WASTE OF RAPESEED FROM BIODIESEL PRODUCTION AS A POTENTIAL BIOSORBENT FOR HEAVY METAL IONS

Lavinia Tofan,[a] Carmen Paduraru,[a,]* Irina Volf,[a,]* and Ovidiu Toma [b]

Rapeseed waste from biodiesel production was explored as a biosorbent for the removal of Cu(II) and Cd(II) ions from aqueous solutions under batch conditions. The optimum value of the initial pH for the sorption of both metal ions was found to be 4.5 to 5. The efficiency of Cu(II) and Cd(II) removal from aqueous solutions varied from 49% to 91% and from 61% to 97%, respectively, by increasing the rapeseed waste dose from 5 to 30 g L^{-1}. According to the evaluation using the Langmuir equation, the monolayer sorption capacity of copper (II) and cadmium (II) ions on rapeseed waste was found to be 15.43 mg g^{-1} and 21.72 mg g^{-1}, respectively at 293 K. The batch sorption systems under study were thermodynamically characterized by means of parameters such as ΔG, ΔH, and ΔS. The kinetic parameters derived from the pseudo-first-order and pseudo-second-order equations were calculated and compared.

Keywords: Rapeseed waste; Biosorption; Copper; Cadmium; Isotherm; Kinetic

Contact information: a: "Gheorghe Asachi" Technical University of Iasi, Environmental Engineering and Management Department, 71A D. Mangeron Street, 700050 Iasi, Romania; b: "Al. I. Cuza" University of Iasi, Department of Biochemistry, Faculty of Biology, 20A Bd. Carol I, 700505 Iasi, Romania
**Corresponding authors: cpadur2005@yahoo.com; iwolf@ch.tuiasi.ro*

INTRODUCTION

The amount of heavy metals released into the environment has increased continuously as a result of industrial activities (electroplating, metal finishing and metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, etc.) and technological developments. The effects of these metals, which are non-biodegradable and persistent, on the ecosystems are of large economic and public health significance (Spurgeon et al. 2003). Therefore, their removal from wastewaters before being discharged into the surrounding water bodies is a critical need.

In recent years research efforts dealing with the removal and recovery of toxic and/or valuable heavy metal ions have been focused on new technologies rather than traditional methods, expensive and suitable only for high concentrations and potentially risky because of the possibility to generate hazardous by-products. In this context, the removal of heavy metal ions has entailed the search for many unconventional materials that may be useful for this purpose (Bailey et al. 1999; Alluri et al. 2007; Whang and Chen 2009; Opeolu et al. 2010; Srinivasa et al. 2010). An emerging field of interest is the use of agricultural materials (waste, by-products, raw materials, etc.) available in large quantities and at low cost for the removal of heavy metals from aqueous solutions (Demirbas 2008; Sud et al. 2008; Faroog et al. 2010; Ray et al. 2010).

High efficiency, high sorption capacity, cost-effectiveness ratio, and renewability are the most important parameters governing which these materials are likely to be economical alternatives for metal removal and waste remediation. The regeneration of these agricultural biosorbents further improves the cost-effectiveness ratio of the process and guarantees its future success following the concept of *Green Chemistry*, which is a principle guiding the next generation products and processes (Ray et al. 2010). Thus, a few recent studies have demonstrated that seed press cakes can be used to remove toxic pollutants. Examples include adsorption of copper by mustard oil seed cake (Ajmal et al. 2005), methylene blue adsorption by oil palm fiber (Tan et al. 2007) and sunflower oil cake (Karagoz et al. 2008), biosorption of pesticides in cold-pressed rapessed, moringa and soybean cakes (Boucher et al. 2007), and removal of cadmium and chromium by Jatropha oil cake (Garg et al. 2008). Another recent study has emphasized the feasibility of employing degreased coffee beans for adsorption of metal ions, including copper(II), zinc(II), lead(II), iron(III), and cadmium(II) (Kaikake et al. 2007).

The agricultural wastes remove heavy metal ions from aqueous solutions by chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface and surface adsorption (Demirbas 2008). The sorptive properties of these agricultural materials can be attributed to the presence of functional groups such as carboxyl, hydroxyl, phenolyc, sulphdryl, amino, amido, etc. (Faroog et al. 2010). Rapeseed posseses these chemical characteristics and it is inexpensive and environmentally friendly. Rapeseed *(Brassica napus)* is a bright yellow flowering member of the mustard family. It has greatly improved its competitive position in the world, being actually a major crop in many countries, including Romania. The seeds of this plant, with very high level of oil, are one of the principal components of the crop. They can be ground into nutritional meals used in animal fodder, or pressed for the oil, which can be used for human food or in the production of biodiesel (Gupta 2007).

In view of the aforementioned, in the present study rapeseed was explored as a sorbent for the removal of copper(II) and cadmium(II) ions from aqueous solutions under batch conditions. Cu(II) was chosen for this work as a result of the fact that copper is one of the most widely used heavy metals and in large amounts it is extremely toxic to living species (Spurgeon et al. 2003). On the other hand, the industrial and potential pollution impact of cadmiun(II) is of major interest. Cadmium has joined lead and mercury to form the group of metals known as the “Big Three”, with the greatest potential hazard (Akar and Tunali 2006).

EXPERIMENTAL

Biosorbent Preparation

The rapeseed used in these experiments resulted from agricultural units in the north-east region of Romania. The seed press cake obtained after the oil extraction in biodiesel production, was washed with doubly distilled water several times to remove surface impurities, dried at 40 ^{o}C for 24 hours, and ground (Retsch-Grindomix-GM-200) to obtain particles whose sizes ranged between 0.1 and 0.2 mm.

Chemicals

Stock solutions of 1156 mg L^{-1} and 1130 mg L^{-1} were prepared through dissolution of analytical grade reagents $CuSO_4\cdot5H_2O$ and $CdSO_4\cdot8H_2O$, respectively, in doubly distilled water and were complexometrically standardized. Working solutions of Cu(II) and Cd(II) were prepared through appropriate dilutions of the stock solutions.

