pH 6 for cadmium (II), pH 5.5 for chromium (VI) & pH 4.5 for lead (II). The pH study values are shown in **Table 1**. The maximum removal of metal ions found to be 88%, 85% & 89% for metal ions cadmium, chromium and lead. The pH studies were shown in the **Figure 2**.



Figure 1. FTIR spectrum of Mirabilis jalapa.

 Table 1. pH studies for the biosorbent *Mirabilis jalapa* for the removal of metal ions cadmium (II), chromium (VI) & lead (II).

| Mirabilis jalapa | | | | | | | | |
|------------------|-----------|-----|-----------|---------|-----------|--|--|--|
| Cd (II) | | С | r (VI) | Pb (II) | | | | |
| pН | % Removal | pН | % Removal | pH | % Removal | | | |
| 3 | 58 | 3 | 56 | 3 | 54 | | | |
| 4 | 66 | 4 | 64 | 3.5 | 61 | | | |
| 5 | 77 | 5 | 74 | 4 | 76 | | | |
| 6 | 88 | 5.5 | 85 | 4.5 | 89 | | | |
| 7 | 79 | 6 | 81 | 5 | 80 | | | |
| 8 | 72 | 7 | 73 | 5.5 | 74 | | | |
| | | 8 | 68 | 6 | 67 | | | |



Figure 2. Adsorption of cadmium (II), chromium (VI) and lead (II) on biosorbent *Mirabilis jalapa* at different pH values. Concentration of metal ions 3 µg/mL.

3.3. Effect of Contact Time

The equilibrium time required for the biosorption of metal ions for *Mirabilis jalapa* with $3 \mu g/mL$ of metal concentrations of cadmium (II), chromium (VI) and lead (II) at different time intervals were studied. **Figure 3** shows that adsorption capacity sharply increased with increase in time and attain equilibrium in 120 minutes. The removal rate of metal ions increases with the increase of the adsorption time. However, it remains constant after an equilibrium time of 120 minutes, which indicates that the adsorption tends towards saturation. Therefore, the adsorption time was set as 120 minutes in each experiment. The rate of adsorption was higher in the beginning due to large available surface area of the biosorbent. After the capacity of the adsorbent gets exhausted, *i.e.* at equilibrium, the rate of uptake was controlled by the rate at which the absorbate was transported from the exterior to the interior sites of the biosorbent particles [20]. The effect of time for the extraction of metal ions by biosorbent *Mirabilis jalapa* was shown in **Table 2**.

3.4. Effect of Biomass Dosage

The effect of biosorbent dosage for the extraction of cadmium (II), chromium (VI) and lead (II) is shown in **Figure 4**. The amount of biosorbent was varied from 25 mg - 125 mg and equilibrated for 120 minutes with the concentration of 3 μ g/mL. The results indicated that the removal percentage of metal ions increased with the increased amount of adsorbent and removal efficiency of *Mirabilis jalapa* was 88 per cent for cadmium (II), 85 per cent for chromium (VI) and 89 per cent for lead (II) respectively. The highest uptake yield was obtained at biosorbent concentration of 100 mg for the biosorbent. The removal of metal ions concentration was increased with the increased biosorbent concentration and attained equilibrium after 100 mg of adsorbent dosage for cadmium (II), chromium (VI) and lead (II). This is due to availability of more biosorbent as well as greater availability of surface area [21]. The effect of biosorbant dose for the extraction of metal ions by biosorbent (*Mirabilis jalapa*) was shown in **Table 3**.

3.5. Adsorption Isotherms

The equilibrium of biosorption of metal ions was modelled using adsorption-type isotherms. The Langmuir and Freundlich isotherm models were used to describe the biosorption equilibrium of biomass. It is also helpful in comparing different biomaterials under different operating conditions. To find out the relationship between aqueous concentration (C_e) and sorbed quantity (Q_e) at equilibrium, mostly isotherms models are used for fitting the data. The C_e and Q_e values for the biosorbent during the study of cadmium (II), chromium (VI) and lead (II) extraction was shown in the **Table 4**. Langmuir parameters can be determined from a linearized form of equation given below.

$$\frac{C_{e}}{Q_{e}} = \frac{1}{K_{L} \cdot Q_{max}} + \frac{C_{e}}{Q_{max}}$$



Figure 3. Adsorption of cadmium (II), chromium (VI) & lead (II) on biosorbent *Mirabilis jalapa* at different time intervals. Concentration of metal ions 3 μ g/mL, at pH 6, pH 5.5 & pH 4.5 for cadmium (II), chromium (VI) & lead (II).



