Removal of Cadmium Ions from Industrial Wastewater Using Iraqi Ceratophyllum Demersum

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ABSTRACT
A new simple method was developed for the removal of cadmium ions from wastewater by using natural and modified dried leaves of (ceratophyllum demersum). This plant is an Iraqi spices grew on the shores of Iraqi rivers. Optimal conditions were obtained (pH was 6, weight of adsorbent was 1.5g, particle size was 300µm, temperature was 30°C, contact time was 60 minute and concentration of cadmium ions was 10 mg/L). These parameters were applied on spiked samples (50 gm./L) and proved to be efficient (95% removal for natural and 98% for sodium hydroxide treated modified). A batch sorption isotherm showed that Temkin model was dominant for natural ceratophyllum demersum but Langmuir model for modified was the dominant. The thermodynamic parameters were given and showed that $\Delta H^\circ$ was endothermic-positive value, $\Delta G^\circ$ was found (a spontaneous process-negative value) and $\Delta S^\circ$ was found positive value- increase of disorder of the process. FTIR was used to identify the activity of adsorption process by knowing of active sites on the surface of adsorbent.

INTRODUCTION
Cadmium is one of toxic heavy metal that discharges from industrial activity, considered as pollution metal ion, which can cause serious damage to the kidneys and liver [1]. Cadmium ion has been found as a human carcinogen [2]. The maximum permissible limits for cadmium in drinking water were 3 -10μg/L (WHO) [3]. Cadmium is released to the environment by different activities, such as electroplating, pigments, plastic, battery and zinc refining industries [4,6]. In order to remove cadmium from polluted wastewater different physical and chemical methods were used [7]. Those methods included; precipitation [8], cementation [9], membrane separation technique [10], ion exchange technique [11], solvent extraction technique [12] and adsorption [13]. Conventional methods have been found with limited application due to poor efficiency, sensitive operating, conditions and high cost of their disposal. Adsorption was also found powerful technique for removal of cadmium [14]. New adsorbents were found successful for removal cadmium and were improved performance of application [15]. Agricultural wastes have been extensively used for wastewater effluent [16,17]. The mechanism of adsorption was attributed to functional groups present in biomass molecules such as: carbonyl, phenol, amino, carboxyl groups, alcohols, amido, ester and other groups [18]. These groups may bind with heavy metals to form complexes [19]. Many
adsorbents were reported as bioadsorbents which were obtained from agricultural materials; These materials such as: saw dust [20], barks [21,22], stems [23,24], shells [25], peels [26,27], husk [28,29], bran [30,31] and leaves [32,33]. Despite the large number of bioadsorbents, there are still other herbs that have not been investigated such as Iraqi natural Ceratophyllum Demersum (NCD) and modified Ceratophyllum Demersum (MCD). This paper is an attempt for study of parameters to develop and new method for removal of Cd (II) from wastewater.

**MATERIALS AND METHODS**

**Chemical and instrumentation;**

**Chemicals:**

Stock solution: stock solution of cadmium (1000 mg/L) was prepared by dissolving (2.74 gm.) of analr (99.9%) (Cd (NO3)2.4H2O) (Obtained from Fluka) in 1liter of distilled-deionized water. The resulting solution was diluted to 100 mg/l and standardized against 0.1N EDTA to obtain the exact concentration of cadmium ion. Other chemicals are 0.1 M HCl and NaOH, both solutions were standardized before use. All measurements were triplicate. Blank values were considered and subtracted from all measurements.

Natural Ceratophyllum Demersum (NCD) (dried leaves): the NCD plants were collected from Al-Kufa River, Najaf, Iraq on October 2011. Then washed with tap water, Then the product was dried at 80 C° for 36 h and broken into many pieces into different particle size (300,500 and 700 µm) using clean mortar and pestle. Finally the dried plants stored in clean plastic envelope.

Modified Ceratophyllum Demersum leaves (MCD): add 300 mL of NaOH (0.1 M) to 30g of natural ceratophyllum demersum. The mixture was heated to 120 C° for 30 min and stirred occasionally. Cool, then separate the plant powder by filtration, and then washed with distilled water until the washing was free of color and the final pH of effluent was 7. The residue was dried at 50C°, overnight to avoid thermal deactivation of the adsorbent surface [34].

**Instrumentations:**

All the following instruments were calibrated by using standard solutions or reference material to obtain the satisfaction:

1- Atomic absorption spectrophotometer used was Shimadzu AA-6200.
2- FT-IR spectrophotometer – Shimadzu 6000.
3- pH meter was Research pH meter Radiometer, Copenhagen, Denmark.
4- Shaker was BS-11 digital, JEIO TECH, Korea.

**Procedures:**
1- Preparation of natural ceratophyllum demersum; weigh 50gm of (NCD) and place in small beaker and washed with deionized water and then crushed into many pieces using mortar and pestle ( particle sizes were 300, 500, and 700um).