In order to study the effect of medium acidity on the sorption process, a solution of H_2SO_4 with concentration of 10^{-2} mol L^{-1} was used (Inolab pH/ion735).

Sorption Procedure

The sorption experiments were performed under batch conditions. For this purpose, samples of about 0.5 g rapeseed waste were equilibrated with 50 mL of each aqueous solution containing a defined amount of Cu(II) and Cd(II) ions, at desired temperature and pH. At the end of predetermined time intervals, rapeseed was removed from the aqueous solutions by centrifugation (Rotofix 32A Hettich) at 4000 rpm for 10 min. The Cu(II) and Cd(II) concentrations in the final solutions were determined through atomic absorption spectrometry. The absorbance measurements were performed using a GBS Avanta 2007 Atomic Absorption Spectrometer with furnace system.

The effects of the experimental parameters such as initial pH, biosorbent dose, metal ion concentration, temperature, and contact time on the Cu (II) and Cd(II) sorption by rapeseed waste were studied. The conditions for the sorption studies are systematized in Table 1.

Table 1. Sorption Experimental Conditions

Studied influence	Tested cations	Initial pH	Rapeseed dose (g L^{-1})	Metal ion concentration (mg L^{-1})	Temperature (°C)	Contact time (hours)
Effect of initial pH of solution	Cu(II) Cd(II)	1-5 1-5	10 10	92.48 90.44	20 20	24 24
Effect of rapeseed dose	Cu(II) Cd(II)	4.5-5 4.5-5	5-30 5-30	69.36 90.44	20 20	24 24
Effect of initial concentration	Cu(II) Cd(II)	4.5-5 4.5-5	10 10	21.38-231 22.61-271	20 20	24 24
Effect of temperature	Cu(II) Cd(II)	4.5-5 4.5-5	10 10	23.12-138.72 22.61-135.66	4; 20; 60 4; 20; 60	24 24
Effect of contact time	Cu(II) Cd(II)	4.5-5 4.5-5	10 10	92.48 90.44	18 18	0.50-24 0.50-24

The parameters of the metal ions sorption by rapeseed waste were calculated using the following equations:

Retention percentage, R (%) $$R = [(C_0 - C)/C_0]\cdot 100 \qquad (1)$$

Retained amount of metal ion, q (mg g^{-1}) $$q = [(C_0 - C)/G]\cdot V \qquad (2)$$

where C_0 is the initial concentration of metal ion (mg L^{-1}), C is the cation concentration after sorption (mg L^{-1}), V is the volume of solution (L), and G is the weight of rapeseed (g).

FT-IR Spectra

The infrared spectra were obtained as KBr pellets, and the equipment used was FT-IR spectrometer Bruker Vertex 70.

RESULTS AND DISCUSSION

Rapeseed Waste Characterization

The chemical composition of the rapeseed waste under study was determined by conventional methods (Budoi 2000). The following relevant results have been obtained: nitrogen 3.61 %, crude protein 22.57 %, fat 48.19 %, moisture 6%, and ash 4.65 %.

FTIR spectroscopy was applied to identify the functional groups of rapeseed responsible for metal adsorption. To reveal the systematic changes in the spectral features upon reaction with metal ions, FTIR spectra were obtained for the sample before and after reacting with Cu(II) and Cd(II) (Fig. 1).

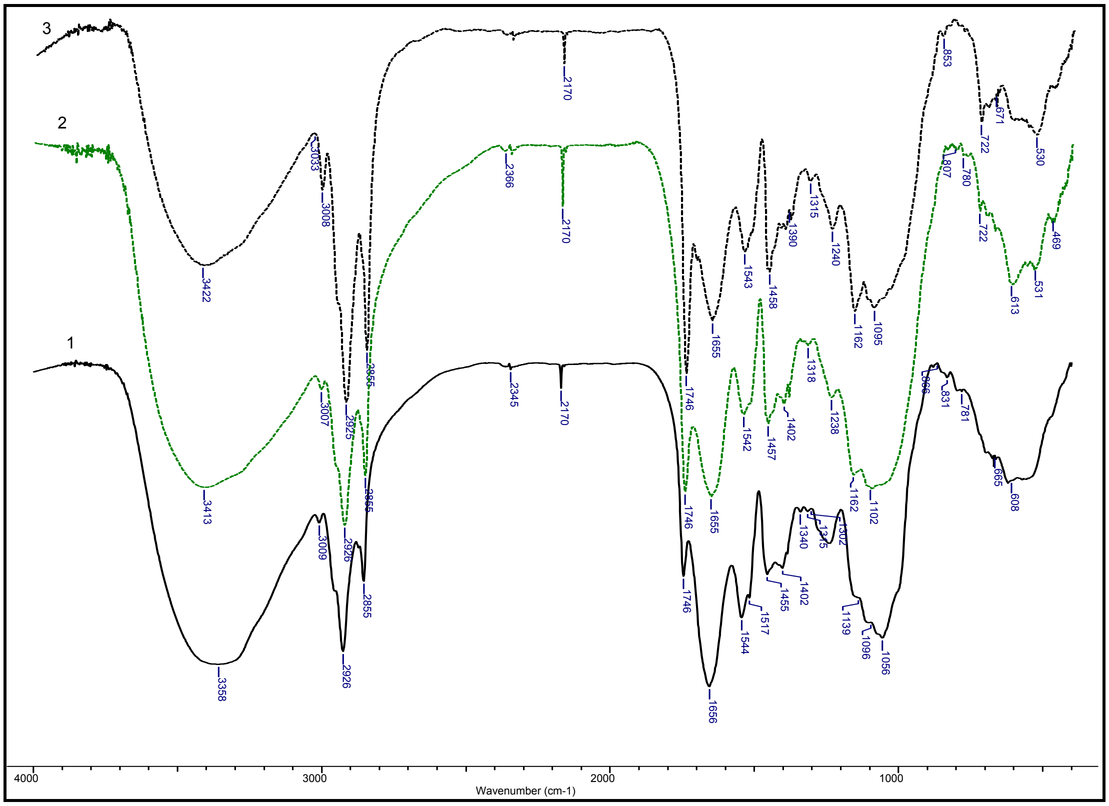

Fig. 1. IR-spectra for (1) rapeseed, (2) rapeseed-Cu(II), and (3) rapeseed-Cd(II) systems

