

## Removal of cadmium(II) from aqueous solution by adsorption onto modified algae and ash

Maria Harja\*, Gabriela Buema\*, Laura Bulgariu\*, Dumitru Bulgariu\*\*\*\*\*,†, Daniel Mircea Sutiman\*, and Gabriela Ciobanu\*

\*Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 Prof. dr. docent D. Mangeron Street, 700050, Iasi, Romania

\*\*Faculty of Geography and Geology, "Alexandru Ioan Cuza" University of Iasi, 20A, Carol I Street, 700506, Iasi, Romania

\*\*\*Filial of Iasi, Collective of Geography, Romanian Academy, 18A, Carol I Street, 700506, Iasi, Romania

(Received 6 June 2014 • accepted 23 January 2015)

**Abstract**—Pollution with cadmium ions has serious negative consequences on human health and environment. Adsorption of low-cost materials represents a viable option for the removal of cadmium ions from aqueous media. In this study are comparatively discussed the adsorption behaviour of cadmium(II) on two low-cost materials, one of biologic nature (marine algae) and other of inorganic nature (ash), after their treatment with alkaline solution. The influence of contact time and initial cadmium ions concentration was studied in batch system, for each type of adsorbent. In optimum experimental conditions (solution pH of 5.0; adsorbent dose of  $8 \text{ g L}^{-1}$ ) and an initial cadmium concentration of  $360 \text{ mg L}^{-1}$ , the obtained uptake capacities reach to  $34.15 \text{ mg g}^{-1}$  for the modified algae and to  $43.12 \text{ mg g}^{-1}$  for the modified ash, respectively. The uptake data were analyzed using two isotherm models (Langmuir and Freundlich) and the models' parameters were evaluated. The results indicate that the Langmuir model provides the best correlation of experimental data for both adsorbents, and the maximum adsorption capacities were  $41.8 \text{ mg g}^{-1}$  for modified algae and  $48.0 \text{ mg g}^{-1}$  for modified ash, respectively. The kinetics of the cadmium uptake was modelled using the pseudo-first order, pseudo-second order and intra-particle diffusion model equations. It was shown that the pseudo-second order kinetic equation could best describe the adsorption kinetics of cadmium ions, whatever the nature of adsorbent.

Keywords: Cadmium, Adsorption, Modified Algae, Modified Ash

### INTRODUCTION

Pollution with heavy metals has become a serious problem for human health and for environment. Heavy metals are hazardous pollutants which can modify the physical and chemical properties of any ecosystem. They are not biodegradable and tend to accumulate in organisms causing various diseases [1].

Toxicological studies show that one of the most toxic heavy metals is cadmium. Initially, its use was in electroplating and for nickel-cadmium batteries manufacturing. Cadmium is also used in the obtaining of paint pigments and polyvinyl chloride plastics. The majority of cadmium present in the atmosphere is the result of human activities, especially smelting of non-ferrous metal ores, fossil fuel combustion and municipal waste incineration [2,3]. Occupational exposure of workers in the non-ferrous smelting industry can be significant. Application of municipal sewage sludge to agricultural soil can also be a significant source of cadmium. Cadmium toxicity causes disorders such as heart disease, cancer and diabetes [3-5]. Cadmium poisoning may also result in lung cancer, anaemia, skin, pulmonary edema, bone diseases, brain damage and trachea-bronchitis [6,7]. The maximum contaminant level (MCL) standard

established by USEPA for cadmium is  $0.01 \text{ mg L}^{-1}$  [8].

The most widely employed methods for removing of heavy metals from wastewaters include flocculation, coagulation, chemical precipitation, electrochemical techniques, ion exchange, membrane-related processes, etc. [9-21]. But most of these methods are expensive, not eco-friendly and inefficient, specially when the heavy metals are present in low concentrations ( $1\text{-}100 \text{ mg dissolved metal L}^{-1}$ ), and may also generate secondary wastes, which are difficult to treat.

In regards to its simplicity, adsorption using low cost adsorbents has gained important credibility, because of the good efficiency, minimization of secondary (chemical or biological) wastes and low cost of these materials [9-13]. In general, there are three main steps involved in pollutant adsorption onto solid adsorbent: (1) the transport of the pollutant from the bulk solution to the adsorbent surface; (2) adsorption on the particle surface; and (3) transport within the adsorbent particle.

Due to the increasing of environmental pollution, currently there is a growing demand to get a large number of novel low cost adsorbents with high efficiency for wastewater treatment [8,14,15]. Thus, non-conventional and low-cost adsorbents, such as natural materials or agricultural and industrial wastes, can be efficiently employed for the adsorptive removal of metal ions from industrial and municipal wastewaters [16].

Recently, ash and modified ashes obtained by different methods were frequently used as adsorbents for wastewater treatment.

†To whom correspondence should be addressed.

E-mail: dbulgariu@yahoo.com

Copyright by The Korean Institute of Chemical Engineers.

However, the specialized literature recommends the use of modified ash for removal of heavy metals due to its higher capacity uptake [8,13,14,17-22]. Modified ash can be realized by especially three methods: direct hydrothermal activation, diffusion and ultrasound. All the methodologies proposed are based on the dissolution of Al-Si-bearing ash phases with NaOH or KOH solutions, at different temperatures and the subsequent precipitation of new material [20].

On the other hand, the literature shows that the algae can be used as a viable option for treated waters containing heavy metals, due to the presence of polysaccharides, proteins and lipids on the cell wall surface [4,23-25]. Algae could be especially useful, as they are fairly abundant in many regions of the world, have a great metal recovery potential and large surface areas [24,25-28]. Also, the alkaline treatment of algae biomass has as an effect a considerable increase of the adsorption capacity of this material for metal ions from aqueous solution [29].

In this study, the modified algae and modified ash (by alkaline treatment) were used as low-cost adsorbents for the removal of cadmium ions from aqueous solution. The ability of these materials for the removal of cadmium(II) ions was studied as a function of initial cadmium ions concentration and contact time, by batch technique. The equilibrium and kinetics data were modelled using two isotherm models (Langmuir and Freundlich) and three kinetics models (pseudo-first order, pseudo-second order and intra-particle diffusion models), in order to understand the adsorption mechanism of cadmium ions onto considered low-cost adsorbents. A detailed characterization of both adsorbents was also presented.

