Removal of Cadmium from Aqueous Solutions Using Low Cost Sorbents

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The pollution of water with heavy metals is a highly important environmental problem, first of all because of the propagation of the pollution and second, because of its unfavorable consequences on the aquatic life and different uses of water. Various agricultural waste could be potentially used as low cost adsorbents for biosorptive removal of heavy metal ions from aqueous solutions. This study presents the results of the adsorption process of Cd$^{2+}$ on some adsorbents: clinoptillolite (CLP), carrot residue (CR) and green tea waste (TW). Removal efficiencies greater than 95% were achieved for clinoptillolite (CLP) and tea waste (TW), whereas carrot residue (CR) showed removal percentages between 80-90%. The suitability of the Freundlich, Langmuir and Temkin adsorption models to the equilibrium data were investigated for each heavy metal - adsorbent system. The results showed that the equilibrium data for these systems fitted the Freundlich model best within the concentration range studied, except for tea waste, for which the Temkin isotherm provides a better fit for the available data. The study points to the potential of use of low cost materials as effective sorbents for the removal of Cd$^{2+}$ from aqueous solution.

Keywords: adsorption, heavy metals, cadmium, isotherms

In the past several decades, extensive research has been conducted to develop innovative and promising adsorbent materials to deal with problem of industrial effluents contamination [1]. The pollution with heavy metals is a highly important environmental problem, first of all because of its propagation and second, because of unfavorable consequences on the aquatic life and different uses of water [1,2]. The concentration of these pollutants is accentuated through bioaccumulation via food chain in living tissues, causing various physiological disorders, as: damage to blood composition, lungs, kidneys, liver and other vital organs. The industrial utilization of cadmium has increased, because of the extensive use in pesticides, pigments and dyes, textile operations, refining, cadmium-nickel batteries, cadmium-silver batteries, phosphate fertilizers or electroplating [2]. Cadmium is an irritant, thiol depletion inducer and is classified as a human carcinogen [3].

Removal of heavy metal ions from wastewater in an effective manner has become an important issue in many countries. Conventional methods has been extensively applied for the removal of heavy metal ions from industrial wastewater: chemical precipitation, chemical oxidation, chemical reduction, ion exchange, filtration, electrochemical treatment and membrane advanced systems. [2,3] All these procedures have some limitations in application: high-energy requirements, an incomplete removal and production of toxic sludge or waste products that also require further treatment [2,4,5].

Adsorption is an efficient method for the removal of tracer contaminants from water. Activated carbon produced by carbonizing different organic materials is widely used as metal ions adsorbent. Activated carbon also requires complexing agents to improve its removal performance for inorganic matters. In spite of its prolific use, the high cost of the activation process limits the use of this sorbent in wastewater treatment [4].

Various functionalized materials, like mesoporous and microporous silicas, clays or organic polymers have been developed for removal of heavy metals from wastewater [5-7]. Zeolites are crystalline microporous aluminosilicates with ion exchange properties, suitable for a wide range of applications: in catalysis, separation of liquid and gaseous mixtures and in wastewater treatment [7-9]. Clinoptilolite, occurring in the zeolitic volcanic tuffs, is a hydrated alumina-silicate member of the heulandite group; it is widespread in our country and in the whole world [7].

There are many recent studies, focused to test and develop various low cost and widely available adsorbents to remove the heavy metal ions. A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry [2]. Waste biomass, industrial waste and mineral waste have been investigated by many researchers and biomass has shown better adsorption properties [2,10]. Adsorbents of agricultural origin possess different polymeric groups: cellulose, hemicellulose, pectin, lignin and proteins as active centers for metal uptake. Various waste materials: almond shell residues, walnut shells, coffee ground, olive stones, pomegranate peel, rice husk are low cost and non-conventional adsorbent for biosorptive removal of heavy metal ions from aqueous solutions [4, 5, 11-16]. Adsorption of heavy metal ions occurs as a result of physicochemical interaction, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface [2]. Various functional groups are involved, such as carboxyl, amine and amides. Ion exchange mechanism considers the model of metal binding and proton releasing reaction [2,17]. The biosorption efficiency by waste biomass depend on physical and surface properties of adsorbent, metal ion properties and operating conditions [18,19]. Therefore, the specific effect of adsorbent properties and operating conditions depends on the biomass-metal ion system [10, 20-22].