A comparison between these spectra shows that the intensity and position of peaks assigned to carboxyl, -NH, and -OH groups from rapeseed were minimized or slightly shifted after sorption of Cu(II) and Cd(II) ions (Table 2). These changes can be attributed to electrostatic interactions between functional groups in the rapeseed structure and the metal cations, confirming the chemical nature of the sorption of Cu(II) and Cd(II).

Table 2. The Main FTIR Spectral Characteristics of Rapeseed Before and After Sorption of Cu(II) and Cd(II)

Transmission band (cm^{-1})			Assignment
Before adsorption	After adsorption Cu(II)	After adsorption Cd(II)	
3358	3413	3424	Strong band indicates the presence of –OH and –NH groups
2855	2855	2855	Aliphatic C-H group
1656	1655	1655	Double bands of carboxylic group
1456	1457	1458	Aromatic groups
1056	1110	1095	Assigned to alcoholic group

Effect of Initial pH of the Aqueous Solution

The initial pH plays a vital role in the removal of heavy metal ions from wastewaters by using agricultural wastes due to its impact on both the surface-binding sites and species distribution of the metal cations. Previous results reported in the specialized literature indicated that the sorption of heavy metals on *Canola* (a specific variety of rapeseed) meal increased with pH up to 5.2, but the differences in the increase from one pH to another were not very large (Al-Aseh and Duvnyak 1999). This trend has been attributed to the large amount of proteins that are contained in *Canola* meal and can act as a buffer in the meal–metal suspension (Al-Aseh and Duvnyak 1999). The influence of pH on the sorption of Cu(II) and Cd(II) from solutions with initial concentrations of 92.48 mg L^{-1} and 91 mg L^{-1}, respectively, by the rapeseed under study was evaluated over a pH range of 1 to 5. Within this pH range the sorption is not influenced by the metal precipitation as metal hydroxides, and the estimation is more reliable. According to the speciation data from literature, in solutions at pH 1 to 5, both metals exist in their divalent positively charged ionic forms (Cu^{2+} and Cd^{2+}) (Fergusson 1990).

The effect of the initial pH on the sorption of the tested cations by rapeseed waste is shown in Fig. 2. As follows from Fig. 2, the sorption of copper and cadmium ions recorded its minimum values at pH = 1 (reached by acidification with H_2SO_4 solution). This negligible extent of sorption is similar to the retention of Cu(II) and Cd(II) on other agricultural materials at lower values of pH and could be due to the positive charge of the rapeseed surface and an increase in competition between H^+ ions and the metallic cations for the active sites of the sorbent (Bhattaacharya et al. 2006). Then there was an increasing of the rapeseed sorption ability with increasing pH in the initial pH range of 1-3.5 for both cations. At the initial pH values higher than 3.5, the amount of sorbed cations did not increase further. This trend may be explained by taking into account the fact that within the pH range of 2 to 5, as a result of superficial functional group dissociation, the surface of rapeseed is negatively charged (Al-Aseh and Duvnyak 1999; Mahmoodi et al. 2011). The sorption increase with increasing pH may be correlated with these negative charges at the active sites on the rapeseed that would allow metallic ions (M^{2+}) to be chemisorbed. These findings are in good agreement with other literature data that reported the influence of the initial pH on the retention of Cu(II) and Cd(II) on agricultural wastes such as rice straw and Ponkan mandarin peels (Rocha et al. 2009; Pavan et al. 2006).

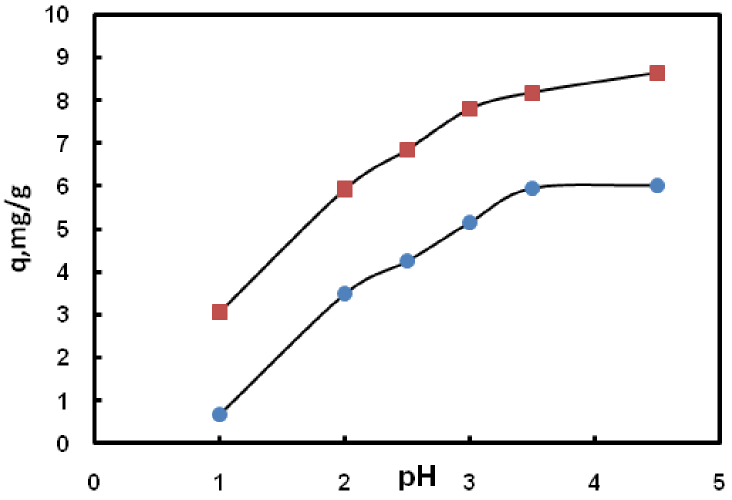

Fig. 2. The influence of initial pH on the Cu(II) (●) and Cd(II) (■) retention by rapeseed waste (C_0= 92.48 mg Cu(II) L^{-1}; C_0= 91mg Cd(II) L^{-1}; rapeseed dose= 10 g L^{-1}, time= 24 h, t= 20 °C)

