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ORIGINAL PAPER

A low-cost sorbent for removal of copper ions from wastewaters based on sawdust/fly ash mixture

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Abstract In the present work, a low-cost sorbent prepared from mixed local conifer sawdust (SW) and fly ash (FA) provided by a Romanian power plant was developed. On the basis of the preliminary studies, both materials were qualified as suitable sorbents for the removal of copper ions; however, the sorption capacity and material structures of the SW is influenced by the FA. Therefore, a sorbent based on SW–FA mixture is proposed in this study for the removal of copper ions to improve the efficiency of the SW alone. The sorption capacity of the novel sorbent toward Cu(II) ion removal from aqueous solution has been investigated by employing the regression modeling techniques. In order to describe the sorption equilibrium, the obtained data were fitted using the classical isotherm models. In addition, the experimental design and response surface methodology have been applied for modeling and optimization of the Cu(II) removal process. The operational parameters used in the experimental design were as follows: the initial copper concentration, pH of initial solution and sorbent dose. The maximum removal efficiency of Cu(II) was 79.56 %, which was experimentally validated.

Keywords Copper ions · Isotherm · Low-cost sorbent · Modeling · Optimization · Response surface methodology

Introduction

The contamination of the surface waters with heavy metal ions stemming from contaminated wastewater discharges is a serious environmental issue and exhibits health hazard as these pollutants are nonbiodegradable, toxic and tend to be accumulated in living organisms (Larous et al. 2005). Therefore, the removal of heavy metals ions from waters and wastewater streams is an important step for upgrading the water quality and to provide healthy water supply (Acar and Eren 2006).

Copper is a widely used element which is basically used in electrical and electroplating industries. According to the report of the World Health Organization, copper is among the most toxic metals that affect the environment. The intake of excessive doses of copper may cause liver and kidney diseases (Kavakh et al. 2007). Moreover, copper is carcinogenic and mutagenic. Such aspects stand as a motivating factor for many research studies regarding the copper removal from the wastewater streams.

Nowadays, the conventional methods for heavy metal removal involve chemical precipitation (Islamoglu et al. 2006); electroflotation (Srinivasan and Subbaiyan 1989); membrane technologies (e.g., polymer-assisted and micellar-enhanced ultrafiltration) (Cojocaru and Zakrzewska-Trznadel 2007; Xiarchos et al. 2008); adsorption on activated carbon (Chen and Wu 2004; Gupta and Ali 2008; Reed and Nonavinakere 1992) and ion exchange (Hamdaoui 2009). These methods are efficient when heavy metals pollutants are present in high concentrations in wastewater streams. At low concentrations of dissolved metal (1–100 mg/L), the conventional methods may be ineffective or too expensive (Cordero et al. 2004). In order to treat wastewaters containing heavy metals in low concentrations, it is preferable to use sorption techniques based

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on inexpensive sorbent materials (Buema et al. 2013; Ciobanu et al. 2013; Mittal et al. 2008, 2009, 2010a, b; Gupta et al. 2007, 2009a, 2011a, b; Jain et al. 2003).

Numerous investigations have been carried out to identify new and low-cost sorbents for heavy metal ion removal (Sharaf and Hassan 2013). Inexpensive materials can be mentioned for this purpose, e.g., natural inorganic materials (Gedik and Imamoglu 2008; Taqvi et al. 2006), fly ash (FA) (Gupta et al. 1998; Gupta and Ali 2004; Harja et al. 2011; Mishra and Tripathi 2008), peat (Brown et al. 2000), peat moss (Gupta et al. 2009b), algae (Davis et al. 2003; Gupta and Rastogi 2008a, b), yeast biomass (Cojocaru et al. 2009; Zamani et al. 2013), rice husk (Nakbanpote et al. 2007), sawdust (SW) (Acar and Eren 2006; Ajmal et al. 1998; Alkam et al. 2002; Khalid et al. 2005; Larous et al. 2005; Memon et al. 2007; Sciban et al. 2006, 2007; Yu et al. 2001) and others. Among these cheap sorbents, the agricultural waste materials have attracted special attention since such materials can be obtained from naturally occurring and renewable biomass (Memon et al. 2007). Particularly, the agricultural by-products could be considered to be used as metal-binding materials. For example, it is well known that the vegetal materials, i.e., wood, peat are able for binding the metal ions by different mechanisms such as ion exchange, complexation, and surface adsorption. The polar functional groups (carbonyl, carboxyl, hydroxyl and phenolic) from the structure of such kind of materials could be involved in metal binding via the above mentioned mechanisms. The use of large quantities of wastes from agricultural production for the treatment of wastewaters is an attractive and promising option with several benefits for the environment. First of all, it reduces the cost of disposal of waste materials, and secondly, it converts the agricultural wastes into useful and inexpensive sorbents for water purification (Gupta et al. 2010; Larous et al. 2005).