Time of stirring at 3 ppm of metal ions con. for biosorbant Mirabilis jalapa

Figure 4. Adsorption of cadmium (II), chromium (VI) & lead (II) on biosorbent *Mirabilis jalapa* with various dosages. Concentration of metal ions 3 μ g/mL, at pH 6, pH 5.5 & pH 4.5 for cadmium (II), chromium (VI) & lead (II).

Table 2. Time of stirring at 3 µg/mL of metal ions cadmium (II), chromium (VI) and lead (II) on biosorbent *Mirabilis jalapa* at different time intervals.

| Time of stirring | Cd (II) | Cr (VI) | Pb (II) | |
|------------------|-----------|-----------|-----------|--|
| - | % Removal | % Removal | % Removal | |
| 30 | 55 | 52 | 56 | |
| 60 | 64 | 63 | 65 | |
| 90 | 75 | 74 | 76 | |
| 120 | 88 | 85 | 89 | |
| 150 | 88 | 85 | 89 | |

Table 3. Dosages of biosorbent at 3 µg/mL of metal ions cadmium (II), chromium (VI) and lead (II) on *Mirabilis jalapa*.

| | | Mirabilis jalapa | |
|----------------------------|-----------|------------------|-----------|
| Dosage of biosorbent in mg | Cd(II) | Cr(VI) | Pb(II) |
| | % Removal | % Removal | % Removal |
| 50 | 65 | 63 | 64 |
| 75 | 71 | 69 | 70 |
| 100 | 88 | 85 | 89 |
| 125 | 88 | 85 | 89 |

Table 4. Aqueous concentration (C_e) and sorbed quantity (Q_e) at equilibrium cadmium (II), chromium (VI) & lead (II) by *Mirabilis jalapa*.

| Metal ions | Ci | C _e mg/L | Q _e mg/g | C _e /Q _e | logC _e | logQe |
|---------------------|----|---------------------|---------------------|--------------------------------|-------------------|--------|
| | 1 | 0.13 | 0.435 | 0.299 | -0.886 | -0.362 |
| | 2 | 0.24 | 0.88 | 0.273 | -0.620 | -0.056 |
| Calmium (II) | 3 | 0.37 | 1.315 | 0.281 | -0.432 | 0.119 |
| Cadmium (II) | 4 | 0.48 | 1.76 | 0.273 | -0.319 | 0.246 |
| | 5 | 0.59 | 2.205 | 0.268 | -0.229 | 0.343 |
| | 6 | 0.71 | 2.645 | 0.268 | -0.149 | 0.422 |
| | 1 | 0.14 | 0.43 | 0.326 | -0.854 | -0.367 |
| | 2 | 0.31 | 0.845 | 0.367 | -0.509 | -0.073 |
| Characteristic (MI) | 3 | 0.44 | 1.28 | 0.344 | -0.357 | 0.107 |
| Chromium (VI) | 4 | 0.59 | 1.705 | 0.346 | -0.229 | 0.232 |
| | 5 | 0.76 | 2.12 | 0.358 | -0.119 | 0.326 |
| | 6 | 0.91 | 2.545 | 0.358 | -0.041 | 0.406 |
| | 1 | 0.12 | 0.44 | 0.273 | -0.921 | -0.357 |
| | 2 | 0.21 | 0.895 | 0.235 | -0.678 | -0.048 |
| | 3 | 0.34 | 1.33 | 0.256 | -0.469 | 0.124 |
| Lead (II) | 4 | 0.43 | 1.785 | 0.241 | -0.367 | 0.252 |
| | 5 | 0.56 | 2.22 | 0.252 | -0.252 | 0.346 |
| | 6 | 0.65 | 2.675 | 0.243 | -0.187 | 0.427 |

The adsorption data obtained for metal ions adsorption, *Mirabilis jalapa* leaves powder used as biosorbent. The values of the Langmuir constants (K_L , Q_{max}) and Freundlich constants (K, n) are presented for the biosorption of cadmium (II), chromium (VI) and lead (II) was shown in **Table 5**. It shows that the R² value for Freundlich isotherm was high than Langmuir isotherms. **Figure 5** shows that Langmuir isotherm model of metal ions adsorption by *Mirabilis jalapa* leaves powder was found with R² of 0.275 for cadmium (II), 0.626 for chromium (VI) and 0.157 for lead (II). **Figure 4 & Figure 6** shows that Freundlich isotherm model of adsorption by *Mirabilis jalapa* leaves powder was found with R² of 0.999 for cadmium (II), 0.997 for chromium (VI) and 0.995 for lead (II).