Effect of Rapeseed Waste Dose

The influence of rapeseed dose on the removal of Cu(II) and Cd(II) from aqueous solutions can be viewed in Fig. 3. The observed cation removal amounts represented a significant improvement with the increase in rapeseed dose. Thus, the percent removal of Cu(II) from solution with an initial concentration of 63.87 mg L^{-1} varied from 49% to 91% for an increase of rapeseed waste dose to 5 at 30 g L^{-1}. At the same time, the efficiency of Cd(II) removal from aqueous solutions of C_0 = 113 mg L^{-1} increased from 61 % to 97 % with an increase in rapeseed dose for 5 to 30 g L^{-1}. This behavior can be attributed to the increase in surface area resulting from the increase in sorbent mass, thus increasing the number of active sorption sites. However, the amount of cation retained on the unit mass of rapeseed decreased with increasing sorbent dose. Thus, for solutions with C_0= 69.36 mg L^{-1} the amount of Cu(II) retained decreased from 9.60 mg g^{-1} at 1.60 mg g^{-1} for an increase in rapeseed dose to 5 at 30 g L^{-1}. The Cd(II) amount sorbed onto rapeseed reached values of 16.74 mg g^{-1} and 2.92 mg g^{-1} at rapeseed doses of 5 and 30 g L^{-1}, respectively. This decrease can be correlated with the reduction of effective surface area and sorbate /sorbent ratio.

Effect of Cu(II) and Cd(II) Concentrations in Initial Solutions

The amount of cation retained on rapeseed waste (q) increased with increasing initial metal ion concentrations, but the Cu(II) and Cd(II) sorption percentages (*R*%) decreased (Table 3). Higher initial concentrations might be closely associated with large values of the ratio between the initial number of mmoles of heavy metal cation and the limited number of available binding sites, thus resulting in an enhancement of the metal uptake. Occupation of the total active sites on the rapeseed may hinder the access of Cu(II) and Cd(II), consequently decreasing the sorption percentages. This trend leads to the conclusion that the rapeseed could be efficiently used in the removal of heavy metals from wastewaters with low contents of Cu(II) or Cd(II).

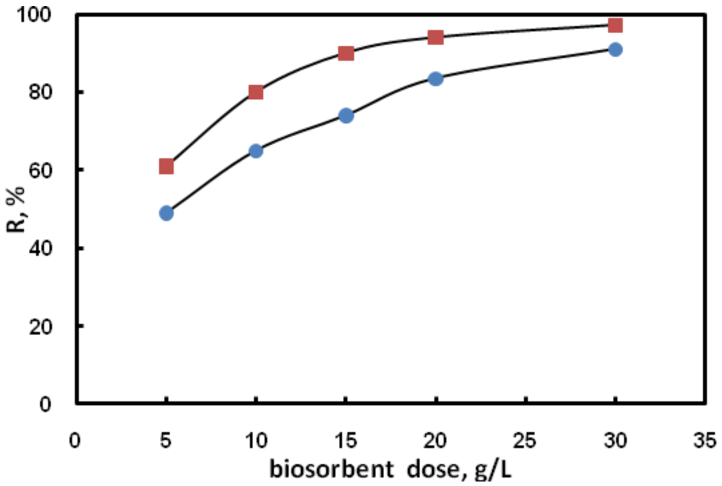

Fig. 3. Removal percentage of Cu(II) and Cd(II) on rapeseed waste as function of sorbent dose (Cu(II) (●)-C_0= 69.87 mg L^{-1}; Cd(II) (■)-C_0=113 mg L^{-1}; pH= 4.5-5; time= 24 h; t= 20 °C)

Table 3. Influence of Initial Concentration on Cu(II) and Cd(II) Sorption by Rapeseed

C_0, mg L^{-1}		**q, (mg g^{-1})**		***R* %**	
Cu(II)	Cd(II)	Cu(II)	Cd(II)	Cu(II)	Cd(II)
21.38	22.61	2.10	1.89	93	95.79
42.76	45.22	3.79	4.09	90.20	92.53
69.36	67	4.46	6.26	86.20	90.60
92.48	91	6.50	7.64	81.50	88.11
115	113	7.79	10.67	78.30	82
138.72	136	9.76	12.45	73.24	76
185	180.88	13.71	15.27	65	69
231	271	17	19.36	59.30	62

Sorption Isotherms

In order to successfully represent the dynamic sorptive behavior, it is important to have a satisfactory description of the equilibrium state between the two phases composing the sorption system. The Langmuir and Freundlich sorption isotherms were tested to fit the experimental data.

The Langmuir sorption isotherm is given by Eq. 3 (Langmuir 1916),

$$q = K_L \cdot C \cdot q_0 / (1 + K_L \cdot C) \tag{3}$$

where K_L is a constant related to the sorption capacity and q_0 is the maximum capacity of sorption. The Langmuir equation assumes the formation of monolayer coverage of metallic ion at the rapeseed surface containing a finite number of homogeneous sites of sorption. The Langmuir isotherms for Cu (II) and Cd(II) on the investigated rapeseed at three different temperatures are presented in Figs. 4 and 5. Table 4 characterizes the Cu(II) and Cd(II) sorption on the rapeseed under study by means of the Langmuir constants obtained from the corresponding linear Langmuir plots.

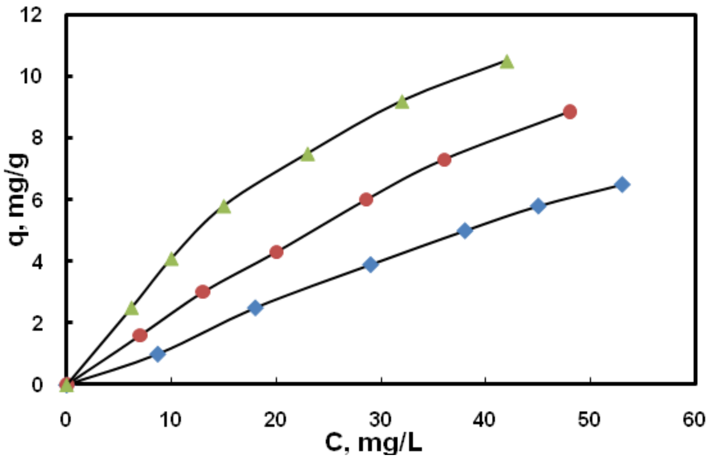

Fig. 4. The Langmuir isotherms of Cu(II) sorption on rapeseed waste at (▲) 60 °C; (●) 20 °C;(♦) 4 °C (pH= 4.5-5; biosorbent dose=10 g L^{-1})