Locally available SW is one of the most attractive waste materials for removing copper from wastewaters. SW is generated as a waste in timber industry, and it is usually used as domestic fuel, packing material or as filler in composite materials (Acar and Eren 2006; Djeribi and Hamadaoui 2008; Khalid et al. 2005; Larous et al. 2005; Sciban et al. 2007; Yu et al. 2001; Zainul et al. 2009). Likewise, the wood SW can be used as low-cost sorbent for copper removal, particularly owing to its lignocellulosic composition (typically, it contains 45–50 % cellulose and 23–30 % lignin). In the SW, the active groups considered for metal-binding function are the hydroxyl, phenol and carboxyl groups in the cellulose and lignin structures (Sciban et al. 2007; Zainul et al. 2009). In spite of large number of works reported for sorption of heavy metal ions by SW and other low-cost sorbents (Acar and Eren 2006; Ajmal et al. 1998; Alkam et al. 2002; Curteanu et al. 2013; Harja et al. 2012a, b, c; Larous et al. 2005; Lim et al. 2012; Khalid et al. 2005; Plazinski 2012; Sciban et al. 2006), this process is still in the stage of laboratory-scale study.

In the present, impressive amounts of ash are worldwide generated. Its valorization as adsorbent could be achieved as an individual component or in mixture with other wastes. This fact is a challenge for the researchers, taking into consideration that the purchasing of the SW is not necessary because there are appreciable SW amounts as waste from the wood processing industry. Also, the FA is known as an efficient sorbent for heavy metal ions (including Cu(II)), especially after some pretreatments according to our previous studies (Harja et al. 2012a). FA is generated by power plants as a waste of the firing technology. It contains various metallic oxides (i.e., silica, aluminum and iron oxides), as well calcium and magnesium hydroxides (Harja et al. 2011) FA exhibits an alkaline character (the pH is around 8 in aqueous solution). This makes the FA suitable for applications in wastewater treatment procedures of acidic waste streams due to its alkaline character. Beside the copper ions removal from acid wastewater using this type of new sorbent (which contains ash with alkaline character), the neutralization of wastewater is also accomplished.

Generally speaking, the reported retention capacity for Cu(II) from aqueous solutions on several sorbent materials widely ranges (i.e., from 1.8 up to 5.2 mg/g), depending on the initial solution concentration, pH, sorbent dose and stirring regime (Harja et al. 2012a, b). According to the literature (Memon et al. 2007; Ngah and Hanafiah 2008; Harja et al. 2012a, b), the SW is slightly better performing than the FA in terms of heavy metal ion removal. However, the FA is more resistant than SW in acidic media due to its oxide composition having alkaline character. As previously mentioned, the addition of small amounts of FA to SW exhibits a neutralizing effect, which in turn allows this mixture to be used in acidic solutions as well.

The main technical disadvantage of the SW as sorbent is related to its low stability outside of the neutral pH value. The main constituents of the SW are polysaccharides which are hydrolyzed into monosaccharide in acidic medium. During the hydrolysis, the structure of the SW is destroyed and the sorption capacity decreases (Yuan et al. 2004). On the other hand, the SW loses weight upon reaction with alkaline components which phenomenon is well known from pulping and in the textile industry. In alkaline media, the reducing glucose group of a cellulose molecule is isomerized that results in migration of the carbonyl group along the carbon chain (Pavasars et al. 2003).