## MATERIALS AND METHODS

### 1. Adsorbents

The ash used for the experimental work was obtained from a thermoelectric power plant in the area of Iasi (Romania). The marine green alga (*Ulva lactuca* sp.) was collected from the Romanian coast of the Black Sea, in August 2011. Both materials were first washed several times with distilled water to remove impurities, and dried in air at 60-65 °C for 24 hours. After drying, the biomass was crushed and sieved to a granulation of 1.0-1.5 mm.

The chemical treatment was done by mixing dried materials (algae biomass and ash) with 1 mol/L NaOH solution, in a solid/liquid ratio of 1 : 3. In case of ash adsorbent the treatment was performed for 72 h at 150 °C, followed by cooling and crystallization for 18 h at room temperature, while in case of algae biomass the chemical treatment was done at room temperature (25±0.5°), for 24 h. After treatment, both modified adsorbents were separated by filtration, washed with distilled water until getting a neutral pH, dried in air and then mortared.

The modified materials were characterized by different techniques such as SEM-EDS, BET surface area, FT-IR and XRD. The characterizations were performed with the following equipment: SEM/EDX with a QUANTA 3D - AL99/D8229 for morphological and elementary analysis; BET surface area - Quantachrome Autosorb 1-MP; FT-IR with Thermo Scientific "Nicolet" 6700; XRD with diffractometer X'PERT PRO MRD.

### 2. Adsorption Experiments

Cadmium ions solutions of initial concentration of 23-360 mg

L<sup>-1</sup> were prepared by Cd(NO<sub>3</sub>)<sub>2</sub> (Sigma Aldrich product) dissolving in 1,000 mL volumetric flask with distilled water. The pH of the solutions was adjusted to 5 using a 0.1 N HCl solution. For the experiments 40 mg of the individual adsorbents were contacted for 24 hours with 50 mL of the cadmium solutions at ambient temperature (25 °C). These values of solution pH and adsorbents dose have been previously established as the optimal for unmodified materials [22,28], and for rigor were maintained the same.

After the separation of the solid from the liquid phase by centrifugation, the equilibrium pH of the supernatant solutions was measured with Hanna Instruments pH meter, and the cadmium concentration was determined spectrophotometrically using xylenol-orange (C<sub>31</sub>H<sub>28</sub>N<sub>2</sub>Na<sub>4</sub>O<sub>13</sub>S) at 575 nm wave length, with spectrophotometer Buck Scientific.

Kinetic data were obtained at 298 K, and modelled using the pseudo-first-order model, pseudo-second-order model and intra-particle diffusion model rate equations. For the kinetics measurements 2 g of the modified ash and the modified algae adsorbents were contacted with 250 mL of cadmium solution of concentration 69.17 mg L<sup>-1</sup> and pH 5. At predetermined time intervals 10 mL samples were withdrawn and their cadmium concentration was determined. The kinetics model parameters were then determined by linear regression. The obtained data were used to calculate the cadmium uptake (in mg g<sup>-1</sup>), according with the relation:

$$q = \frac{(C_0 - C) \cdot V}{m} \quad (1)$$

where: q is the uptake (mg g<sup>-1</sup>), C<sub>0</sub> and C are the liquid phase concentration of cadmium at initial and equilibrium (mg L<sup>-1</sup>), V is the volume (L) and m is the amount of adsorbent (g).

## RESULTS AND DISCUSSION

### 1. Characterization of Adsorbents

The scanning electron micrographs (SEM) of the modified adsorbents are shown in Fig. 1. In case of modified ash the particles have different shapes, intersecting and interconnecting semi-disc to each other, frequently being presented in the form of spherical agglomerates on the parent ash surface. Also, in case of modified algae, the SEM images indicate that the adsorbent surface is wrinkled, porous and has cracks, which will facilitate the binding of cadmium ions.

The BET surface area for modified ash was 121 m<sup>2</sup> g<sup>-1</sup>, and V<sub>pores</sub> 0.246 cm<sup>3</sup> g<sup>-1</sup>, for modified algae 42 m<sup>2</sup> g<sup>-1</sup> and 0.091 cm<sup>3</sup> g<sup>-1</sup>. The surface area of adsorbent synthesized by the conventional hydrothermal treatment using ash sample is nearly 17 times higher than unmodified ash [22], and for algae surface area increases about 4.5 times. The elementary compositions (EDAX) of low cost adsorbents, presented in Table 1, show that these materials are mainly composed of the elements O, Si, Al, Fe, Ca, Mg, K, Na and Ti.

XRS analysis was performed only for modified ash adsorbent, because the algae biomass has not a crystalline structure and cannot be investigated by this technique. Fig. 2 shows X-ray diffraction patterns of modified ash.

From the Fig. 2 the modified ash shows the most intense peaks at 15 °, respectively, 25 °, corresponding to faujasite (Fau) and