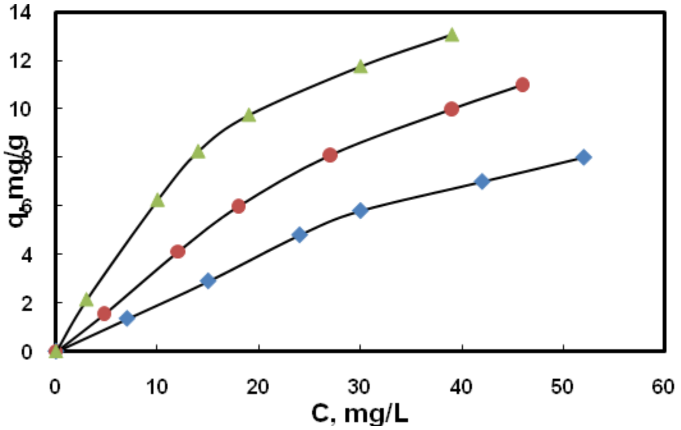

Fig. 5. The Langmuir isotherms of Cd(II) sorption on rapeseed waste at (▲) 60 °C; (●) 20 °C;(♦) 4 °C (pH= 4.5-5; biosorbent dose=10 g L^{-1})

Table 4. Quantitative Description of the Cu(II)–Rapeseed and Cd(II)–Rapeseed Batch Sorption Systems on the Basis of Langmuir and Freundlich Models

Metal ion	T, K	Langmuir isotherm				Freundlich isotherm		
		R^2	q_0,		K_L ($L\ mol^{-1}$)	R^2	K_F	n
			($mmol\ g^{-1}$)	($mg\ g^{-1}$)				
Cu(II)	277	0.992	0.217	13.88	878	0.987	1.38	1.061
	293	0.990	0.243	15.55	1310	0.986	3.47	1.104
	333	0.994	0.305	19.52	1736	0.983	6.51	1.35
Cd(II)	277	0.995	0.156	17.53	1799	0.988	1.32	1.106
	293	0.985	0.194	21.80	2418	0.984	2.24	1.162
	333	0.993	0.223	25.06	3649	0.980	4.016	1.32

It can be seen from Table 4 that the rapeseed under study may be considered as a reasonable sorbent for Cu(II) and Cd(II) ions removal from aqueous solutions. It was found that the low values for q_0 obtained for rapeseed are in good agreement with literature data describing the sorption of Cu (II) and Cd (II) by other agricultural sorbents

(Table 5). The K_L values reflect that the relative sorption affinity of the investigated rapeseed is higher for cadmium ions than for copper ions. The same order of the sorption affinity (Cd(II) > Cu(II)) has been reported in literature for other agro-waste materials, such as rice straw (Rocha et al. 2009) and banana trunk fibers (Sathasivam and Haris 2010). This behavior may be justified on the basis of the ionic size of the hydrated metal ion or the different electronegativites of two divalent cations (Yao et al. 2010).

Table 5. Comparison of Maximum Sorption Capacity of Cu(II) and Cd(II) on Different Low-cost Sorbents

	Low – cost sorbent	Initial pH	Sorbent dose, g L^{-1}	Maximum capacity of sorption, mg g^{-1}	Ref.
Cu(II)	Banana trunk fibers	5.0	4	63.69	Sathasivam and Haris 2010
	Waste tire rubber ash	4.5-6.0	1.5	34.3	Mousavi et al. 2010
	Thermal power plant ash	4.5-5	10	4.71	Tofan et al. 2008
	Chestnut shell	5.0	10	12.56	Yao et al. 2010
	Peanut hulls	5.0	4	13.84	Oliveira et al. 2010
	Sawdust of Meranti wood	5.0	250	37.17	Ahmad et al. 2009
	Peach stones	5.0	25	10 – 15	Hansen et al. 2010
	Spent tea leaves	5.0	0.2	90.90	Bajpai and Jain 2010
	Coconut copra meal	6.0	200	2.59	Ofomoja and Ho 2008
	Rapeseed waste	4.5-5	10	15.43	This study
Cd(II)	Pomelo peel	5.0	1	21.83	Saikaew et al. 2009
	Rice husk	6.0	2.5	21.28	Senthil Kumar et al. 2010
	Grape stalk waste	5.5	-	27.77	Villaescisa et al. 2006
	Olive cake	6.0	-	65.4	Al-Anber and Matong 2008
	Ground pine cone	7.0	6	13.5	Izanlov and Nasseri 2005
	Banana peel	8.0	-	35.52	Memon et al. 2008
	Rapeseed waste	4.5-5	10	21.72	This study

The Freundlich equation can be described by the following linearized form (Freundlich 1906),

$$\log q = \log K_F + (1/n)\log C \qquad (4)$$

where q is the amount of divalent cation taken up per 1 gram of rapeseed (mg g^{-1}); C is the divalent cation concentration left in solution at equilibrium (mg mL^{-1}); K_F and n are the Freundlich constants relating to all factors affecting the retention process: sorption capacity (K_F) and energy of sorption (n), respectively. The Freundlich equation is based on a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites (Katal et al. 2011) The values of Freundlich constants for the Cu(II)-rapeseed and Cd(II)-rapeseed sorption systems are given in Table 4. The n values are above unity, indicating favorable sorption of the tested cations by rapeseed at all working temperatures.