Wood is a composite material based on the carbohydrates and lignin linked in a 3D structure, with a chaotic orientation in all spatial directions. Thus, the structure of the cell wall of a wood tissue consists of polymers with a spatial structure such as cellulose–lignin–hemicelluloses–lignin–polyuronides. On studying the stability, the size and shape of ligno-polysaccharide macromolecules Brownell et al. (1986) showed that the chemical bonds between lignin and carbohydrates are stable in alkaline environments, while the ester bonds are destroyed under the same conditions. Moreover, the acidic media has a negative action toward the stability of the wood by destroying the chemical bonds from cellulose, acetal (ketal), phenyl glycosidic and ester bonds from the ligno-polysaccharide macromolecules.

Because both FA and SW are considered wastes with negative environmental impact, we proposed the valorization of these wastes as low-cost sorbent. Of course, each of these wastes can be used as low-cost sorbent, but by mixing of them, the pH working range of the sorbent increases (due to the alkaline character of FA) even if the total sorption capacity decreases (this is explained due to the low capacity of ash in comparison with the sorption capacity of SW; the diminishing of the total capacity is proportional with the rate of the FA and SW). So, the mixed sorbent could be used even in acid media due to the alkaline character of FA that actions as a neutralizer of the wastewater.

Thus, utilization of the SW and FA for wastewater treatment has the advantages of the abundant availability in supply at no or low cost and the elimination of wastes that could exhibit environmental problems if not utilized. Based on these premises, the idea to combine these two inexpensive materials in order to develop a new mixture with higher sorption capacity and better stability in acidic media was the main objective of this work with a special emphasis on the process intensification and optimization.

Materials and methods

Aqueous solutions containing copper have been prepared by dissolution of copper sulfate of analytical reagent grade in distilled water. The adjustments of solution pH were made using 0.1 N sulfuric acid and 0.1 N sodium hydroxide solutions.

The conifer wood was converted to SW in the frame of the furniture factory from Iasi city, from where we took it as waste in order to be valorized. The SW used had the particle size ranging between 0.5 and 1.5 mm after sieving. The samples of FA were obtained from thermal power plant of Municipality of Iasi (CET II, Iasi, Romania), having spherical shape with diameter of 100–150 μm and dark gray color (Harja et al. 2011). Both sorbents were prepared by washing with deionized water several times and drying in a hot air oven at 105 °C for 24 h and stored in desiccator for further use.

A new sorption material (SWFA) was obtained by mixing the SW and FA in a weight ratio of 4:1 according to preliminary tests that showed the advantages of combining the two materials. Particularly, this study was basically focused on the utilization of the SW and the FA was mainly used as an adjuvant for improving the SW resistance toward chemical agents, without significantly influencing the sorption capacity of the initial material (SW). The mixture of both sorbents is packed into a textile mesh veil, having the following dimensions: 10 × 10 × 5 mm with mesh of 0.1 mm.

A pH meter with a combined glass electrode, included in the Multi-Parameter Consort C831, was used for pH measurements. The concentration of Cu(II) in aqueous solutions has been determined with using spectrophotometer Buck Scientific for heavy metal detection by atomic adsorption spectroscopy.

The sorption process was studied in batch scale experiments by shaking 1.5 g of SW–FA mixture (4:1 weight ratio) with 100 mL of copper solution of different initial concentrations varying from 25 up to 200 mg/L. The pH of the solution was ranged between 3 and 5, and shaking was performed at 300 rpm at 20 °C. Samples were left for 24 h to reach the equilibrium. The filtrate obtained was analyzed for copper concentration by atomic absorption in order to establish the content of copper ions. The sorption metal uptake at equilibrium was calculated from the sorption mass balance as follows:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m \cdot 1000} \tag{1}$$

where q_e: the equilibrium adsorption capacity (mg/L); C_0 and C_e: the initial and final copper concentrations, respectively (mg/L); V: the solution volume (mL); m: the weight (g) of the sorbent used in the experiments.

The experiments were carried out with the objective to optimize the efficiency of the sorption process. The removal efficiency (Y, %) of the copper ions from aqueous solution was specified as the optimization criteria for the objective function, which was determined with using the following equation:

$$Y = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e are the initial and final copper ion concentrations, respectively (mg/L).

All experiments regarding the optimization were carried out in batch mode and the initial copper concentrations varied from 20 up to 80 mg/L. The samples were left for

24 h to reach the sorption equilibrium. The final copper concentrations were analyzed, and the removal efficiency was determined in accordance with Eq. (2).

