



*Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary*

Cd²⁺ REMOVAL FROM AQUEOUS SOLUTIONS USING AN ORGANO-INORGANIC IMMOBILIZED ADSORBENT

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This paper presents the potential use of the organic-inorganic immobilized mixtures green algae *Scenedesmus armatus* – bentonite (hybrid adsorbent) for removal of Cd²⁺ from aqueous solution. Experimental parameters affecting the adsorption process such as biomass dosage, Cd²⁺ initial concentration, pH and temperature were studied. An increase of biomass dosage and heavy metal concentration led to an increase of adsorption capacity values, while low pH values and increased temperatures led to a decrease of adsorption capacity values. Langmuir and Freundlich isotherm models describe well the adsorption process, and kinetic of the process was best described by the pseudo-second-order model.

INTRODUCTION

The release of different pollutants into environment has increased noticeable as a result of industrialization, and thereby lowered the quality of the environment to alarming level.¹ Between these pollutants, heavy metals are important from environmental point of view due to their non-biodegradability, with cadmium ions being one of the most poisonous, whose toxicity is attributed in part to its ability to accumulate in tissues.² There are some reports on the destruction of chloroplast by heavy metal ions at higher concentration.³ Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects.⁴ There are many processes that can be used for removal of metals from

wastewaters including precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange and adsorption.⁵ However, technical or economic factors limit sometimes the feasibility of such processes.

Biosorption, which uses the ability of biological materials, is a relatively new technology to remove heavy metals from industrial wastewater. The major advantages of the biosorption technology are its effectiveness in reducing the concentration of heavy metals from aqueous solutions to very low levels and the use of inexpensive adsorbent materials such as naturally abundant algae, by-products of fermentation industries,⁶ wood wastes⁷ or microorganisms.⁸

Among the biological materials, marine algae otherwise known as seaweeds have been reported to have high metal binding capacities due to the

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presence of polysaccharides, proteins or lipid on the cell wall surface, containing functional groups such as amino, carboxyl, hydroxyl and sulphate, which can act as binding sites for metals.⁹ Some investigations have been carried out for the removal of Cd²⁺ using algae^{6,10-13} and bentonite.^{2,14,15} However, according to author's survey, there is no study on the adsorption of Cd²⁺ using the mixture of *Scenedesmus armatus* and bentonite. In addition, these new material was chosen as adsorbent in this study due to the fact that it is natural, renewable and thus, low cost material.

The present work focused on the potential use of the organic-inorganic immobilized mixtures green algae *Scenedesmus armatus* (SA) – bentonite (B) for removal of Cd²⁺ from synthetic aqueous solutions. Experimental parameters affecting the adsorption process such as biomass dosage, Cd²⁺ initial concentration, pH and temperature were studied. Also equilibrium and kinetics models were considered to characterize the adsorption process.

RESULTS AND DISCUSSION

Effects of biomass dosage, Cd²⁺ concentration, pH and temperature

The effect of biomass dosage on the adsorption of Cd²⁺ ion was studied using different biomass suspension volumes in 1-3 mL range (1 g B as a blank sample and 1 g B in mixture with 1, 2 or 3 mL green algae – the samples were labeled as follows: B, SA1, SA2, SA3). Adsorption capacity values obtained in this case are presented in Fig. 1a. From Fig. 1a it can be observed, that an increase of the biomass dosage led to a slight improvement of the adsorption process. The highest Q_e value was obtained when 3 mL green algae suspension was used (SA3, 2.5907 g adsorbent), therefore all the experiments were further conducted using this dosage. An increase of

Cd²⁺ concentration from 7 to 43 mg L⁻¹ Cd²⁺ led to an increase of Q_e values, Fig. 1b, suggesting that the organic-inorganic adsorbent system has the ability to retain high quantities of heavy metal ions. A closer inspection of the adsorption process allows us to conclude that the equilibrium was reached in 150 minutes in all cases.