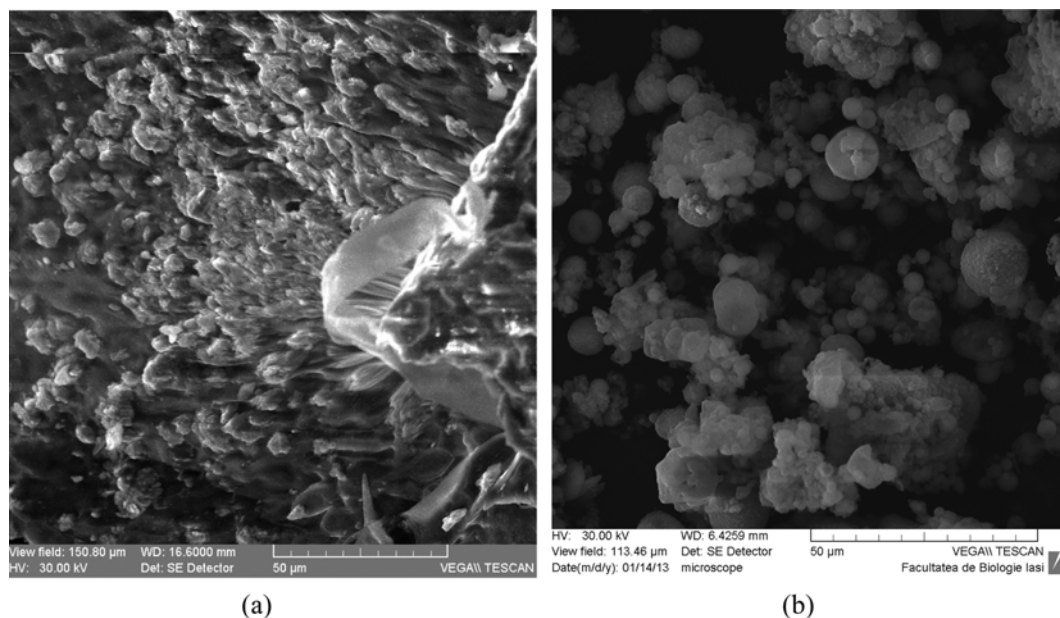


Fig. 1. SEM image for low cost adsorbents ((a) modified algae; (b) modified ash).

Table 1. Chemical composition of modified adsorbents, %

| Element | Modified algae | Modified ash |
|---------|----------------|--------------|
| C       | 24.12          | 2.45         |
| O       | 46.78          | 38.15        |
| Na      | 8.52           | 11.18        |
| Mg      | 5.74           | 0.66         |
| Al      | 0.35           | 17.50        |
| Si      | 2.09           | 24.35        |
| K       | 0.11           | 0.16         |
| Ca      | 1.40           | 2.67         |
| Ti      | -              | 0.71         |
| Fe      | 0.23           | 2.63         |

Linde L zeolites. Widened and less intense peaks are obtained between 30-70  $2\theta$  lengths. Peaks at values lower than 15  $2\theta$  overlap and due to were very hard to identify.

The quartz and mullite compounds could not be completely dissolved during the hydrothermal treatment under mentioned conditions, and remained in the samples after the chemical modification. Sodalite has high stability with variations in temperature and can occur during the synthesis of adsorbents using ash as the raw material crystallized between 353.15 K and 413.15 K [30,31]. Also, the material contains analcime (A), but it appears in small quantities.

FT-IR spectra for both adsorbents are illustrated in Fig. 3. The IR spectrum of ash shows the presence of absorption band at 458  $\text{cm}^{-1}$ , which can be attributed to the O-Si-O or Si-O-Si stretching vibrations. The bands from at 621  $\text{cm}^{-1}$  and 689  $\text{cm}^{-1}$  indicate the presence of quartz in the ash [32,33].

The sharp peak from 998  $\text{cm}^{-1}$  corresponds to the presence of Al atoms in the tetrahedral forms of silica frame work. The region from high wave numbers, 1,656  $\text{cm}^{-1}$ -3,440  $\text{cm}^{-1}$ , was generally

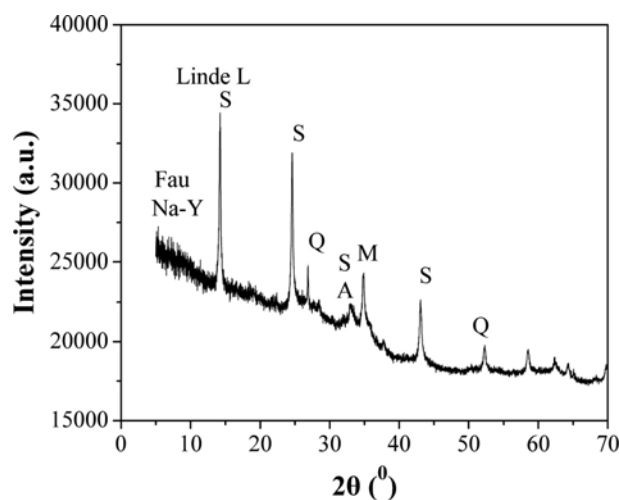


Fig. 2. X-ray diffraction patterns of modified ash (A: analcime; Fau: faujasite; M: mullite; Q: quartz; S: sodalite).

attributed to the O-H stretching of the intermolecular hydrogen bond or the O-H in the water molecular-OH [32]. It can be observed that the ash presented a peak at 1,493  $\text{cm}^{-1}$  corresponding to Na-Y zeolite, fact confirmed by XRD analysis, also. The bonds in the spectra at 3,440  $\text{cm}^{-1}$  suggest that the new substance loaded in the modified ash exists in the form of hydroxyl compound [34,35].

On the other hand, in case modified algae, several important peaks, corresponding to the essential functional groups of the algae cell wall, are observed. The broad and strong band from 3,441  $\text{cm}^{-1}$  is attributed to the overlapping of O-H and N-H stretching vibrations. Peak at 2,919  $\text{cm}^{-1}$  corresponds to carboxylic / phenolic vibrations. The peaks at 1,631  $\text{cm}^{-1}$  and 1,425  $\text{cm}^{-1}$  can be attributed to the HO<sup>-</sup> bonds of quinine, and the peak of 1,656  $\text{cm}^{-1}$  to the C=N and C=O stretching. The peak at 1,101  $\text{cm}^{-1}$  can be assigned to C-OH stretching vibrations, due to different functional groups on algae