Results and discussion

Adsorption isotherms

The sorption process of copper ions could be considered to be complex procedure, due to the different retention mechanisms and considering the different compositions and structures of the studied composite sorbent. However, the models proposed by different researchers for the adsorption processes can represent a suitable tool for the investigation of such complex sorption processes. The study of the adsorption isotherm is fundamental and plays an important role in the design of sorption systems and in the determination of the maximum sorption capacity (Ho et al. 2002). The equilibrium models which can describe with high reliability the experimental results were considered in this study. The studied models deal with equilibrium models with two parameters such as the Freundlich and Langmuir isotherm equations, as well as equilibrium models with three parameters, i.e., Toth and Sips isotherm equations. The well-known expressions of the Freundlich and Langmuir isotherm equations with two parameters are given by Eqs. 3, 4 (Ho et al. 2002; Nethaji et al. 2013; Mohammadi et al. 2010):

The Freundlich isotherm is as follows:

$$q_e = K_F C_e^{1/n_F} \tag{3}$$

where q_e: the equilibrium adsorption capacity (mg/g); C_e: equilibrium concentration (mg/L); K_F: the Freundlich adsorption equilibrium constant (L/g); n_F: Freundlich isotherm parameters.

The Langmuir isotherm is as follows:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4}$$

where C_e: the equilibrium concentration (mg/L); q_e: the amount of copper adsorbed at equilibrium (mg/g); q_{max}: q_e for a complete monolayer (mg/g), which gives the maximum sorption capacity of sorbent; K_L: the Langmuir adsorption equilibrium constant (L/g).

The easiest method to determine the isotherm constants for two parameter models is to use the linearization technique (Ho et al. 2002). Thus, the applicability of Freundlich and Langmuir adsorption isotherms was analyzed by plotting $\log(q_e)$ against $\log(C_e)$ and (C_e/q_e) against (C_e), respectively. The values of the Freundlich constants (K_F and n_F) and Langmuir constants (q_{max} and K_L) computed by linearization method are summarized in Table 1.

Table 1 Isotherm constants for copper sorption by SWFA from aqueous solutions at $T = 293$ K

Type of isotherm	pH = 3	pH = 4	pH = 5
Freundlich	$n = 3.11$	$n = 4.47$	$n = 4.61$
	$K_F = 0.58$	$K_F = 1.15$	$K_F = 1.34$
Langmuir	$q_{max} = 2.68$	$q_{max} = 3.05$	$q_{max} = 3.22$
	$K_L = 1.3986$	$K_L = 4.34$	$K_L = 4.59$
Toth	$K_t = 13.92$	$K_t = 16.12$	$K_t = 10.37$
	$a_t = 32.57$	$a_t = 18.25$	$a_t = 14.7$
	$z = 0.773$	$z = 0.762$	$z = 0.809$
Sips	$q_{sm} = 2.98$	$q_{sm} = 3.256$	$q_{sm} = 3.299$
	$b = 1.4971$	$b = 3.9064$	$b = 4.5057$
	$n_S = 5.6242$	$n_S = 5.704$	$n_S = 8.5689$

The Toth isotherm model, according to Eq. (5), could describe the adsorption process in heterogeneous systems:

$$q_e = \frac{K_t C_e}{(a_t + C_e)^{1/z}} \tag{5}$$

where C_e: equilibrium concentration (mg/L); q_e: the amount of copper adsorbed at equilibrium (mg/g); K_t: the Toth adsorption equilibrium constant (L/g); a_t and z: the Toth model parameters.

It is well known that the Sips model is based on a combination of the Langmuir and Freundlich models, as defined by the Eq. (6):

$$q_e = \frac{q_{sm} b C_e^{1/n_s}}{1 + b C_e^{1/n_s}} \tag{6}$$

where C_e: the equilibrium concentration (mg/L); q_e: the amount of copper adsorbed at equilibrium (mg/g); q_{sm}: maximum adsorption capacity of sorbent for Sips model (mg/g); b and n_S: the Sips model parameters.

The isotherm parameters of Toth (K_t, a_t, z) and Sips (q_{sm}, b, n_S) models were calculated with using the nonlinear regression method from MATLAB software, according to data presented in Table 1.