Considering these aspects, our study presents the results of the adsorption process of Cd$^{2+}$ on some adsorbents: clinoptilolite, carrot residue and green tea waste. The cation exchange and/or adsorptive properties of tea and...
carrot residue can be attributed to the presence of carboxylic, phenolic and other functional groups, which exist in caffeine either the cellulosic matrix or in the materials associated with cellulose such as hemicellulose, lignin, peptides [4,10].

Carrot residue and tea waste were investigated as low cost non-conventional adsorbents for the sorption of cadmium ions from the contaminated water under various experimental conditions: pH, adsorbent amount and initial metal concentration. The equilibrium data were examined using Langmuir, Freundlich and Temkin isotherm models. The adsorption capacity can be described by equilibrium sorption isotherms, which are characterized by definite constants whose values express the surface properties and the affinity of an adsorbent support [15].

**Experimental part**

**Materials and methods**

**Adsorbents**

In the present study, clinoptilolite (CLP) and some waste materials: carrot residues (CR) and green tea waste (TW) were used as adsorbents for the removal of cadmium from synthetic wastewater.

The *clinoptilolite (CLP)* sample was conditioned as in our previous study [7], with the following composition: [Ca_{1.24}Na_{1.84}K_{1.76}Mg_{0.2}] Al_{3}Si_{30}O_{72}(H_{2}O)_{21.32}]. The clinoptilolite sample was ground and sieved and the particles that passed through a 0.05 mm sieve were used for this study. The selected fraction was washed three times with distilled water, to remove any soluble salts and dried at 40°C in the oven, for 24 h.

Carrot residue (CR) was oven dried for 24 h, at 80°C, then ground and sieved, to get homogenous particle sized material. In order to eliminate soluble components such as tannin, coloring substances and resins reducing sugars, the carrot residue was washed with 0.5 M HCl and distilled deionized water, until a constant pH was achieved.

Surface impurities, soluble and coloured components from green tea waste (TW) were removed by washing with boiling distilled water. This was repeated until the water was colourless. The tea residues were then washed with distilled water and dried in oven for 12h at 105°C. The dried tea waste was ground and sieved and the fine powder retained was then used for the sorption studies.

**Synthetic wastewater preparation**

Synthetic wastewater solutions were prepared by dissolving analytical grade Cd(NO₃)₂, 4H₂O in distilled water, to obtain 1000 mg of Cd²⁺/L stock solution. The standard solutions of Cd²⁺ (20-80 mg/L) were prepared by serial dilution of the stock solution.

**Equipment**

In order to evidence the surface structure of clinoptilolite, morphological analysis was performed by scanning electron microscopy (SEM), using a FEI Quanta 200 field emission SEM.

X-ray diffraction (XRD) analysis was carried out with a BRUKER D8 ADVANCE X-ray diffractometer, equipped with a software DIFFRACplus XRD Commender (Bruker AXS).

A Varian AA 240 FS type atomic absorption spectrometer with an air-acetylene flame and a hollow cathode lamp for Cd was used for metal ion analysis. The absorbance of the samples was read in triplicate.

For pH adjustment throughout the experiment, solutions of HCl and NaOH 0.1 M were used as necessary. A pH-meter CYBERSCAN PCD 6500 with a combined glass electrode was used for pH measurement. Final pH of the sorbate-sorbent adsorption system was measured at sorption equilibrium.

**Equilibrium studies**

The adsorption capacity qₑ (mg/g) after equilibrium was calculated by mass balance relationship equation as follows [5]:

\[ qₑ = \frac{(C₀-Cₑ)}{W} \]

where C₀ (mg/L) is the initial metal concentration, Cₑ (mg/L) is the metal concentration at equilibrium, W is the mass of adsorbent (g).