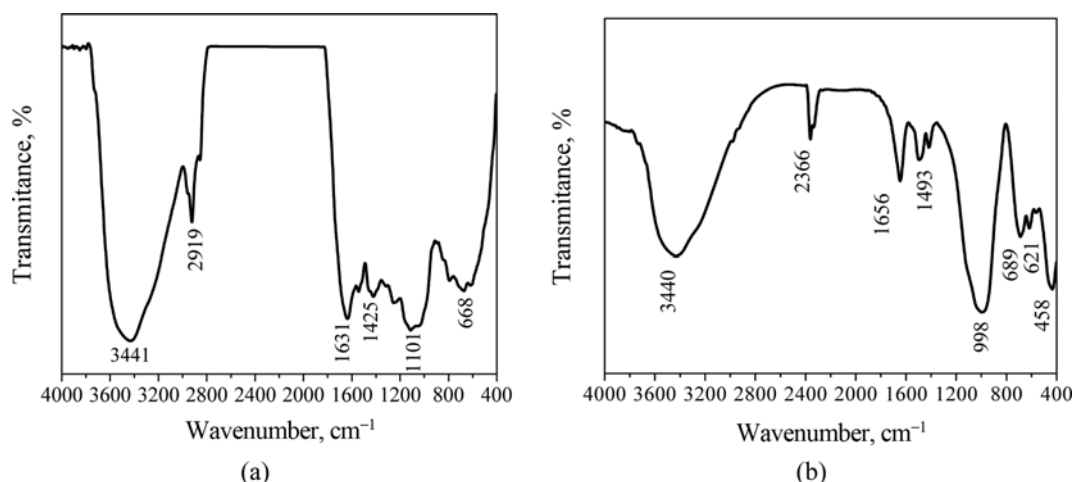


Fig. 3. FT-IR spectra of low cost adsorbents ((a) modified algae; (b) modified ash).

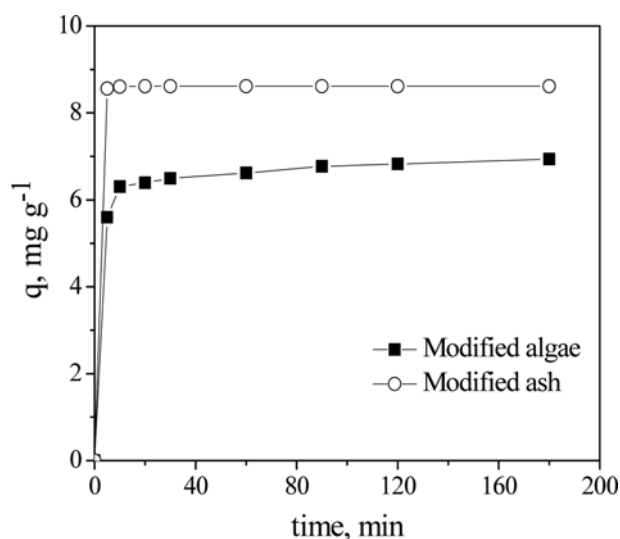


Fig. 4. Plot of the cadmium ions adsorbed onto modified algae and modified ash versus time.

cell. The band from  $668\text{ cm}^{-1}$  corresponds to the C-N-S shearing due to polypeptides structure of algae cells.

## 2. Adsorption Studies

### 2-1. Influence of the Contact Time and Type of Adsorbent

The influence of the contact time of removal process of  $\text{Cd}^{2+}$  by modified algae and modified ash was studied using a solution with initial cadmium concentration of  $69.17\text{ mg L}^{-1}$  and initial pH of 5, from 0 to 180 minutes (Fig. 4).

The experimental results presented in Fig. 4 show that by increasing contact time, the amount of metal ion retained per unit mass of the adsorbent increases. The adsorption process is very fast in the initial stage, during the first 30 minutes retaining over 80% of the total amount of  $\text{Cd}^{2+}$  in the case of modified algae, which corresponds to a capacity uptake of  $6.94\text{ mg g}^{-1}$ , and almost 99% of the total amount of  $\text{Cd}^{2+}$  for modified ash, which corresponds to a capacity uptake of  $8.62\text{ mg g}^{-1}$ . In the case of  $\text{Cd}^{2+}$  ions adsorption, a contact time of 120 minutes can be considered sufficient, in

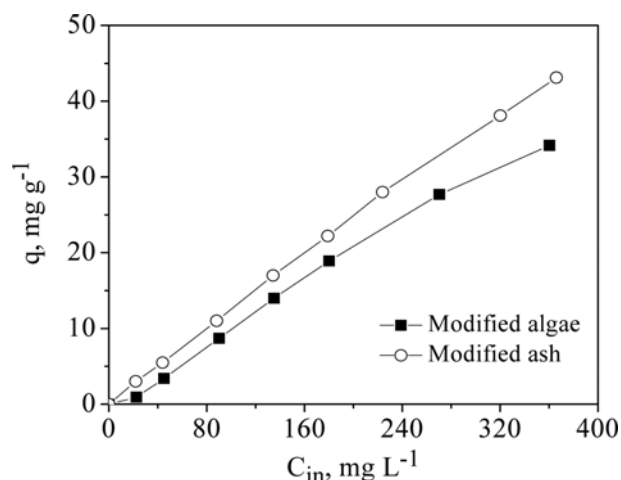


Fig. 5. Isotherms for the cadmium uptake from aqueous solutions of  $\text{pH}_{in}$  5.

order to achieve a state of equilibrium. According to the results presented in Fig. 4, at the initial concentration of cadmium ions of  $69.17\text{ mg L}^{-1}$ , both adsorbents showed ability to remove cadmium ions from aqueous solutions at initial pH of 5.

### 2-2. Influence of Initial Concentration

In Fig. 5 is illustrated the effect of metal concentration on the adsorption behavior of cadmium(II) on considered low cost adsorbents, in the range of metal concentration of  $23\text{--}360\text{ mg L}^{-1}$ . As already expected, with the increasing of initial concentration from  $22$  to  $360\text{ mg L}^{-1}$ , the adsorption capacity of cadmium ion increases.

This behavior can be explained by the strong attraction between the positive charge of the cadmium ions and the negative sites from the adsorbent materials. Thus, for an initial cadmium(II) concentration of  $360\text{ mg L}^{-1}$ , the obtained adsorption uptakes were  $34.15\text{ mg g}^{-1}$  for modified algae, and  $43\text{ mg g}^{-1}$  for modified ash, respectively. Also, in the case of modified ash the increase of pH can be observed, after the equilibrium was reached. This is most probably due to simultaneous retention of protons from aqueous solutions (Fig. 6).