2- Preparation of modified ceratophyllum demersum ; weigh 30 gm of (NCD) plant and place in small beaker. Heat to 120 c° ,and thoroughly add 300 ml of NaOH (0.1M), then the final solution was placed in shaker water bath for 30 min. Cool and filter , then washed with distill-deionized water, dry overnight at 50C°. The material was finally ready for use.

3-Prepartion of spiked wastewater; Prepare series of diluted cadmium solutions (10-50mg/L) from stock solution .all measurements of cadmium before and after adsorption were measured by atomic absorption spectrophotometer (shemadzu AA 6200).

4-Batch adsorption procedures; to measure the adsorption of cadmium ion on (Ceratophyllum demersum) different weights of adsorbents were used at different concentration of metal ion (10-50 mg/L). All parameters were kept constant at optimum values. Measure concentration of cadmium ion before and after adsorption by flame atomic absorption.

RESULTS AND DISCUSSION

Characterization of adsorbents
In order to evaluate the adsorption properties of ceratophyllum demersum. FTIR was used to obtain spectra as shown in (Fig 1). This figure gave vibration absorption bands which were identified; 3412 cm$^{-1}$ for (-OH) group, 2926 cm$^{-1}$ for alkyl group (-CH$_2$-). The bands at 1660 and 1095 cm$^{-1}$ were considered indicator of the presence of (c=c) and (c-o-c) respectively [35].

Optimization of adsorption process; In order to obtain maximum removal of cadmium ions from waste water conditions have to be found , these are ,contact time ,pH , weight of adsorbent , concentration of cadmium , particle size and temperature. The following are procedures for these studies:

1- Effect of contact time; The following parameters are fixed as follows (pH at 6, cadmium concentration at 50mg/L, weight of natural and modified plant at 1 gm at 50ml of metal ion solution and temperature at 30°C). The only variable in this optimization was contact time. Use different times (30, 60, 90, and 120 min) carry out batch adsorption of each solution and results are given in Fig. 2. It is shown that optimal time is 120 min for both, but (MCD) is slightly higher than
(NCD) in removal of cadmium ions; and these results are similar to efficiency of plant used before [36, 37].

2- Effect of pH; in order to optimize the pH, all the parameters were fixed (amount of both adsorbents were 1gm, concentration of cadmium was 50mg/L., time of adsorption was 1hour.). But pH was varied from 2 to 8 (pH was adjusted by using buffer solution). Results are given in fig 3. pH was optimum at 6 for both (NCD) and (MCD). At acidic pH the adsorbent surface will be converted to carboxylate and phenolate which give active site on the surface of adsorbent, at alkaline medium, hydrogen ions removed by hydroxide ion, and therefore adsorption decrease [38].

3- Effect of weight of adsorbent; to observe the highest amounts of adsorbent that give optimum adsorption at fixed concentration of cadmium, temperature and time of adsorption. Variable amounts of (NCD) and (MCD) (1, 2, 3, 4, and 5gm) at 50 ml of metal ion solution were added independently to the reaction mixture and carry out batch adsorption, finally cadmium was measured before and after adsorption. Results are given in fig 4. Optimum adsorbent was found 1.5gm/50ml for (NCD) and 1gm/50ml for (MCD).

4- Effect of concentration of cadmium ions; using optimum adsorbent amount, pH, temperature, time of adsorption and all these parameter were fixed to measure the efficiency of cadmium removal from wastewater. Different concentration (10, 20, 30, 40, and 50 mg/L) were prepared and the adsorption process was carried out and results are given in fig 5. Optimum concentration was 10mg/L for (NCD), while 10-20 mg/L for (MCD). At initial concentration the ratio of metal to adsorbent was reached maximum at 10mg/L and concentration of metal ions above the normal value did not increase because all sites on the surface were occupied [39].

5- Effect of particle size; particle size was considered important factor because it is related to surface area of adsorbent, therefore it has been studied. Fixing pH, time of adsorption, temperature, weight of adsorbent, and initial concentration, but varying particle size (300-750 µm), then complete adsorption batch process and measure cadmium ion concentration before and after adsorption. Results are given in fig 6. Optimum particle size was found 300 for both (NCD) and (MCD). Increase of surface area accompanied with decrease particle size but increase particle size more than 300µm will not added more active sites,
because a metal ion will be saturated and adsorption will be decrease due to desorption of cadmium [40].

6- Effect of temperature; the efficiency of adsorption of cadmium was affected by change of temperature, therefore the effect of temperature from 20 to 50°C was obtained by fixing of all parameters except temperature ,and batch adsorption process was completed . results were given in fig 7. Optimum removal efficiency was 95% for natural and 98% for modified at 50°C. Heating the dried plant above 50°C resulted penetrating cadmium ion to the surface and produce swelling [41].

Adsorption models
Adsorption process is considered important for removal of cadmium ions, therefore batch adsorption process was carried out to study distribution of metal ion between the liquid phase and the solid adsorbent. The adsorption equilibrium can be expressed by one model or many other models following isotherm pattern [42].Three different common models of isotherm were studied (Langmuir, Freundlich and Temkin isotherms). R² values and slope both measured and found to be related to Temkin isotherm model for NCD and Langmuir model for MCD. Fig.8 and fig.9 gave linear plot, which suggested that adsorption was Temkin isotherm for natural and Langmuir isotherm for MCD respectively [43].