To compare Langmuir and Freundlich isotherm models, the experimental data were statistically processed through linear regression. High values of the linear regression correlation coefficients (R^2) for both Langmuir and Freundlich plots (Table 4) suggest that monolayer sorption as well as heterogeneous surface conditions may coexist under the applied experimental conditions.

Effect of Temperature and Thermodynamic Parameters

It is obvious from Fig. 4 and 5 that the temperature had a favorable effect within the sorption systems under study. Both Langmuir and Freundlich constants (Table 4) increased with increasing temperature, showing that the sorption capacity and the intensity of sorption were enhanced at higher temperatures. Furthermore, this trend indicates the endothermic and chemical nature of the studied metal sorption on rapeseed. Another reason for the observed influence of the temperature may be the increased accessibility of the sorption sites in the rapeseed.

In order to evaluate the thermodynamic feasibility of the Cu(II) and Cd(II) sorption process and to confirm its nature, the thermodynamic parameters, the free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were calculated. Based on the values of the Langmuir sorption constant K_L at different temperatures, the following equations were used (Tofan et al. 2008),

$$\Delta G = - RT \ln K_L \quad (5)$$

$$\ln K_L = \text{constant} = - \Delta H/RT \quad (6)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (7)$$

where R is the gas constant and T is the absolute temperature. The obtained data are reported in Table 6. The negative values of ΔG at all working temperatures validate the feasibility of the sorption process and the spontaneity of the divalent cations retention by rapeseed. The positive value of ΔH shows the endothermic nature of the Cu(II) and Cd(II) sorption process, favored by temperature increasing. The positive value of entropy change suggests the increase in randomness at the solid-liquid interface during the sorption of Cu(II) and Cd(II) ions on rapeseed.

Table 6. Thermodynamic Quantities of the Sorption Process of Cu(II) and Cd(II) on rapeseed.

	T, K	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Cu(II)	277	-15.606	7.47	0.084
	293	-17.457		0.0842
	333	-20.643		0.084
Cd(II)	277	-17.241	9.67	0.0971
	293	-18.967		0.0977
	333	-22.696		0.0971

Effect of Contact Time and Kinetics of Cu(II) and Cd(II) Sorption by Rapessed Waste

The kinetics of sorption, describing the Cu(II) and Cd(II) sorption rate is an important characteristic for efficiency of sorption assessment. The kinetic data for the sorption of the tested cations on rapeseed are shown in Fig. 6.

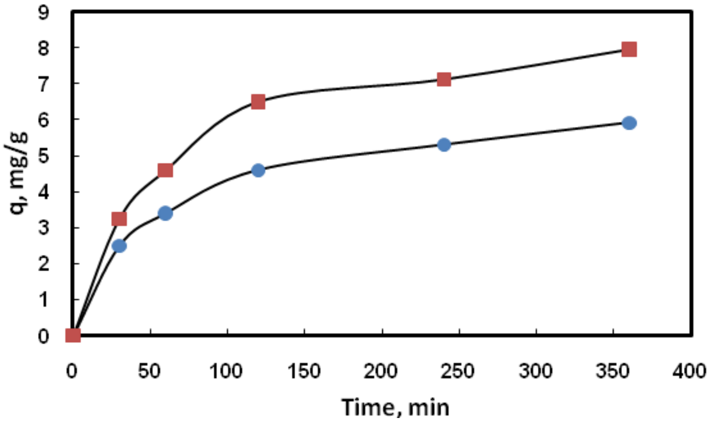

Fig. 6. Effect of the contact time on the Cu(II) and Cd(II) retention by rapeseed waste. (Cu(II) (●) ,C_0= 92.48 mg L^{-1}; Cd(II) (■), C_0= 91 mg L^{-1})

The kinetic curves in Fig. 6 show that in the initial stages of the sorption process the amounts of Cu(II) and Cd(II) retained on rapeseed increased sharply with increasing contact time of phases, attaining values that stayed almost constant.

In order to investigate the mechanism of sorption and potential rate-controlling steps, the pseudo-first-order and pseudo-second-order rate equations were used to test the experimental data. The pseudo-first-order rate expression is given by Lagergren equation (Lagergren 1898),

$$\log (q - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \qquad (8)$$

where q and q_t are the amounts of cation (mg g^{-1}) sorbed at equilibrium and at time t, respectively, and k_1 is the pseudo-first-order sorption rate constant (min^{-1}). The kinetic parameters obtained from the linear Lagergren plots are given in Table 7, together with the corresponding coefficients of determination (R^2).

Table 7. Kinetic Characterization of the Sorption Systems based on Rapeseed Waste

Metal ion	Initial concentration C_0 (mg L^{-1})	q mg g^{-1}	Pseudo-first-order		q mg g^{-1}	Pseudo-second-order		
			k_1, min^{-1}	R^2		k_2, g $mg^{-1}min^{-1}$	h, mg $g^{-1}min^{-1}$	R^2
Cu(II)	92.48	6.35	$4.6X10^{-3}$	0.989	7.04	$2.52x10^{-3}$	0.121	0.997
Cd(II)	91.00	8.25	$6.9x10^{-3}$	0.990	9.00	$2.37x10^{-3}$	0.165	0.993

The pseudo-second-order kinetic model is based on Equation 9 (Ho and McKay 1999),

$$1/q_t = 1/h + (1/q).t \qquad (9)$$

where k_2 is the rate constant for the pseudo-second-order model and the quantity $h = k_2 \cdot q^2$ (mg g^{-1} min^{-1}) can be regarded as the initial sorption rate constant of the pseudo-second-order sorption. The kinetic parameters derived from the plots of the liniarized form of the pseudo-second-order equation are recorded in Table 7, along with the corresponding coefficients of determination. Comparing the R^2 values, it is obvious that the sorption of Cu(II) and Cd(II) ions on the tested rapeseed follows better the pseudo-second-order kinetic model, which is in agreement with chemisorption being the rate-controlling step (Ho 2006). A similar behavior has been observed with the sorption of copper(II) and cadmium(II) ions onto other agricultural wastes (Tofan et al. 2008; Hansen et al. 2010; Sentil Kumar et al. 2010).