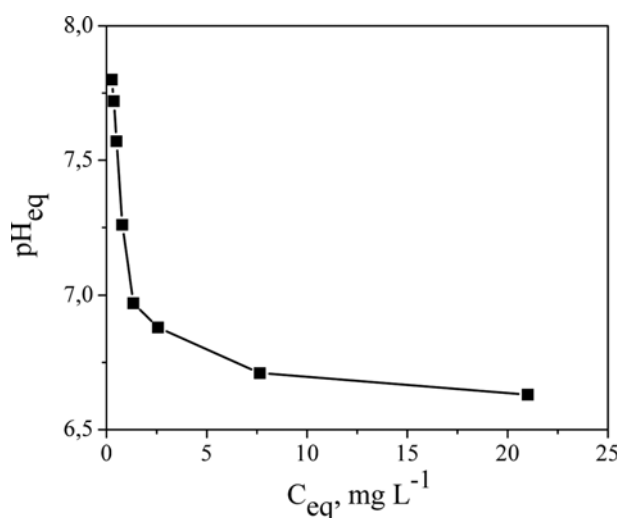


Fig. 6. Variation of the  $pH_{eq}$  as a function of  $C_{eq}$  for the interaction of modified ash with cadmium-containing aqueous solutions ( $pH_{in}$  5).

The pH values for the solutions after the adsorption processes were also measured, and the average values for modified ash were found to be between 6.63 and 7.80, respectively. These final pH values were lower than the precipitation pHs for  $Cd^{2+}$  (that occur at pH around 8.4), which means that cadmium remains as free ions, during of adsorption process.

The uptake capacities of adsorbents used in this study for Cd(II) adsorption were compared with those of others reported in the literature. The values presented in Table 2 were all expressed as monolayer adsorption capacity. From Table 2 the data obtained in present study are comparable with those obtained in other experimental investigations.

### 2-3. Adsorption Isotherm

Adsorption isotherm models are commonly used to describe a relationship between concentration of the metal ions in solution and the amount of metal ion adsorbed on adsorbent, when both the phases are at equilibrium. Such studies are useful for the evaluation of the characteristics and applicability of the adsorption process, and for the design of operational units.

In literature are presented various adsorption isotherms models. The Langmuir and Freundlich models are the most widely used isotherm models for the mathematical description of adsorption processes [40-43], whose mathematical equations are summarized in Table 3.

The Langmuir isotherm, suggesting that enthalpy of adsorption is independent of the amount adsorbed, while data-based Freundlich equation can be attained based on adsorption on heteroge-

Table 2. Comparison of the maximum adsorption capacities of different adsorbents for  $Cd^{2+}$  ions

| Adsorbent                               | Uptake, mg g <sup>-1</sup> | References |
|---|----------------------------|------------|
| Modified algae                          | 41.8                       | This study |
| Modified ash                            | 48.0                       | This study |
| Rice husk                               | 2.0                        | [36]       |
| Fly ash, treated                        | 14.33                      | [32]       |
| Na-P                                    | 38.55                      | [30]       |
| Na-S                                    | 29.76                      | [30]       |
| Unmodified ash                          | 0.08-0.29                  | [34]       |
| Algae, Nile water                       | 37.43                      | [36]       |
| Iron ore slime                          | 34.75                      | [1]        |
| Syzygium cumini leaf powder             | 34.54                      | [37]       |
| Mixed alginate/pectin gel beads         | 1.71-2.79                  | [20]       |
| ZFA                                     | 26.0                       | [38]       |
| Activated sludge                        | 9.6                        | [39]       |
| Dried sludge                            | 6.6                        | [39]       |
| Chorfa silt material (Mascara, Algeria) | 0.35                       | [39]       |

neous surface, which assumes a logarithmic decline in the enthalpy of adsorption as the fraction of occupied sites increases [40,41]. The Freundlich equation is strictly empirical and based upon adsorption on heterogeneous surface.

The adsorption equilibrium data for cadmium ions on modified algae and modified ash evaluated by the Langmuir and Freundlich equations are presented in Fig. 7. The isotherm parameters calculated from the intercepts and slopes of linear equations associated with each model are presented in Table 4.

According to the linear regression coefficients ( $R^2$ ) presented in Table 4, the experimental data for both adsorbents used in this study complied with the Langmuir models.

The fundamental characteristics and practicability of Langmuir isotherm regarding a dimensionless constant separation factor or equilibrium parameter  $R_L$ , are defined as [44]:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (2)$$

where  $K_L$  is the Langmuir constant and  $C_0$  is the initial concentration of Cd(II). The value of  $R_L$  indicates the type of isotherm; thus the adsorption process is reversible when  $R_L=0$ , favorable when  $0 < R_L < 1$ , linear when  $R_L=1$ , or unfavorable when  $R_L > 1$ . Values of  $R_L=0.13$  demonstrate that the uptake process of cadmium ions on studied materials is favorable.

### 2-4. The Kinetics of the Adsorption Process of $Cd^{2+}$

The study of adsorption kinetics helps us to find the solute uptake rates which clearly can be used to control the residence time of ad-

Table 3. Mathematical equations of Langmuir and Freundlich isotherm models

| Isotherm types | Equations   | Nomenclature  |
|----------------|---|---|
| Langmuir       | $q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$ | $C_e$ - is equilibrium solute concentration in solution, (mg/L); $q_e$ - equilibrium metal adsorption capacity, (mg/g); $q_{max}$ - maximum adsorption capacity (mg/g); $K_L$ - Langmuir constants, (L/g) |
| Freundlich     | $q_e = K_F \cdot C_e^{1/n}$                                   | $K_F$ - Freundlich constants, (L/g); $n$ - is a constant indicative of adsorption intensity   |