The main advantage of the nonlinear regression method comparing with the linear regression stems from the fact that the nonlinear technique provides a mathematically rigorous method for the determination of the isotherm parameters using the original form of the isotherm equation (He et al. 2010). In this way, the calculus errors (issued due to the linearization algorithm) can be avoided.

The values of the parameters of Langmuir isotherm (Table 1) point out that the maximum sorption capacity for Cu(II) ions, q_{max}, is about 3.22 mg/g at room temperature and at pH of 5. Under the same conditions, the Sips isotherm exhibits almost the same result, i.e., a sorption capacity of 3.29 mg/g. The predicted sorption

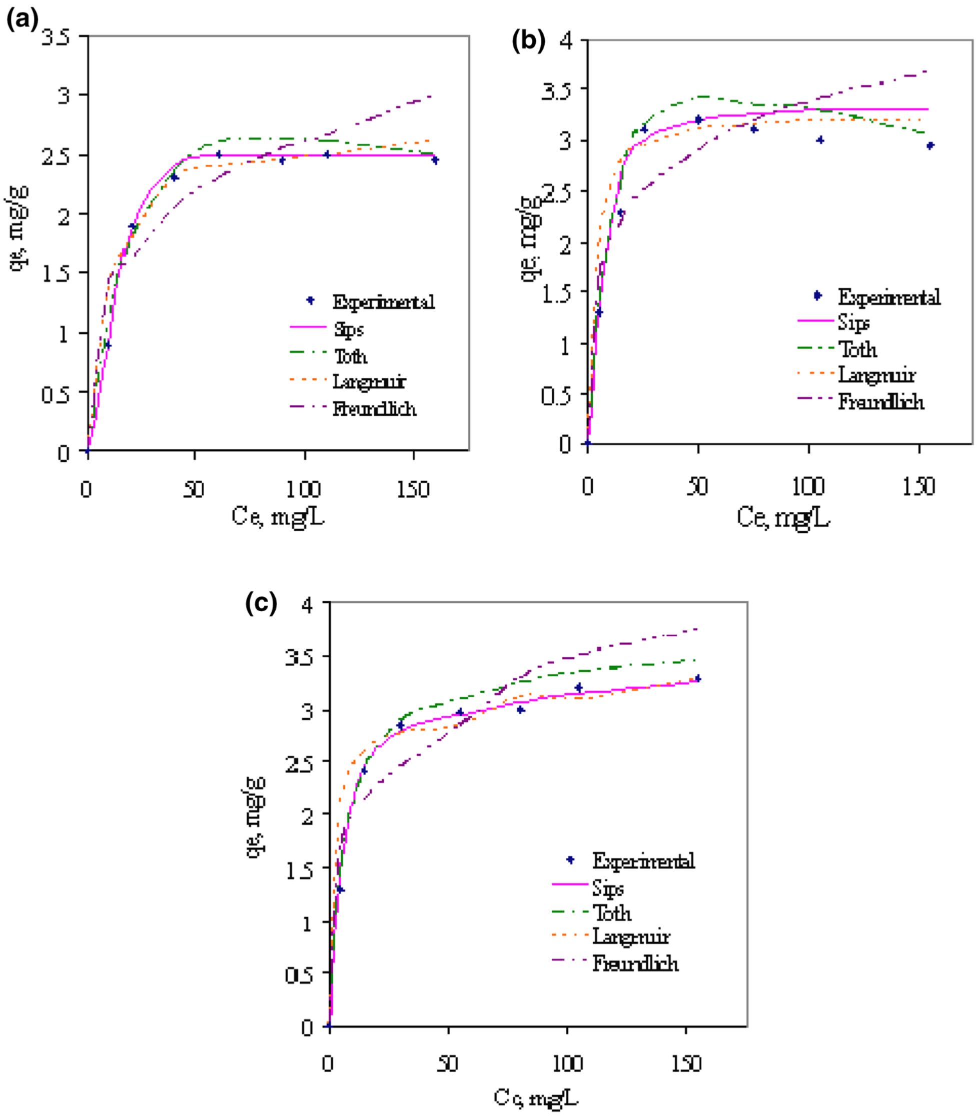

Fig. 1 Sorption isotherms obtained at 293 K for different pH values for SWFA sorbent **a** solution pH = 3, **b** solution pH of 4 and **c** solution pH of 5

capacities were determined by means of isotherm constants and mass balance equations and were compared with the experimental data of Fig. 1, where the influence of pH on the sorption capacity can be observed. An increase in pH from 3 to 5 results in a slight increase in the sorption capacity.