Thermodynamic Studies:
Adsorption process was found useful to calculate thermodynamic parameters such as change in free energy ∆G°, enthalpy ∆H° and entropy ∆S°. Using the following equations;

\[ K = \frac{(Q_e \times W)}{(C_e \times V)} \]  
\[ \Delta G^\circ = -RT \ln K \]  
\[ \log K = (\Delta S^\circ/2.303R) - (\Delta H^\circ/2.303RT) \]  
\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]

As K is the equilibrium constant, Q_e is adsorption efficiency (mg/g), C_e is final concentration of metal ions (mg/L), W is weight of adsorbent (g), V is the volume of solution (litter), T is the absolute temperature (K°) and R is the gas constant [44, 45].

Van’t Hoff equation was used to estimate the values of ∆H° and ∆S° from the intercept, and slope of the plot which was ln K vs. 1/T (fig. 10). Table (1) showed the thermodynamic parameters values for the adsorption processes. From this table, adsorption process was found endothermic (ΔH° was positive), reaction was spontaneous (ΔG° was negative), and solid solution interface was random because ΔS° was
increased. The change in adsorption enthalpy was measured and found -20 to 40 KJ.mol⁻¹, compared to chemisorption which was -400 and -80 KJ.mol⁻¹ [46]. values of ΔH° physisorption was found the dominant mechanism.

**Application**

From experimental results, it was clear that cadmium ions can be removed from industrial waste using NCD and MCD at optimum conditions. Three samples were taken from three different Iraqi factories: Babylon batteries factory, Kufa cement factory and Babylon tiers factory. From results, it was found that NCD and MCD gave high efficiency (100%) for the removal of Cd ions at optimum conditions. Results were given as in table 2. Therefore this method was recommended for industrial application.

**Conclusions:**

NCD and MCD Were found successful for removal of cadmium ions from waste water (95.3% for NCD and 98.8% for MCD). And this percentage considered higher than other adsorbents, therefore this method is recommended as efficient method for treatment of waste water polluted with cadmium in spiked and real sample. The Temkin adsorption isotherm model was better used to represent the experimental data on NCD and Langmuir model for MCD. MCD was found slightly higher than natural.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature K°</th>
<th>ΔH° KJ.mole⁻¹</th>
<th>ΔG° KJ.mole⁻¹</th>
<th>ΔS° KJ.mole⁻¹.K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Ceratophyllum demersum</td>
<td>303</td>
<td>19.496</td>
<td>-7684.296</td>
<td>25.425</td>
</tr>
<tr>
<td>Modified Ceratophyllum demersum</td>
<td>303</td>
<td>31.177</td>
<td>-7695.481</td>
<td>25.50</td>
</tr>
</tbody>
</table>

Table -2: practical applications of removal of cadmium ions from Iraqi factories wastewater by using of natural and artificial Iraqi Ceratophyllum Demersum as adsorbents.

<table>
<thead>
<tr>
<th>Factory</th>
<th>Optimum conditions</th>
<th>Conc. before treatment (mg/L)</th>
<th>Conc. after treatment (mg/L)</th>
<th>R%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Babylon batteries</td>
<td>pH 6 Contact time (min.)</td>
<td>30</td>
<td>1.5</td>
<td>300</td>
</tr>
<tr>
<td>Kufa cement</td>
<td>pH 6 Contact time (min.)</td>
<td>30</td>
<td>1.5</td>
<td>300</td>
</tr>
<tr>
<td>Babylon tiers</td>
<td>pH 6 Contact time (min.)</td>
<td>30</td>
<td>1.5</td>
<td>300</td>
</tr>
</tbody>
</table>
Fig.-1: FTIR for Ceratophyllum Demersum

Fig.-2: effect of time on adsorption process at pH=2.3, temperature=30 c°, initial concentration=50 mg/L and adsorbent weight=1gm
fig.-3: effect of pH on adsorption process at time=60 min, temperature=30°C, initial conc.=50mg/L and adsorbent weight=1 gm.

Fig.-4: effect of loading weight on adsorption process at time=60min, pH=2.3, temperature=30°C, and initial conc.=50mg/L.
Fig. 5: Effect of initial concentration on adsorption process at time = 60 min, temp. = 30°C, weight of adsorbent = 1 gm/50 ml of solution and pH = 2.3

Fig. 6: Effect of particle size on adsorption process at pH = 2.3, time = 60 min, initial conc. = 50 mg/L, temperature = 30°C and weight of adsorbent = 1 gm
Fig.-7: effect of temperature on adsorption process at pH=2.3, time=60min, initial conc.=50mg/L and adsorbent weight=1gm

Fig.-8: the Temkin isotherm model for natural Ceratophyllum Demersum (NCD) as adsorbent
Fig. 9: the Langmuir isotherm for modified ceratophyllum demersum (MCD) as adsorbent.

Fig. 10: plot of Van’t Hoff equation for adsorption process with NCD and MCD as adsorbents

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