The Langmuir constants (Q_{max}) defined as the amount of adsorbate per unit weight of adsorbent to form a complete multi molecular layers on a sorbate surface was found to be 38.461 for cadmium (II), 23.255 for chromium (VI) and 38.461 for lead (II) by using biosorbent *Mirabilis jalapa* while K_L values which reflects quantitatively the affinity between the adsorbent and adsorbate were found to be 0.077 for cadmium (II), 0.145 for chromium (VI) and 0.100 for lead (II) Lower value corresponds to more affinity of metal ions to biomass.

| Table 5. Linear regression | data for Langmu | ir and Freundlich | isotherms for | metal ions | cadmium (II), | chromium | (VI) a | & lead |
|----------------------------|-----------------|-------------------|---------------|------------|---------------|----------|--------|--------|
| (II) by Mirabilis jalapa. | | | | | | | | |

| | | Lang | umuir paramete | Freundlich parameters | | | |
|------------------|---------------|-------------------------|-----------------------|-----------------------|---|----------------|-------|
| Biosorbent | Metal ions | Q _{max} (mg/g) | K _L (L/mg) | R ² | Kr N Kr 0.946 0.583 1.041 0.442 0.959 0.622 | R ² | |
| | Cadmium (II) | 38.461 | 0.077 | 0.275 | 0.946 | 0.583 | 0.999 |
| Mirabilis jalapa | Chromium (VI) | 23.255 | 0.145 | 0.626 | 1.041 | 0.442 | 0.997 |
| | Lead (II) | 38.461 | 0.100 | 0.157 | 0.959 | 0.622 | 0.995 |

Isotherm studies (F) for metal ions by Mirabilis jalapa



Figure 5. Freundlich isotherm model for adsorption of metal ions cadmium (II), chromium (VI) and lead (II) by *Mirabilis jalapa* as biosorbent.



Figure 6. Langmuir isotherm model for adsorption of metal ions by Mirabilis jalapa as biosorbent.

In the present work Freundlich isotherm fits the data it may be due to heterogeneous distribution of active sites and the supply of these adsorption sites were infinite on studied adsorbent surface. The fitting of the Freundlich isotherm to the experimental data for the developed adsorbent can be explained by the fact that this model can only be applied in the low to intermediate concentration range. The Langmuir isotherm failed to apply in this instance could indicate that the adsorption of cadmium (II), chromium (VI) & lead (II) metal ions does not assume monolayer mechanism. Thus, the present adsorption process involves coverage of multi molecular layers, as the most actively energetic sites are occupied first and thereafter the surface was occupied until the lowest energy sites were filled at the final stage of the adsorption process. In addition, physical adsorption may also be responsible for the interaction between adsorbent and metal ions because adsorbent had a large surface area.

The Freundlich model is expressed as:

$$Q_{e} = K_{f}C_{e}^{1/1}$$

Above equation can be rearranged into following form:

$$\log Q_{e} = \log K_{f} + \frac{1}{n} \log C_{e}$$

Q_e is metal ions cadmium (II), chromium (VI) and lead (II) sorbed (mg/g). C_e the equilibrium concentration of metal ions solution (mg/L), Kf and N are Freundlich constants. The constants Kf and 1/n are used as an indication of whether adsorption remains constant (at 1/n = 1) or decreases with increasing adsorbate concentrations. It appears from the Figure 4 & Figure 6 that Freundlich model fits best for the experimental results which was not similar to Langmuir over the experimental range with good correlation co-efficient. The n values by biosorbent Mirabilis jalapa from the Figure 4 & Figure 6, 0.946 for cadmium (II) 1.041 for chromium (VI) and 0.959 for lead (II) The K_f values are 0.583 for cadmium (II), 0.442 for chromium (VI) and 0.622 for lead (II).