Algae biomasses have high content of carboxyl groups from mannuronic and guluronic acids on the cell polysaccharides which suggests that the adsorption could be affected by changes in the solution pH.^{16,17} The effect of pH on Cd²⁺ adsorption was studied on the SA3 adsorbent mixture, by changing pH values in 2-9 pH units range. The obtained results are presented in Fig. 2a. Hybrid adsorbent has weak acidic groups (-COOH and -OH), which in low pH environments (2-4 pH) are less ionized, therefore a competition between proton and heavy metal ions for the ionic exchange sites exists. Consequently, the amount of Cd²⁺ retained on the hybrid material is smallest at 2 pH. In contrast, when the pH value increased, competition between the positive ions is less intense and the adsorption of the Cd²⁺ was reached maximum around pH 5.5. Decrease in adsorption at higher pH values is probably due to the formation of soluble hydroxylated complexes of Cd²⁺ and their competition with the active sites. Consequently, the retention of cadmium ions would decrease. Towards more basic environment (9 pH) Cd²⁺ precipitation could also contribute to the decrease of heavy metal ions concentration in the aqueous solution. The influence of the temperature on the adsorption capacity of Cd²⁺ on organo-inorganic adsorbent is presented in Fig. 2b. From this figure it can be observed, that an increase in temperature led to a decrease of the adsorption capacity, suggesting that the adsorption process is exothermic (the calculated value of the enthalpy was -10.8 kJ mol⁻¹).

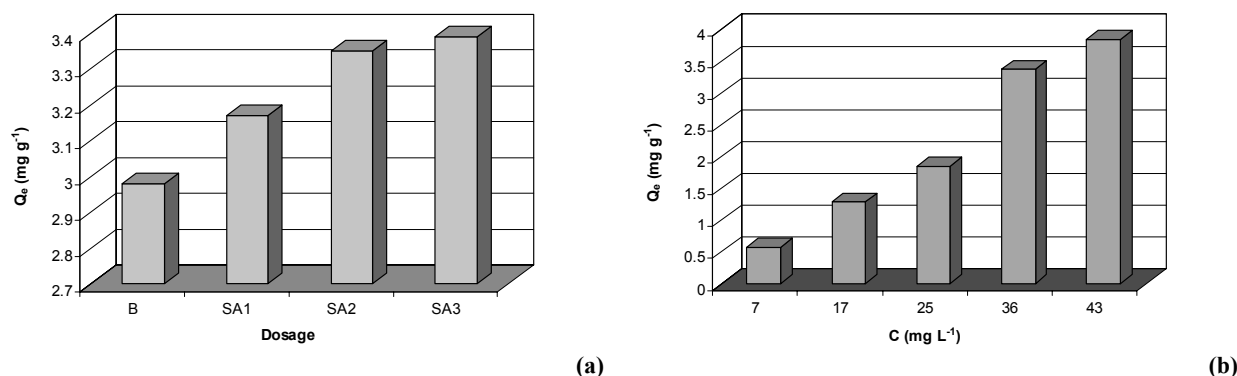


Fig. 1 – Effect of biomass dosage (a) and initial Cd²⁺ concentration (b) over the adsorption capacity values; 100 mL solution, 2.5868-2.5907 g, pH 5.5, 298 K, 750 rpm, 36 mg L⁻¹ Cd²⁺ (a) and 7-45 mg L⁻¹ Cd²⁺ (b).

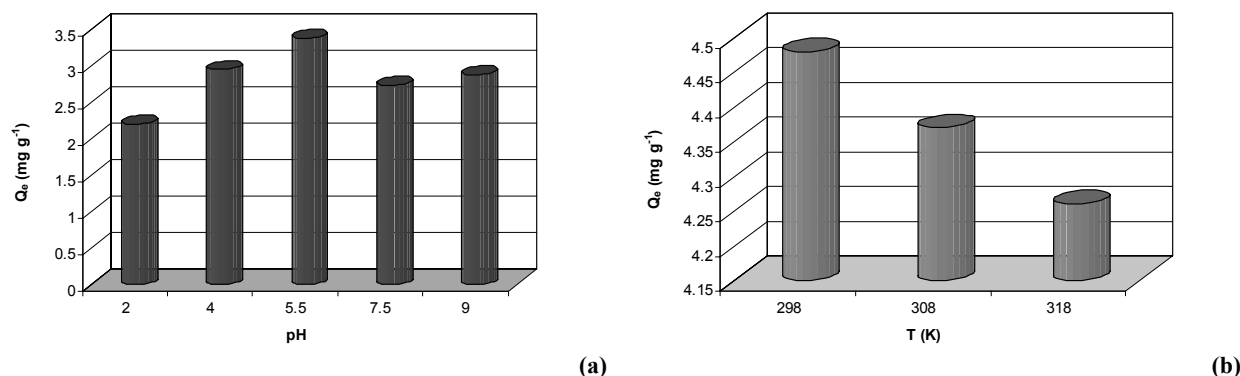


Fig. 2 – Effect of pH (a) and temperature (b) over the adsorption capacity values; 100 mL solution, 2.5907 g (SA3 sample), 750 rpm, 36 mg L⁻¹ Cd²⁺, 298 K (a) and 5.5 pH (b).