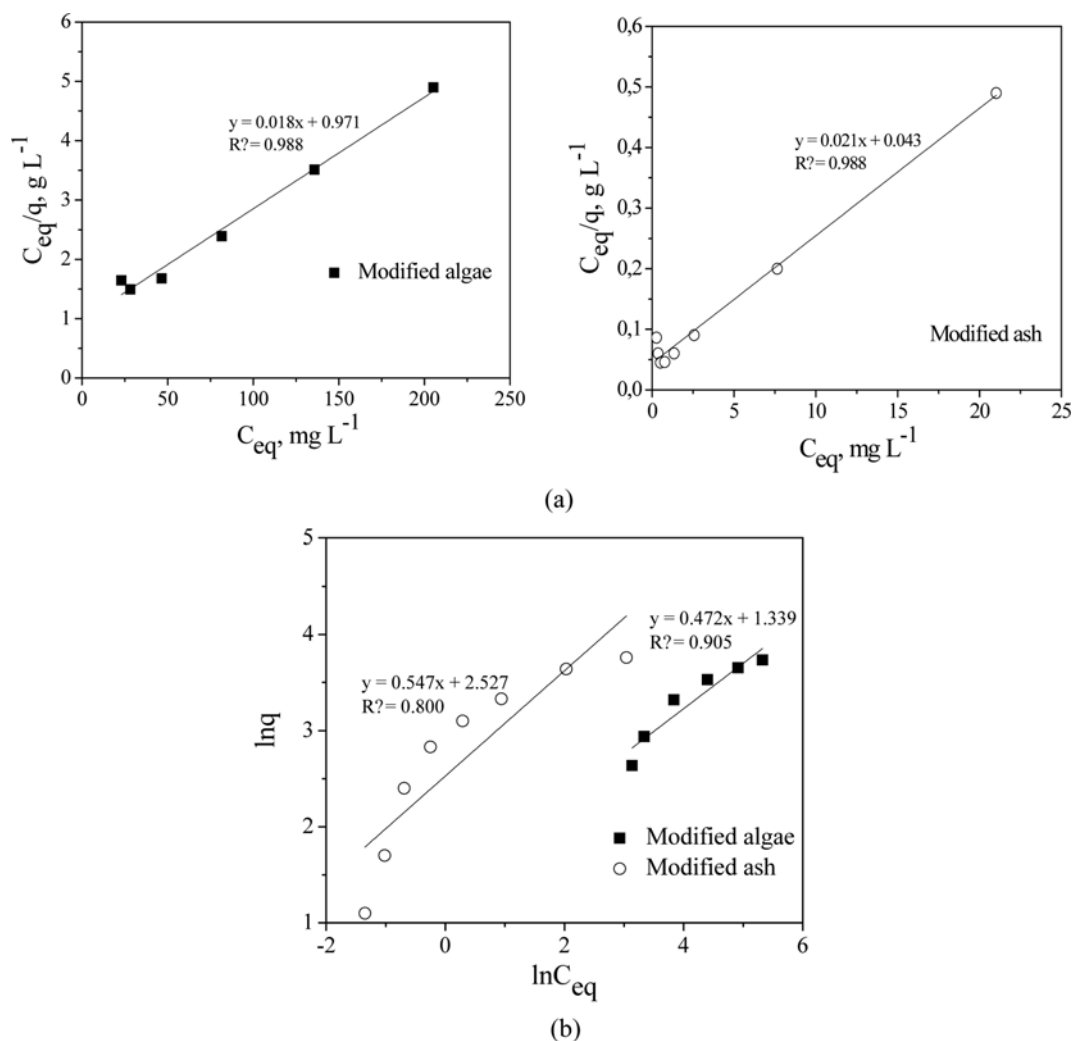


Fig. 7. Linear representations of Langmuir (a) and Freundlich (b) isotherm models for cadmium adsorption onto modified algae and modified ash.

Table 4. Values of the Langmuir and Freundlich parameters for considered low cost adsorbents

| Adsorbent      | Langmuir                     |                         |       | Freundlich   |      |       |
|----------------|------------------------------|-------------------------|-------|--|------|-------|
|                | $q_{max}$ mg g <sup>-1</sup> | $K_L$ L g <sup>-1</sup> | $R^2$ | $K_F$ (mg g <sup>-1</sup> )/(L mg <sup>-1</sup> ) <sup>n</sup> | 1/n  | $R^2$ |
| Modified algae | 41.8                         | 18                      | 0.988 | 3.81   | 2.12 | 0.905 |
| Modified ash   | 48.0                         | 21                      | 0.988 | 12.51  | 1.82 | 0.800 |

sorbate uptake at solid-solution interface including the diffusion process [45-48].

Three different kinetics models--pseudo-first order, pseudo-second order and intra-particle diffusion model--have been used to analyze the kinetics of adsorption process of cadmium ions onto the modified algae and modified ash. For the kinetic study pseudo-first-order model was used one in linearized form, plotted  $\log(q_e - q)$  against  $t$  (Fig. 8(a)). Pseudo-second-order model was done by plotting  $t/q$  against  $t$  (Fig. 8(b)), and intra-particle diffusion model verification  $q$  against  $t^{1/2}$  (Fig. 9).

To determine which of the considered kinetic models verify the experimental data, the linear equations obtained in each case, to-

gether with the values of correlations coefficients ( $R^2$ ), are illustrated in Figs. 8 and 9.

The pseudo-second order equation agrees very well with the experimental results (values  $R^2$  are the highest). This suggests that adsorption is a mechanism of pseudo-second-order, which means that the rate limiting step is the chemical interaction (involving electrostatic or covalent bonds) between Cd(II) ions from aqueous solution and functional groups from adsorbents surface. The pseudo-second-order equation fitted the adsorption data in a large quantity of literature reported, and indicates that the chemical adsorption process is predominant [18,29,49-51].