CONCLUSIONS

1. Batch sorption capability of rapeseed for the removal of copper (II) and cadmium (II) ions from diluted aqueous solutions has been investigated as function of initial pH, sorbent dose, metal ion concentration, temperature, and contact time.
2. Within the initial pH range of 1 to 5 under study, the rapeseed sorption ability increased with increasing pH until 3.5. At initial pH values higher than 3.5, the amount of sorbed Cu(II) and Cd(II) did not increase further.
3. The percentages of Cu(II) and Cd(II) sorption increased with increasing rapeseed doses. At a maximal rapeseed dose of 30 g L^{-1}, the values of the retention percentage exceeded 90%.
4. The amount of Cu(II) or Cd(II) retained on rapeseed increased with increasing metal ion concentration, but the Cu(II) and Cd(II) sorption percentages decreased.
5. The dependence between the equilibrium concentrations of Cu(II) and Cd(II) in the rapeseed phase and aqueous solution phase was well described by both Langmuir and Freundlich models. The relative sorption affinity of the rapeseed is higher for cadmium(II) than for copper(II) ions. Both Langmuir and Freundlich constants increased with increasing temperature, showing that the sorption capacity and the intensity of sorption are enhanced at higher temperatures. In addition, the obtained values for the thermodynamic parameters indicated the endothermic and chemical nature of the studied metal ions sorption on rapeseed.
6. In the concentration range under investigation, the sorption kinetics for Cu(II) and Cd(II) ions at pH 4.5 to 5 were very well described by the pseudo-second-order model, indicating the chemisorption as the rate-controlling step.
7. From the findings of this study it is obvious that the rapeseed could be efficiently used in the removal of heavy metals from wastewaters with low contents in Cu(II) or Cd(II).

REFERENCES CITED

Ahmad, A., Rafatullah, M., Sulaiman, O., Ibrahim, M. H., Chii, Y. Y., and Siddique, B. M. (2009). "Removal of Cu(II) and Pb(II) from aqueous solutions on sawdust of Meranti wood," *Desalination* 250, 300-310.

Ajmal, M., Rao, R. A. K, and Khan, M. A. (2005). "Adsorption of copper from aqueous solution on *Brassica cumpestris* (mustard oil cake)," *J. Hazard. Mater*. 122(1-2), 177 – 183

Akar, T., and Tunali, S. (2006). "Biosorption characteristics of *Aspergillus flavus* biomass for the removal of Pb(II) and Cu(II) ions from aqueous solution," *Bioresour. Technol*. 97, 1789-1797.

Al-Anber, Z. A., and Matong, M. A. D. (2008). "Batch adsorption of cadmium ions from aqueous solution by means of olive cake," *J. Hazard. Mater*. 151(1), 194-201.

Al-Aseh, S., and Duvnyak, Z. (1999). "Sorption of heavy metals *by Canola* meal," *Water Air Soil Pollut*.114, 251-276.

Alluri, H. K., Ronda, S. R., Setalluri,V.S., Bondili, J. S, Suryanaraya, V., and Venkateshwari, P. (2007). "Biosorption: An eco-friendly alternative for heavy metal removal," *Afr. J. Biotechnol*. 6(25), 2924-2931.

Bailey, S. E., Olin, T. J., Bricka, R. M., and Adrian, D. D. (1999). "A review of potentially low–cost sorbents for heavy metals," *Water Res*.33, 2469-2479.

Bajpai, S. K., and Jain, A. (2010). "Removal of copper(II) from aqueous solutions using spent tea leaves(STL)as a potential sorbent," *Water SA* 36(3), 221- 228.

Bhattaacharya, A. K, Mandal, S. N., and Das, S. K. (2006). "Adsorption of Zn(II) from aqueous solution by using different adsorbents," *Chem. Eng. J* .123, 43-51.

Boucher, J., Steiner, L., and Marison, I. W. (2007). "Biosorption of atrazine in the press–cake from oilseed," *Water. Res*. 41(15), 3209-3216.

Budoi, G. (2000). *Agrochemistry,* Ed. Didactică şi Pedagogică, Bucharest.

Demirbas, A. (2008). "Heavy metal adsorption onto agro-based waste materials: A review," *J. Hazard. Mater*. 157(2-3), 220- 229.

Faroog, U., Kozinski, J. A., Khan, M. A., and Athar, M. (2010). "Biosorption of heavy metal ions using wheat based materials – A review," *Bioresour. Technol*. 10(14), 5043-5053.

Fergusson, J. E. (1990). *The Heavy Elements: Chemistry, Environmental Impact and Health Effects,* Pergamon Press Inc., New York.

Freundlich, H. M. (1906). "Uber die adsorption in lusungen," *Z. Phys. Chem*. 57, 385-470.

Garg, U., Kaur, M. P.,Jawa, G. K., Sud, D., and Garg, V. K. (2008). "Removal of cadmium(II) from aqueous solution by adsorption on agricultural waste biomass," *J. Hazard. Mater*. 154(1-3), 1149-1157.

Gupta, S. K. (2007). *Advances in Botanical Research, Vol. 45: Rapeseed Breeding,* Elsevier, San Diego.

Hansen, H. K., Aranciba, F. A., and Gutierrez, C. (2010). "Adsorption of copper onto agricultural waste materials," *J. Hazard. Mater*. 180, 442-448.

Ho, Y. S. (2006). "Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non–linear methods," *Water Res*. 40(1), 111-125.

Ho,Y. S., and McKay, G. (1999). "Pseudo–second order for the sorption process," *Biochemistry* 34, 451-465.

Izanlov, H., and Nasseri, S. (2005). "Cadmium removal from aqueous solution by ground pine cone," *Iranian J. Env. Health Sci. Eng.* 2(1), 33-42.