The degree of fitting the equilibrium models with the experimental data was ascertained by residual analysis using absolute errors (EABS) and average relative error (ARE) which can be calculated with using the following equations (Ng et al. 2002; Kumar et al. 2008a, b):

$$\mathrm{ARE} = \frac{100}{n}\sum_{i=1}^{n}\left(\frac{\left|q_{e,\exp} - q_{e,\mathrm{calc}}\right|}{q_{e,\exp}}\right)_i \tag{7}$$

$$\mathrm{EABS} = \sum_{i=1}^{n}\left|q_{e,\exp} - q_{e,\mathrm{calc}}\right|_i \tag{8}$$

Table 2 The residual error analysis of isotherm data for copper sorption on SWFA sorbent

Experimental conditions	Isotherm model of	ARE	EABS
pH = 3	Sips	1.26	0.21
293 K	Toth	6.72	0.78
	Langmuir	9.34	0.80
	Freundlich	17.38	2.03
pH = 4	Sips	7.54	1.35
293 K	Toth	7.15	1.30
	Langmuir	14.32	1.95
	Freundlich	14.47	2.58
pH = 5	Sips	4.27	0.61
293 K	Toth	3.92	0.55
	Langmuir	12.26	1.47
	Freundlich	13.84	2.23

where $q_{e,\mathrm{exp}}$: the experimental sorption capacity at equilibrium (mg/g); $q_{e,\mathrm{calc:}}$ the calculated sorption capacity by means of model (mg/g); n: the number of data points.

All statistical functions were employed for the residual analysis and for testing goodness of fit of equilibrium models with experimental data. The results concerning the residual error analysis are summarized in Table 2.

As it can be seen from Table 2 and Fig. 1, the Sips isotherm provided the best model for the copper sorption on SWFA sorbent at $T = 293$ K. The Toth model provides also a good prediction for the sorption equilibrium state. The Langmuir model describes satisfactorily the experimental data under the same conditions, while the Freundlich isotherm exhibits the highest lack of fit. The last model (i.e., Freundlich) predicts adsorption capacities lower than the experimental data at lower copper concentration and higher than the experimental values at high copper concentrations. Thus, it may be concluded that the equilibrium models with three parameters (Sips and Toth) provide a better fit for the experimental data than the models working with two parameters (Langmuir and Freundlich).

Based on the equilibrium constant values K_L, (Langmuir model), the change in the apparent free energy of Cu(II) sorption onto SWFA was evaluated using the following thermodynamic equation:

$$\Delta G = -R_g T \ln K_{\mathrm{L}} \tag{9}$$

where ΔG: variation of apparent free energy (J/mol); T: the absolute temperature (K); R_g: the gas constant (J/mol K).

At pH 4 and 5, the calculation of apparent free energy parameter gives the average numerical value of $\Delta G = -3.775 \pm 0.231$ kJ/mol. The negative value of ΔG shows the spontaneous nature of the sorption process under the experimental conditions.

On the basis of Langmuir equation analysis, the dimensionless parameter of the equilibrium R_{L}—known as separation factor—has been calculated as follows:

$$R_{\mathrm{L}} = \frac{1}{1 + K_{\mathrm{L}} C_0} \tag{10}$$

where C_0 is the initial concentration of solute (mg/L).

Depending on the value of the separation factor R_L, several types of sorption can be distinguished (Sari and Soylak 2007):

Case 1: favorable sorption, when $0 < R_{\mathrm{L}} < 1$;
Case 2: unfavorable sorption, when $R_{\mathrm{L}} > 1$;
Case 3: linear sorption, when $R_{\mathrm{L}} = 1$;
Case 4: irreversible sorption, when $R_{\mathrm{L}} = 0$.