However, the experimental data indicate a limited contribution

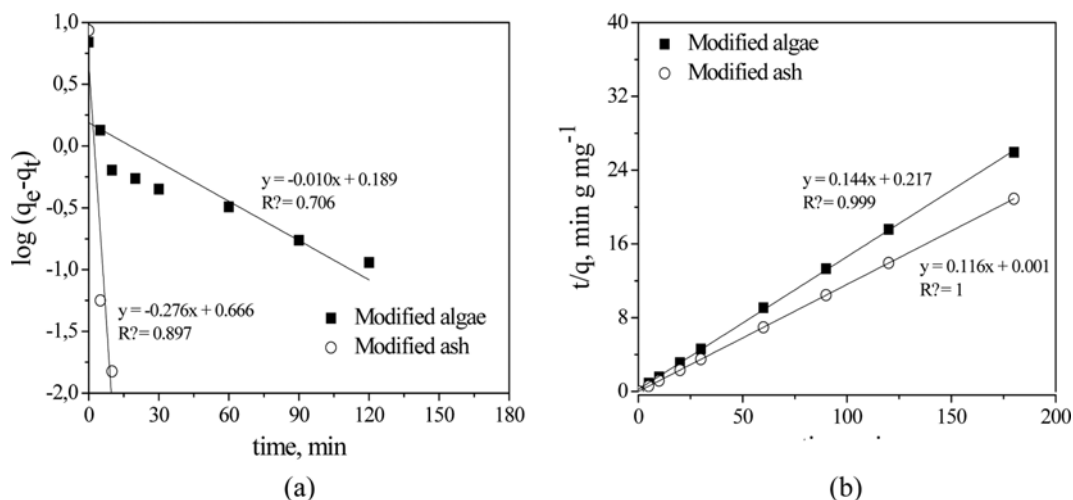


Fig. 8. Kinetics for the adsorption of Cd<sup>2+</sup> on modified algae and modified ash ((a) pseudo-first order; (b) pseudo-second order).

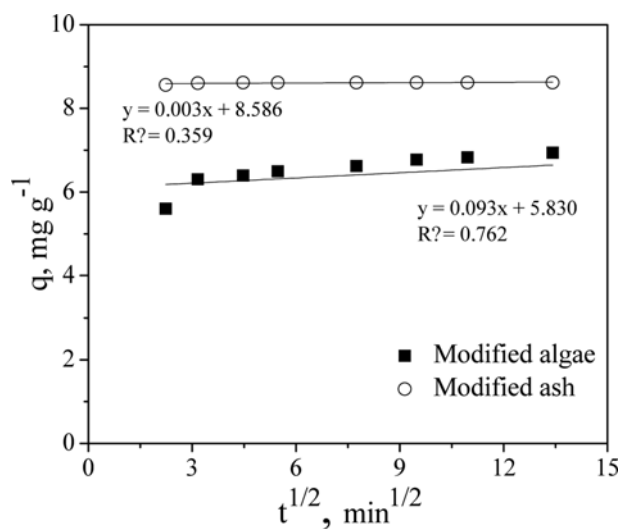


Fig. 9. Plots of the intra-particle diffusion order kinetics for the adsorption of Cd<sup>2+</sup> on modified algae and modified ash.

of mass transfer and boundary layer diffusion in the adsorption process of Cd(II) ions on considered adsorbents. However, the values of intra-particle diffusion coefficients (0.093 mg/(g min<sup>1/2</sup>) in case of modified algae and 0.003 mg/(g min<sup>1/2</sup>) in case of modified ash, respectively), suggest that the intra-particle diffusion influences the Cd(II) adsorption process up to a certain degree.

The results obtained from kinetics modelling show that Cd(II) adsorption on modified algae and ash occurs through two sequential equilibrium stages. Adsorption occurs very fast at surface in the first stage, where the chemical interactions are effective in Cd(II) binding to adsorbent surface, followed by a more slow second stage where the diffusion of metal ions to the pores of adsorbents is predominant.

### CONCLUSIONS

We focused on the adsorption of cadmium ions onto modified algae and modified ash, obtained by treating the raw materials with

sodium hydroxide solution. The choice of Cd(II) ions was justified by the high toxic potential.

Effective parameters were chosen considering different experiments. The uptake capacity of cadmium ions increased with increasing in the initial concentration. For an initial cadmium concentration of 360 mg L<sup>-1</sup>, the uptake capacities obtained in mentioned experimental conditions were by 34.15 mg g<sup>-1</sup> for modified algae and 43 mg g<sup>-1</sup>, respectively for modified ash. Also, the adsorption capacity of Cd<sup>2+</sup> ions is dependent on the contact time. The results show that the adsorption process is very fast in the first 30 minutes, and a contact time of 120 minutes can be considered as sufficient to achieve a state of equilibrium. In the case of modified ash, the equilibrium pH (pH<sub>eq</sub>) of the solution was always higher than the initial one.

Langmuir isotherm provides the best correlation of the experiment data of Cd<sup>2+</sup> absorption onto modified ash adsorbent, and the maximum adsorption capacities ( $q_{max}$ ) are comparable or even higher with those of various materials tested as low-cost adsorbents in literature.

The analysis of kinetic data showed that the adsorption of bio-adsorption of cadmium ions onto modified algae and modified ash followed well the pseudo-second order kinetics model, which means that the rate controlling step is the chemical interaction (probably by ion exchange type) between superficial functional groups of adsorbents and metal ions from aqueous solution.

Our experimental results demonstrate that both low-cost materials can be an efficient alternative for the removal of cadmium ions from aqueous solution, because they are available in large quantities and have considerable adsorption capacity for cadmium ions.

### REFERENCES

1. M. Mohapatra, K. Rout, B. K. Mohapatra and S. Anand, *J. Hazard. Mater.*, **166**, 1506 (2009).
2. F. Ouadjenia-Marouf, R. Marouf, J. Schott and A. Yahiaoui, *Arab. J. Chem.*, **6**, 401 (2013).
3. A. Voegelin and R. Kretzschmar, *Eur. J. Soil. Sci.*, **54**, 387 (2003).