The Langmuir and Freundlich isotherms used to describe the equilibrium of the adsorption process, presented linear plots, Fig. 3, with R^2 values > 0.96, Table 1, and yielding good fits with the experimental data. Values of Langmuir coefficient, Table 1, show that organo-inorganic immobilized adsorbent has good potential for Cd²⁺ removal. The high value of Q_{max} indicated the fact that the considered adsorbent has ability to retain cadmium ions from more concentrated solutions with good efficiencies. Also, value of Freundlich constant n , indicated that the considered adsorbent has good potential (high adsorption intensity) for Cd²⁺ ions adsorption. The obtained results suggested that the experimental data fitted better on Langmuir isotherm model.

Correlation coefficients obtained when the pseudo-first-order kinetic model was applied to Cd²⁺

adsorption on the organo-inorganic adsorbent, ranging between 0.8395 and 0.9231, led us to the conclusion that the considered adsorption process cannot be classified as first-order, Fig. 4a, Table 2. Also values of calculated adsorption capacities show great differences by comparison to experimental values. Application of the pseudo-second-order kinetic model for Cd²⁺ adsorption on organo-inorganic adsorbent is presented in Fig. 4b and Table 2. The similarity between calculated and experimental adsorption capacities and R^2 values indicated that the pseudo-second-order kinetic model describes well the removal of Cd²⁺ ions on the considered organo-inorganic adsorbent, suggesting that the considered process takes place as chemisorption.

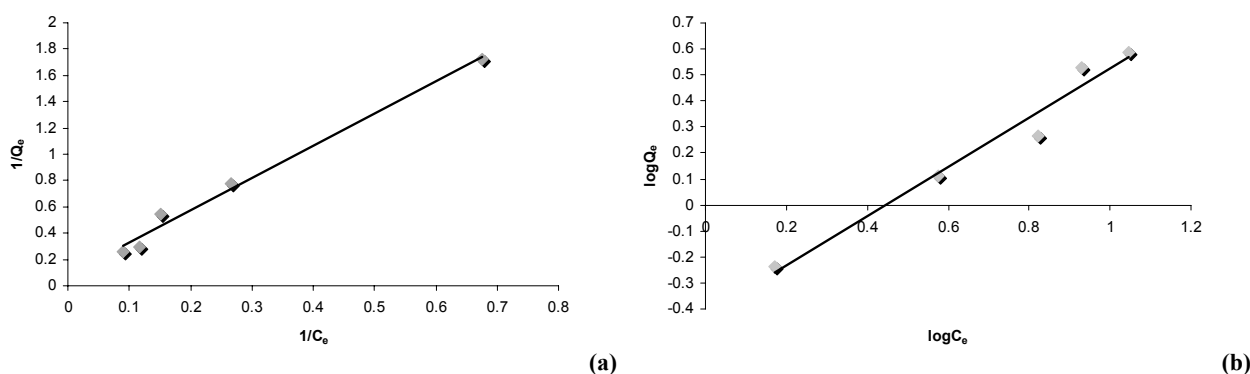


Fig. 3 – Langmuir (a) and Freundlich (b) plots for Cd²⁺ adsorption on the hybrid adsorbent; 100 mL solution, 2.5907 g (SA3 sample), $C_i = 7-45$ mg L⁻¹ Cd²⁺, 298 K, 5.5 pH, 750 rpm.