3.6. Application to Real Water Samples

The developed procedure was used for the removal and determination of cadmium (II), chromium (VI) & lead (II) in the real water samples. Water samples were collected from industrial and around agricultural sites of Tirupati. To the volume of 50 mL of real samples (ground water/tap water), known amount of metal ions concentrations were spiked, and then the spiked samples were stirred with biosorbent by maintaining the pH 6, 5.5 & 4.5 for Cd (II), Cr (VI) & Pb (II) respectively. Metal ions were determined by conducting batch adsorption studies through FAAS. Results are shown in Table 6.

4. Conclusions

The effect of different factors on the sorption ability of Mirabilis Jalapa leaves powder as adsorbent was studied for the removal of cadmium (II), chromium (VI) & lead (II) from aqueous solution. The following conclusions can be drawn from the present study.

| Table 6. Recovery of metal ion by using biosorbent <i>mirabuls jalapa</i> from the real water samples. | | | | | | | | | | |
|---|----------------|---------------|--------------------------|----------------|------------------|--------------------------|----------------|---------------|--------------------------|--|
| Sample | | | | M | lirabilis jalapa | | | | | |
| | | Cadmium (II) |) | | Chromium (VI |) | Lead (II) | | | |
| | Spiked mg/L | Found mg/L | % of Recovery mg/L | Spiked mg/L | Found mg/L | % of Recovery mg/L | Spiked mg/L | Found mg/L | % of recovery mg/L | |
| Industrial Site 1 | 3 | 2.64 ± 0.02 | 88 | 3 | 2.55 ± 0.01 | 85 | 3 | 2.67 ± 0.05 | 89 | |
| Industrial Site 2 | 3 | 2.64 ± 0.03 | 80 | 3 | 2.55 ± 0.04 | 83 | 3 | 2.67 ± 0.03 | 82 | |
| Agricultural Site | 3 | 2.64 ± 0.02 | 78 | 3 | 2.55 ± 0.02 | 80 | 3 | 2.67 ± 0.04 | 76 | |

- The selected herbal leaves powder *Mirabilis jalapa* is a suitable material for the removal of metal ions cadmium (II), chromium (VI) & lead (II).
- Effect of pH, biomass dose and contact time highly affects the overall cadmium (II), chromium (VI) & lead (II) uptake of biosorbent.
- The sorption was pH dependent and the percentage removal of cadmium (II), chromium (VI) and lead (II) was increased with increasing adsorbate solution pH. Maximum removal found to be at pH 6.0 for cadmium (II), 5.5 for chromium (VI) and 4.5 for lead (II).
- The optimum time was observed to be 2 hours with optimum dosage 100 mg.
- Present results show that Freundlich isotherm models fit for the adsorption equilibrium data in the examined concentration range of (1 - 6 μg/mL).
- The selected *Mirabilis jalapa* leaves powder was an effective, novel and eco-friendly biosorbent for the removal of cadmium (II), chromium (VI) & lead (II).