The percent removal of heavy metal from solution (R%) was calculated by the following equation: [4]

\[ R\% = \frac{C₀-Cₑ}{C₀} \times 100 \]

The Freundlich model can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer sorption. The Freundlich model is described as follow (Freundlich, 1906): [15-17]

\[ q = K_f \cdot C^{1/n} \]

where C is the equilibrium concentration (mg L⁻¹ or mmol L⁻¹), K_f (mg g⁻¹) and n (value between 0 and 1) are Freundlich equilibrium constants; 1/n is an empirical parameter relating the adsorption intensity, which varies with the heterogeneity of the material.

The Langmuir model assumes that adsorption occurs at specific homogeneous sites on the adsorbent and is used in many monolayer adsorption processes. This model is described as follow (Langmuir, 1918): [15,17]

\[ q = \frac{q_m \cdot K_L \cdot C}{1 + K_L \cdot C} \]

where C is the equilibrium concentration (mg L⁻¹ or mmol L⁻¹), K_L (mg g⁻¹) and qₑ is the amount of heavy metal ions required to form a monolayer (mg g⁻¹), C is the equilibrium concentration (mg L⁻¹ or mmol L⁻¹), qₑ is the amount of metal ions adsorbed per specific amount of adsorbent (mg g⁻¹), C is the equilibrium concentration (mg L⁻¹ or mmol L⁻¹), Kₑ (mg g⁻¹) and n (value between 0 and 1) are Freundlich equilibrium constants; 1/n is an empirical parameter relating the adsorption intensity, which varies with the heterogeneity of the material.

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The crystal structure analysis of clinoptilolite (CLP) particles was performed, using X-ray diffraction and the obtained diffractogram is represented in figure 2. The main characteristic peaks from figure 2 shows that clinoptillolite is the main mineral from zeolitic sample which was analyzed. The specific diffraction peaks show the presence of other phases like albite, biotite, quartz and cristoballite.

X-ray diffractometry (XRD) analysis indicated also the presence of the clinoptillolite well-crystallized, which can be observed from the intensity of the diffraction lines.

**Effect of operating parameters**

**Effect of initial metal concentration**

The initial concentration of heavy metal is one of the parameters which have a pronounced effect on the removal of adsorbate species from aqueous solution. (fig.3)

The effect of the initial cadmium concentration on the adsorption rate was investigated in the range 20–80mg/L, adsorbent dose of 0.5 g/100mL, at 24h contact time and at pH 6.

The influence of initial heavy metal concentration could be explained as follow: at low concentrations, metals are adsorbed by specific sites; increasing concentrations, the specific sites are saturated and the exchange sites are filled. [4] With increasing initial concentrations of cadmium, the percent metal removal (R%) decreases. Also, the figure 3 indicates that CLP and TW had better percentage removal than CR.

**Effect of adsorbent dosage**

Adsorbent amount is also an important parameter in the determination of adsorption capacity. As the adsorbent dosage increases, the adsorbent sites available for metal ions are also increased and consequently better adsorption takes place [19-24].

In our study, the adsorbent dosages were varied from 0.10 to 1.00 g / 100mL, at 24h contact time and at pH 6. The effect of the adsorbent dose on the removal cadmium ions is shown in figure 4. The dosage increase of CLP from 0.10 to 1.00 g enhances Cd^{2+} uptake from 69.9 % to 99.5 %; in case of TW, the percent of metal removal...
increased from 42.9% to 92.79% and for CR from 66.1% to 80.45%.

**Effect of pH**

The pH value of the aqueous solution is an important variable which controls the adsorption and plays an important role in the precipitation and adsorption mechanisms.[18] The equilibrium established in solution between metal ions and the sorbent may be described as following[21]:

\[ M^{n+} + B H_0 \rightleftharpoons BM + n H^+ \]  \( (9) \)

where M represents the metal, n its charge and B the active sorption sites of the adsorbent.[21] According to eq. (9), pH influences metal ion sorption due to the competition between the metal and H\(^+\) ions for active sorption sites; pH affects both the solubility of metal ions and the ionization states of functional groups, such as carboxyl and hydroxyl [16, 17].