Kaikake, K., Hoaki, K., Dkakal, R. P., and Baba, Y. (2007). "Removal characteristics of metal ions using degreased coffee beans: Adsorption equilibrium of cadmium(II)," *Bioresour. Technol.* 98*,* 2787- 2791.

Katal, R., Zare, H., Fani, A., Omraei, M., and Najafpour, G. D. (2011). "Removal of zinc from aqueous phase by charcoal ash," *World Appl.Sci. J.* 13(2), 331- 340.

Karagoz, S. T., Ucar, S., and Erdem, M. (2008). "Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption," *Bioresour. Technol*. 99(14), 6214-6222.

Lagergren, S. (1898). "About the theory of so-called adsorption of solid substance," *Handlinger* 24, 1-39.

Langmuir, I. (1916). "The constitution and fundamental properties of solids and liquids," *J. Am. Chem. Soc.* 38, 2221-2295 .

Mahmoodi, N. M., Arami, M., Bahrami, H., and Khorramfar, S. (2011). "The effect of pH on the removal of anionic dyes from colored textile wastewater using a biosorbent," *J. Appl. Polym. Sci.* 120(5), 2996-3003.

Memon, J. R., Memon, S. Q., Bhanger, M. I., Memon, G. Z., El–Turki, A., and Allen, G. C. (2008). "Characterization of banana peel by scanning electron microscopy and FT–IR spectroscopy and its use for cadmium removal," *Colloids and Surfaces:B: Biointerfaces* 66(2), 260-265.

Mousavi, H. Z., Hoseinfar, A., and Jahed, V. (2010). "Removal of Cu(II) from wastewaters by waste tire rubber ash," *J. Serb. Chem. Soc.* 75(6), 845-853.

Ofomoja, A. E., and Ho, Y. S. (2008). "Kinetic biosorption of cadmium onto coconut copra meal," *Int. J. Environ. Pollut.* 34, 466-476.

Oliveira, F. D, Soares, A. C., Freitas, O. M., and Figuerido, S. A. (2010). "Copper, nickel and zinc removal by peanut hulls: Batch and column studies in mono, tri- component systems and with real effluents," *Global Nest: J*. 12(2), 206 -214.

Opeolu, B. O., Bamagbose, O., Arowolo, T. A., and Adetunji, M. T. (2010). "Utilization of biomaterials as adsorbents for heavy metals removal from aqueous matrices," *Sci. Res. Essays* 5(14), 1780-1787.

Pavan, F. A., Lima, I. S.,Lima, E. C., Airoldi, C., and Gushikem, Y. (2006). "Use of Ponkan mandarin peels as biosorbent for toxic metal uptake from aqueous solutions," *J. Hazard. Mater*. B 137, 527-523.

Ray, K.R., Kardan, A., Arrora, J.K., Srivatava, M.M.,and Srivastava, S.(2010). "Neural network modeling for Ni(II) removal from aqueous system using agricultural waste," *J. Water Resource Prot.* 2, 331-338.

Rocha, C. G., Morzin Zaia, D. A., da Silva Alfaya, R. V., and da Silva Alfaya, A. A. (2009). "Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents," *J. Hazard. Mater.* 166, 383-388.

Saikaew, W., Kaewsarn, P., and Saikaew, W. (2009). "Pomelo peel: Agricultural waste for biosorption of cadmium ions from aqueous solution," *World Academy of Sci. Eng.&Technol*. 56, 287-291.

Sathasivam, K., and Haris, M. R. H. M. (2010). "Banana trunk fibers as an efficient biosorbent for the removal of Cd(II), Cu(II), Fe(II) and Zn(II) from aqueous solutions," *J. Chil. Chem. Soc*. 55(2), 278-282.

Senthil Kumar, P., Ramakrishnan, K., Dinesh Kirupha, S., and Sivanesan, S. (2010). "Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk," *Braz. J. Chem. Eng.* 27(2), 347-355.

Spurgeon, D. J., Svendsen, C., Weeks, J. M., Hankard, P. K., Stubbert, H. E., and Kammenga, J. E. (2003). "Quantigiying copper and cadmium impacts on intrinsic rate of population increase in the terrestrial oligochaete *Lumbricus rubellus*," *Environ. Toxicol. Chem.* 22(7),1465-1472.

Srinivasa Rao, K. S., Anand, S., and Venkateswarlu, P. (2010). "Adsorption of cadmium(II) ions from aqueous solution by *Tectona grandis* l.f.(teak leaves powder)," *BioResources* 5(1), 438-454.

Sud, D., Majayan, G., and Kaur, M. P. (2008). "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review," *Bioresour. Technol*. 99(14*)*, 6017- 6027.

Tan, I. A. W., Hameed, B. H., and Ahmad, A. F. (2007). "Equilibrium and kinetic studies on basic dye adsorption by oil palm fiber activated carbon," *Chem. Eng. J*. 127, 111-119.

Tofan, L., Păduraru, C., Bîlbă, D., and Rotariu, M. (2008). "Thermal power plants ash as sorbent for the removal of Cu(II) and Zn(II) ions from wastewaters," *J. Hazard. Mater.* 156, 1-8.

Villaescusa, I., Miralles, N., and Hidalgo, S. (2006). "Removal of lead(II) and cadmium(II) from aqueous solution using grape stalk waste," *J. Hazard. Mater*. 133(1-3), 233-241.

Whang, J., and Chen, C. (2009). "Biosorbents for heavy metals removal and their future," *Biotechnol. Adv*. 27(2), 195-226.

Yao, Z.-Y., Qi, J.-H., and Wang, L. H. (2010). "Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) ions onto chestnut shell," *J.Hazard. Mater*. 174, 137-143.

Article submitted: June 5, 2011; Peer review completed: July 28, 2011; Revised version received and accepted: August 3, 2011; Published: August 5, 2011.