References

- Volesky, B. (1994) Advances in Biosorption of Metal: Selection of Biomass Types. FEMS Microbiology Reviews, 14, 291-302. <u>http://dx.doi.org/10.1111/j.1574-6976.1994.tb00102.x</u>
- [2] Igwe, J.C. and Abia, A.A. (2003) Maize Cob and Husk as Adsorbents for Removal of Cd, Pb and Zn Ions from Wastewater. *The physical Science*, **2**, 83-94.
- [3] Nordberg, G.F., Kjellstrom, T., Nordberg, M., In Friberg, C. and Elinder, G. (1985) Cadmium and Health: A Toxicological and Epidemiological Appraisal. CRC Press, Boca Raton.
- [4] Oehme, F.W. (1978) Toxicity of Heavy Metals in the Environment. Marcel Dekker, New York.
- [5] Fergusson, J.E. (1989) The Toxicity of Heavy Elements to Human Beings. In: *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*, Pergamon Press, Oxford, 548.
- [6] Ullah, M.R. and Enamul Haque, M. (2010) Spectrophotometric Determination of Toxic Elements (Cadmium) in Aqueous Media. *Journal of Chemical Engineering*, **25**, 1-2.
- Barnhart, J. (1997) Occurrences, Uses, and Properties of Chromium. *Regulatory Toxicology and Pharmacology*, 26, S3-S7. <u>http://dx.doi.org/10.1006/rtph.1997.1132</u>
- [8] Costa, M. (2003) Potential Hazards of Hexavalent Chromate in Our Drinking Water. *Toxicology and Applied Pharma-cology*, **118**, 1-5. <u>http://dx.doi.org/10.1016/S0041-008X(03)00011-5</u>
- [9] Ko, D.C.K., Porter, J.F. and Mckay, G. (2000) Optimized Correlation for the Fixed Bed Adsorption of Metal Ions on Bone Char. *Chemical Engineering Science*, 55, 5819-5829. <u>http://dx.doi.org/10.1016/S0009-2509(00)00416-4</u>
- [10] Koller, K.B.T., Spurgeon, A. and Levy, L. (2004) Recent Development in Low Level Exposure and Intellectual Impairment in Children. *Environmental Health Perspective*, **112**, 987-994. <u>http://dx.doi.org/10.1289/ehp.6941</u>
- [11] Axtell, N.R., Sternberg, S.P.K. and Claussen, K. (2003) Lead and Nickel Removal Using *Microspora* and *Lemna minor. Bioresource Technology*, 89, 41-48. <u>http://dx.doi.org/10.1016/S0960-8524(03)00034-8</u>
- [12] Qiu, Y., Cheng, H., Xu, C. and Sheng, S.D. (2008) Surface Characteristics of Crop-Residue-Derived Black Carbon and Lead (II) Adsorption. Water Resource, 42, 567-574. <u>http://dx.doi.org/10.1016/j.watres.2007.07.051</u>
- [13] Patterson, J.W. (1985) Industrial Wastewater Treatment Technology. 2nd Edition, Butterworth Publishers, Stoneham.
- [14] Bhatti, H.N., Mumtaz, B., Hanif, M.A. and Nadeem, R. (2007) Removal of Zinc Ions from Aqueous Solution Using *Moringa oleifera* Lam. (Horseradish Tree) Biomass. *Process Biochemistry*, 42, 547-553. http://dx.doi.org/10.1016/j.procbio.2006.10.009
- [15] Schumann, K. (1990) [The Toxicological Estimation of the Heavy Metal Content (Cd, Hg, Pb) in Food for Infants and Small Children]. Z Ernahrungswiss, 29, 54-73.
- [16] Aziz, A., Ouali, M.S., Elanddaloussi, E.H., De Menorval, L.C. and Lindheimer, M. (2009) Chemically Modified Olive Stone: A Low-Cost Sorbent for Heavy Metals and Basic Dyes Removal from Aqueous Solutions. *Journal of Hazardous Materials*, 163, 441-447. <u>http://dx.doi.org/10.1016/j.jhazmat.2008.06.117</u>
- [17] Schiewer, S. and Volesky, B. (1997) Ionic Strength and Electrostatic Effects in Biosorption and Protons. *Environmental Science and Technology*, 31, 1863-1871. <u>http://dx.doi.org/10.1021/es960434n</u>
- [18] Subhankar, C., Sujoy K., D., Rjdeep, C., Adrita, C., Subrata, G. and Arun K., G. (2010) Interactive of Malathion, an Organophosphorus Pesticide with Rhizopus Oryzae Biomass. *Journal of Hazardous Materials*, **174**, 47-53. http://dx.doi.org/10.1016/j.jhazmat.2009.09.014
- [19] Yadamari, T., Yakkala, K., Battala, G. and Gurijala, R.N. (2011) Biosorption of Malathion from Aqueous Solutions

Using Herbal Leaves Powder. *American Journal of Analytical Chemistry*, **2**, 37-45. <u>http://dx.doi.org/10.4236/ajac.2011.228122</u>

- [20] Mathew, S.B., Pillai, A.K. and Gupta, V.K. (2007) A Rapid Spectrophotometric Assay of Some Organo Phosphorus Pesticide Residues in Vegetable Samples. *Spectrochimica Acta Part A*, 67, 1430-1432. <u>http://dx.doi.org/10.1016/j.saa.2006.11.020</u>
- [21] Verma, A., Chakraborty, S. and Basu, J.K. (2006) Adsorption Study of Hexavalent Chromium Using Tamarind Hull-Based Adsorbents, *Separation and Purification Technology*, **50**, 336-341. <u>http://dx.doi.org/10.1016/j.seppur.2005.12.007</u>