The effect of pH on Cd\(^{2+}\) removal was studied by performing equilibrium adsorption experiments at different pH values (3, 6 and 9). The results are illustrated in figure 5. As can be observed, Cd\(^{2+}\) removal increases with increasing the initial pH of the solution. Very little sorption was observed at the initial pH 3. The low metal sorption at this pH may be explained on the basis of active sites protonation, resulting in H\(^+\) and Cd\(^{2+}\) competition to occupy the binding sites [18-20]. At lower pH, the concentration of H\(^+\) ion is high, causing a competition for vacant adsorbent site between the H\(^+\) ion and heavy metal cations. Therefore, at low pH the heavy metals removal efficiency is low. On the other hand, the value of pH also affects the ionic state of the functional groups presented in some biosorbents and involved in the metal binding [20,21]. In our case, at low pH, carboxylic and amino functional groups of carrot residue are protonated, thus active sites are less available for metal ion binding and cadmium ions are less absorbed. The optimum pH value for the removal of Cd\(^{2+}\) was found to be 6, using CLP, TW and CR as adsorbent materials. (fig.5) The best adsorption results at pH value 6 could be also attributed to the cellulose component of the CR substrates, where site binding component might be occurring. The slightly decrease in Cd\(^{2+}\) ion removal capacity at pH >6.0 may be caused by hydrolysis accompanying by precipitation of metal hydroxide. This effect weakens electrostatic interactions and decreases adsorption.

From the point of view of an industrial application, this may provide an important advantage, since working at extreme pH would be avoided.

**Adsorption isotherm models for cadmium**

Equilibrium adsorption data were used to determine the maximum capacities of the adsorbents during the experiment.

The linearized Langmuir, Freundlich and Temkin isotherms of Cd\(^{2+}\) are shown in figure 6-8.

The adsorption intensities and adsorption capacities (\(q_m\)) were determined from the intercept and slope data, respectively, for each adsorbent.

A comparison of the three isotherms reveals that the correlation coefficients for the Freundlich isotherm were higher and showed better fits for all adsorbents, except for tea waste (TW); for this adsorbent, the Temkin isotherm provides a better fit for the available data. Table 1 shows that CLP and TW exhibited greater adsorption capacities than those of CR adsorbent.

The Freundlich model can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer sorption. [1] The result in table 1 show that the value of n' Freundlich parameter is greater than 1, which indicates that the adsorption of cadmium on all materials (CLP, CR and TW) is favourable. A value of n Freundlich parameter greater than unity suggests also stronger adsorption intensity.

The Temkin isotherm model considers that the heat of the adsorption of all the molecules would decrease linearly with coverage due to adsorbate/adsorbate interactions [23-26]. The Temkin parameter \(b_T\), (KJ/mol) related to heat of sorption, is less than 8 for all adsorbents, that indicate weak
interaction between metal and sorbent. The process, as indicated by $b_T$ parameter, can be expressed as physiosorption.

**Conclusions**

The present study shows that clinoptilolite (CLP) and some waste materials: carrot residues (CR) and green tea waste (TW) are effective adsorbents for the removal of cadmium ions from aqueous solutions.

Removal efficiencies greater than 95% were achieved for CLP and TW, whereas CR showed removal percentages between 80-90%.

The equilibrium adsorption data was described in this study by Freundlich, Langmuir and Temkin isotherm. The correlation coefficients for the Freundlich isotherm were higher and showed better fits for all adsorbents, except for tea waste (TW); for this adsorbent, the Temkin isotherm provides a better fit for the available data.

The values of $\Delta G^c < +10 \text{ KJ/mol}$ suggested the feasibility of the present adsorption process and the spontaneous nature of the adsorption of $\text{Cd}^{2+}$ onto CLP, TW and CR.

Due to their low cost and a good adsorption capacity, the two solid wastes studied in this work (carrot residue and green tea waste) are promising biosorbent materials. Because tea consumption is worldwide and tea wastes can easily be acquired, it is speculated that tea waste has a high potential for practical applications in treating wastewater. Carrot residue is also an environmentally friendly, biodegradable, low cost and potential biosorbent for the removal of heavy metals.

The present study can conclude that instead of many chemicals, non-hazardous waste materials can be used as heavy metal removers from wastewaters and industrial effluents to overcome water pollution.

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