Taking into account that the initial solute concentration changed in these experiments from 25 to 200 mg/L, the corresponding values of the separation factor R_{L} was found to be in the range of 0.0035–0.0279. The results support the notion that the sorption of Cu(II) onto the SWFA is favorable under the conditions used in this work.

Response surface modeling

The determination of the empirical model expression for the simulation of the system response to the variation of the input controllable variables is the main step in the response surface methodology (RSM)-based optimization process. RSM is a widely used optimization technique that allows the location of optimum point on the modeled response surface, which corresponds to the optimum conditions where the optimum system response is observed (Rajkumar and Muthukumar 2012; Cicek et al. 2008; Marchitan et al. 2010; Soreanu et al. 2009). The most common models used in RSM are polynomial regression equations having the general expression (i.e., Marchitan et al. 2010):

$$\hat{Y} = b_0 + \sum b_i x_i + \sum b_{ii} x_i^2 + \sum b_{ij} x_i x_j \tag{11}$$

where $\hat{Y}$: predicted response (e.g., predicted removal efficiency); x_i: factors (input variables); b_0, b_i, b_{ii}, b_{ij}: regression coefficients (offset term, main, quadratic and interaction terms).

It should be noted that in the frame of RSM, the factors are usually scaled up to coded levels in order to facilitate the calculations. Basically, the extent of each factor involves three different coded levels from low (−1) to medium (0) and to high (+1). In addition, depending on the type of the experimental design, the axial levels (±α) can be also considered.

Development of the polynomial model requires the selection of an appropriate experimental design so that information on the response can be obtained in an efficient way. The central composite design (CCD) is the most popular one due to its ease of use in sequential experimentation. Comparing with conventional methods of experimentation where the factors are varied one by one, the experimental design involves the simultaneous variation of the factors. Such approach is very useful for the detection of the interaction effects between different factors, and this technique results in reduction in experimental time, use of reagents and expenditures.

The regression coefficients for empirical (polynomial) model are calculated based on information extracted from experimental design matrix. The ordinary least squares (OLS) method is usually used, and the estimations of the regression coefficients can be written as follows (Akhnazarova and Kafarov 1982; Bezerra et al. 2008; Marchitan et al. 2010; Myers and Montgomery 2002):

$$\mathrm{b} \ = (X^{\mathrm{T}} X) X^{\mathrm{T}} Y \tag{12}$$

Table 3 Central composite orthogonal design and experimental response

Run number (*N*)	Factors (input variables)						Response
	Initial concentration of Cu(II) (mg/L)		pH of aqueous solution		Sorbent dose (% w/v)		Removal efficiency *Y* (%)
	C_0 (mg/L)	Level[a] x_1	*pH*	Level[a] x_2	*D*[b]	Level[a] x_3	
1	75.00	1	5.00	1	2.20	1	68.14
2	25.00	−1	5.00	1	2.20	1	77.01
3	75.00	1	3.00	−1	2.20	1	56.37
4	25.00	−1	3.00	−1	2.20	1	66.75
5	75.00	1	5.00	1	1.50	−1	46.74
6	25.00	−1	5.00	1	1.50	−1	54.24
7	75.00	1	3.00	−1	1.50	−1	35.57
8	25.00	−1	3.00	−1	1.50	−1	40.95
9	80.38	α	4.00	0	1.85	0	46.88
10	19.63	$-\alpha$	4.00	0	1.85	0	57.74
11	50.00	0	5.22	α	1.85	0	71.29
12	50.00	0	2.79	$-\alpha$	1.85	0	55.21
13	50.00	0	4.00	0	2.28	α	75.26
14	50.00	0	4.00	0	1.42	$-\alpha$	50.77
15	50.00	0	4.00	0	1.85	0	63.42
16	50.00	0	4.00	0	1.85	0	64.05

[a] -1 = low value, 0 = center value, $+1$ = high value, $\pm\alpha$ = star point value

[b] Sorbent dose of 2.20 % w/v corresponds to 2.20 g added sorbent per 100 mL solution

where b: the vector of the regression coefficients; X: the design matrix for the input variables; Y: the column vector of experimental response obtained according to the experimental design.