Table 1

Langmuir and Freundlich coefficients for Cd²⁺ adsorption on the hybrid adsorbent; 100 mL solution, 2.5907 g (SA3 sample), $C_i = 7-45$ mg L⁻¹ Cd²⁺, 298 K, 5.5 pH, 750 rpm

Langmuir coefficients			Freundlich coefficients		
K_L (L mg ⁻¹)	Q_{max} (mg g ⁻¹)	R^2	n	K_f (mg ^(1-1/n) L ^{1/n} g ⁻¹)	R^2
0.03	12.69	0.9880	1.06	0.38	0.9684

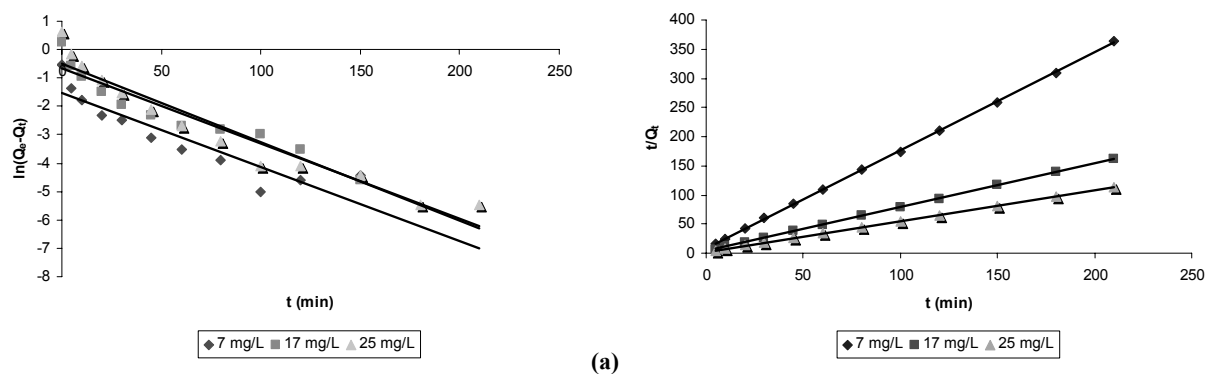


Fig. 4 – Plots of the pseudo-first-order (a) and pseudo-second-order kinetic (b) models for Cd^{2+} adsorption on the hybrid adsorbent; 100 mL solution, 2.5907 g (SA3 sample), $C_i = 7\text{-}25 \text{ mg L}^{-1} \text{ Cd}^{2+}$, 298 K, 5.5 pH, 750 rpm

Table 2

Kinetic parameters for Cd^{2+} adsorption on the hybrid adsorbent; 100 mL solution, 2.5907 g (SA3 sample), $C_i = 7\text{-}25 \text{ mg L}^{-1} \text{ Cd}^{2+}$, 298 K, 5.5 pH, 750 rpm

C (mg L^{-1})	$Q_{e, \text{exp}}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		$Q_{e, \text{calc}}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$Q_{e, \text{calc}}$ (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	R^2
7	0.58	4.63	2.62×10^{-2}	0.8395	0.59	0.36	0.9999
17	1.29	1.94	2.64×10^{-2}	0.9063	1.33	0.17	0.9999
25	1.85	1.63	2.77×10^{-2}	0.9231	1.89	0.12	0.9999

EXPERIMENTAL

The considered organo-inorganic adsorbent system was prepared by immobilization of *Scenedesmus armatus* (SA) green algae (private laboratory, Hungary) and Valea Chioarului bentonite, B, (Maramures County, Romania). The unicellular green alga, *Scenedesmus armatus* IMK-203 strain, was used as received, suspension at the exponential growth phase (10 mL containing 0.0131 g dried algae). Bentonite was used as micronized powder ($< 0.045 \text{ mm}$) without other treatments (a full characterization of the bentonite sample is presented elsewhere).¹⁸ In order to obtain the organo-inorganic adsorbent (hybrid adsorbent) the encapsulation procedure with calcium alginate was used. Thus, various volumes of green algae suspension (1, 2, 3 mL) and 1 g of bentonite were introduced under stirring in 50 mL distilled water. This suspension was next blended with a mixture formed from 1 g Na-alginate and 1 mL ethanol. The mixture was then dropped with a syringe (1.2 mm diameter needle) into a 0.2 M CaCl_2 solution. During this process, alginate-algae-bentonite drops were gelled into beads with a diameter of $4.0 \pm 0.2 \text{ mm}$. The Ca-alginate immobilized adsorbent beads were stored in 0.2 M CaCl_2 solution at 4°C for 1 hour to cure and to form the cross-linking bonds. The beads were rinsed with distilled water, removing excess of calcium ions and stored at 277 K prior to use.¹⁵ For the adsorption study we used synthetic monocomponent solutions containing Cd^{2+} (7-45 mg L^{-1}), prepared by dilution from a 1000 mg L^{-1} stock solution obtained from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ salt, analytically pure reagent.