4. S. B. Deng and Y. P. Ting, *Langmuir*, **21**, 5940 (2005).
5. U. U. Jadhav and H. Hocheng, *Environm. Technol.*, **35**(10), 1263 (2014).
6. L. Jarup and A. Akesson, *Toxicol. Appl. Pharm. J.*, **238**, 201 (2009).
7. J. Thompson and J. Bannigan, *Repr. Toxicol. J.*, **25**, 304 (2008).
8. M. O. Omorogie, J. O. Babalola, E. I. Unuabonah and J. R. Gong, *Environm. Technol.*, **35**(5), 611 (2014).
9. A. Mittal, J. Mittal, A. Malviya, D. Kaur and V. K. Gupta, *J. Colloid Interface Sci.*, **342**, 518 (2010).
10. V. K. Gupta, R. Jain, A. Mittal, T. Saleh, A. Nayak, S. Agarwal and S. Sikarwar, *Mater. Sci. Eng. C*, **32**, 12 (2012).
11. T. A. Saleh and V. K. Gupta, *Environ. Sci. Pollut. Res.*, **19**, 1224 (2012).
12. W. S. Shin, K. Kang and Y. K. Kim, *Environ. Eng. Res.*, **19**, 15 (2014).
13. D. H. Kumar Re, S. M. Lee and K. Seshiah, *Environ. Eng. Res.*, **17**, 125 (2012).
14. V. K. Gupta, S. K. Srivastava, D. Mohan and S. Sharma, *Waste Manage.*, **17**, 517 (1998).
15. A. K. Jain, V. K. Gupta, A. Bhatnagar and Suhas, *Sep. Sci. Technol.*, **38**, 463 (2003).
16. R. Halim, B. Gladman, M. K. Danquah and P. A. Webley, *Biore-sour. Technol.*, **102**, 178 (2011).
17. S. Curteanu, G. Buema, C. G. Piuleac, D. M. Sutiman and M. Harja, *J. Ind. Eng. Chem.*, **20**, 597 (2014).
18. G. Buema, P. Misaelides, F. Noli, D. M. Sutiman, I. Cretescu and M. Harja, *J. Radioanal. Nuclear Chem.*, **299**, 381 (2014).
19. G. Buema, S. M. Cimpeanu, D. M. Sutiman, R. D. Bucur, L. Rusu, I. Cretescu, R. C. Ciocinta and M. Harja, *J. Food Agr. Env.*, **11**, 1137 (2013).
20. R. C. Ciocinta, M. Harja, D. Bucur and G. Buema, *J. Food Agr. Env.*, **11**, 1108 (2013).
21. M. Harja, G. Buema, D. M. Sutiman, C. Munteanu and D. Bucur, *Korean J. Chem. Eng.*, **29**, 1735 (2012).
22. M. Harja, G. Buema, D. M. Sutiman and I. Cretescu, *Chem. Pap.*, **67**, 497 (2013).
23. L. Deng, Y. Su, H. Su, X. Wang and X. Zhu, *J. Hazard. Mater.*, **143**, 220 (2007).
24. A. A. Hamdy, *Current Microb.*, **41**, 232 (2000).
25. P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira and T. F. Marhaba, *Biore-sour. Technol.*, **97**, 2321 (2006).
26. A. Singh, P. Singh Nigam and J. D. Murphy, *Biore-sour. Technol.*, **102**, 10 (2011).
27. M. M. Montazer-Rahmati, P. Rabbani, A. Abdolali and A. R. Kesht-kar, *J. Hazard. Mater.*, **185**, 401 (2011).
28. D. Bulgariu and L. Bulgariu, *Biore-sour. Technol.*, **103**, 489 (2012).
29. L. Bulgariu and D. Bulgariu, *J. Bioproc. Biotechniq.*, **4**, 146 (2014).
30. A. Derkowski, W. Franus, E. Beran and A. Czimerova, *Powder Tech-nol.*, **166**, 47 (2006).
31. B. Shah, C. Mistry and A. Shah, *Chem. Eng. J.*, **220**, 72 (2013).
32. S. Chaiyasith, P. Chaiyasith and C. Septhum, *Thammasat Int. J. Sci. Technol.*, **11**, 13 (2006).
33. A. Mittal, D. Kaur, A. Malviya, J. Mittal and V. K. Gupta, *J. Colloid Interface Sci.*, **337**, 345 (2009).
34. V. C. Srivastava, I. D. Mall and I. M. Mishra, *Sep. Sci. Technol.*, **41**, 2685 (2006).
35. A. Mittal, J. Mittal, A. Malviya and V. K. Gupta, *J. Colloid Interface Sci.*, **340**, 16 (2009).
36. N. R. Bishnoi, M. Bajaj, N. Sharma and A. Gupta, *Biore-sour. Tech-nol.*, **91**, 305 (2003).
37. Y. E. Sherif, A. Ashmawy and S. Badr, *J. Appl. Sci. Res.*, **4**, 391 (2008).
38. H. Javadian, F. Ghorbani, H. Tayebi and S. M. H. Asl, *Arab. J. Chem.*, (2013), DOI:10.1016/j.arabjc.2013.02.018.
39. S. A. Ong, E. Toorisaka, M. Hirata and T. Hano, *Appl. Water Sci.*, **3**, 321 (2013).
40. K. S. Rao, S. Anand and P. Venkateswarlu, *Korean J. Chem. Eng.*, **27**, 1547 (2010).
41. V. K. Gupta, S. Agarwal and T. A. Saleh, *J. Hazard. Mater.*, **185**, 17 (2011).
42. V. K. Gupta, I. Ali, T. A. Saleh, A. Nayak and S. Agarwal, *RSC Adv.*, **2**, 6380 (2012).
43. V. K. Gupta and A. Nayak, *Chem. Eng. J.*, **180**, 81 (2012).
44. T. W. Weber and R. K. Chakraborti, *AIChE J.*, **20**, 228 (1974).
45. H. Khani, M. K. Rofouei, P. Arab, V. K. Gupta and Z. Vafaeil, *J. Haz-ard. Mater.*, **183**, 402 (2010).
46. V. K. Gupta, I. Ali, T. A. Saleh, A. Nayak and S. Agarwal, *RSC Adv.*, **2**, 6380 (2012).
47. V. K. Gupta and A. Nayak, *Chem. Eng. J.*, **180**, 81 (2012).
48. T. A. Saleh and V. K. Gupta, *J. Colloid Interface Sci.*, **371**, 101 (2012).
49. S. Karthikeyan, V. K. Gupta, R. Boopathy, A. Titus and G. Sekaran, *J. Mol. Liq.*, **173**, 153 (2012).
50. A. Mittal, J. Mittal, A. Malviya and V. K. Gupta, *J. Colloid Interface Sci.*, **344**, 497 (2010).
51. V. K. Gupta, R. Jain, A. Nayak, S. Agarwal and M. Shrivastava, *Mater. Sci. Eng. C*, **31**, 1062 (2011).