Effects of biomass dosage (1 g B as a blank sample, 1g B + 1, 2, 3 mL SA suspension), Cd^{2+} concentration (7-45 mg L^{-1}), pH (2-9) and temperature (298, 308, 318 K) on Cd^{2+} adsorption were considered. The final mass of the adsorbent was determined after the fresh beads were dried in air for 24 hours and then in a desiccator until constant mass, and

varies from 2.5868 (B) to 2.5907 (SA3) grams. Cadmium ions in solution were determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia). Adsorption process was carried out in a batch reactor under magnetic stirring (750 rpm), using the fresh beads obtained as described before and 100 mL Cd^{2+} solution. In order to determine the concentration of Cd^{2+} , aqueous solution samples were taken at previous established time intervals until equilibrium was reached. The initial pH was adjusted from the initial 5.5 towards acidic and basic environment, using 0.1 M HCl and 0.1 M NaOH solutions, respectively.

The quality of the considered material as an adsorbent in the heavy metal ion removal process was followed using adsorption capacity (amount of pollutant adsorbed at equilibrium, Q_e , mg g^{-1}) values, calculated according to the equation:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{w} \cdot \frac{1}{1000} \quad (1)$$

where, C_0 and C_e are the initial and equilibrium cadmium concentration, respectively ($\text{mg L}^{-1} \text{ Cd}^{2+}$), $V = 100 \text{ mL}$, and w is the quantity of the dry adsorbent (g).

The calculated values of the adsorption capacity should be considered with respect to the precision of the determination method used (relative standard deviation 0.45%).

Adsorption equilibrium can be described by a variety number of isotherm models. These models are all describing the solute-adsorbent interactions. In this work the most applied ones, the Langmuir (linear form equation 2) and the Freundlich models (linear form equation 3), were considered.^{19,20}

$$\frac{1}{Q_e} = \frac{1}{Q_{\text{max}} \cdot K_L} \cdot \frac{1}{C_e} + \frac{1}{Q_{\text{max}}} \quad (2)$$

where, Q_e is the solid-phase adsorbate concentration at equilibrium (mg g^{-1}), Q_{max} is the maximum adsorption capacity corresponding to the monolayer adsorption capacity (mg g^{-1}), C_e is the concentration of pollutant in solution at equilibrium (mg L^{-1}), and K_L is a constant related to the strength of adsorbent-adsorbate affinity (L mg^{-1}).

$$\log Q_e = \log K_f + \frac{1}{n} \cdot \log C_e \quad (3)$$

where, K_f ($\text{mg}^{(1-1/n)} \text{L}^{1/n} \text{g}^{-1}$) is related to adsorption capacity, and n is related to intensity of adsorption.

Langmuir model assumes a monolayer adsorption, with no lateral interaction between the adsorbed molecules on specific sites. Freundlich model assumes heterogeneous adsorption due to the diversity of adsorption sites or diverse nature of the adsorbed metal ions, free or hydrolyzed species or other adsorbents.²¹

In order to establish the adsorption kinetic model, pseudo-first- (Lagergren, linear form equation 4) and pseudo-second-order (Ho, linear form equation 5) models were considered.²²⁻²⁴

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (4)$$

where, Q_e and Q_t are the amounts of pollutant adsorbed (mg g^{-1}) at equilibrium and time t , respectively, and k_1 is the first-order adsorption rate constant (min^{-1}).

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

where, Q_e and Q_t are the amounts of pollutant adsorbed (mg g^{-1}) at equilibrium and time t , respectively, and k_2 is the second-order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

Adsorption enthalpy was calculated using the equilibrium constant, K_d (Q_e/C_e) and van't Hoff equation.²⁵

CONCLUSIONS

This paper presents the potential use of the organic-inorganic immobilized mixtures green algae *Scenedesmus armatus* – bentonite for removal of Cd²⁺ from aqueous solution. In order to obtain the organo-inorganic adsorbent the encapsulation procedure with calcium alginate was used. Experimental parameters affecting the adsorption process such as biomass dosage, Cd²⁺ initial concentration, pH and temperature were studied. An increase of adsorbent dosage and heavy metal concentration led to an increase of adsorption capacity values, while low pH values and increased temperatures led to a decrease of adsorption capacity values. The obtained results suggested that the experimental data fitted better on Langmuir isotherm model and kinetic of the process was best described by the pseudo-second-order model.

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