In this work, the central composite experimental design CCD of orthogonal type has been applied for developing the polynomial regression model in order to set up a functional relation between the removal efficiency (metal uptake efficiency) and the experimental factors. The most important factors that influence the removal efficiency (response) are the initial concentration of copper ions in aqueous solutions (C_0, mg/L), initial pH of the solution and the sorbent dosage (*D*, % w/v). The real values of these factors as well as their coded limits are specified in Table 3 where the central composite experimental design is given.

In accordance with the results given in the experimental design (Table 3.), the coefficients of the polynomial regression equation have been computed by means of OLS method and the obtained polynomial model (with coded variables) can be written as follows:

$$\hat{Y} = 63.3 - 4.14x_1 + 6.03x_2 + 11.00x_3 - 7.54x_1^2 - 0.796x_1x_3$$
$$\text{subjected to}: x_j \in \text{Surf}; \text{Surf} = \{x_j | -\alpha \le x_j \le +\alpha\}; \quad j = 1, 2, 3; \tag{13}$$

where: x_1, x_2 and x_3: the coded levels of factors; $\alpha = 1.215$ is the star point in experimental design that gives the limits of the valid region; *Surf*: the region of experimentation.

In Eq. (13), only the significant regression coefficients were kept, in concordance with the Student's *t* test, which gives the statistical validation of the significance for each regression coefficient (Akhnazarova and Kafarov 1982). The goodness of fit between model and experimental data was checked using *F*-ratio test (Akhnazarova and Kafarov 1982) for a confidence level $p = 0.05$ and degrees of freedom $f_1 = 9$ and $f_2 = 1$. The F_C-ratio was calculated as the ratio between the variance of residual and the variance of experimental error. The F_C-ratio was found to be smaller than the tabulated value $F_{\text{tab}}\ (p,\ f_1,\ f_2)$, leading to the conclusion that the response surface model is statistically validated for the prediction in the experimental range. In addition, the empirical model in terms of real variables has been deduced based on substitution technique and may be written as follows:

$$\hat{Y} = -49.0 + 1.21\text{C}_0 + 6.03\text{pH} + 35.8\ \text{D} - 0.0121\ \text{C}_0^2 - 0.0894\ \text{C}_0\text{D}$$
$$\text{subjected to}: 19.63 \le C_0 \le 80.38(\text{mg/L}); \quad 2.79 \le pH \le 5.22; 1.42 \le D \le 2.28(\%\ \text{w/v}) \tag{14}$$

In Fig. 2, the experimental data are compared with the predicted figures obtained on the basis of the regression model. As it can be seen, the model provides a good fit for the experimental data.

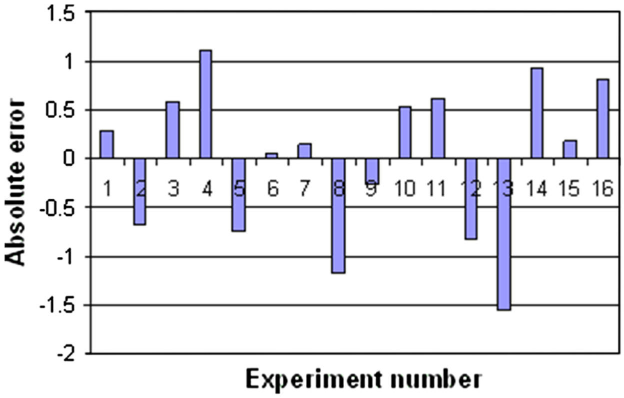

Fig. 2 Absolute error between the experimental removal efficiency data and the predicted values given by the model

Based on statistically validated model, the graphical representations of the response surface were plotted. The most relevant response surface plots and their associated contour-lines maps are illustrated in Figs. 3, 4, 5.

The response surface plots from Figs. 3, 4, 5 show the influence of the experimental factors on the copper removal efficiency. According to the response surface plots, all factors (variables) have significant influence on the sorption process. However, these factors have different impacts. For example, the decrease in initial copper concentration leads to a nonlinear increase in removal efficiency, while the increase in the initial solution pH and the sorbent dose results in linear and, respectively, nonlinear increase in the response. The nonlinear influence of the initial copper concentration and sorbent dose on the response is attributed to the quadratic term and interaction effects in case of initial concentration and to the interaction effect in case of the sorbent dose. Therefore, the increase in C_0 factor up to 41 mg Cu(II)/L leads to an increase in the

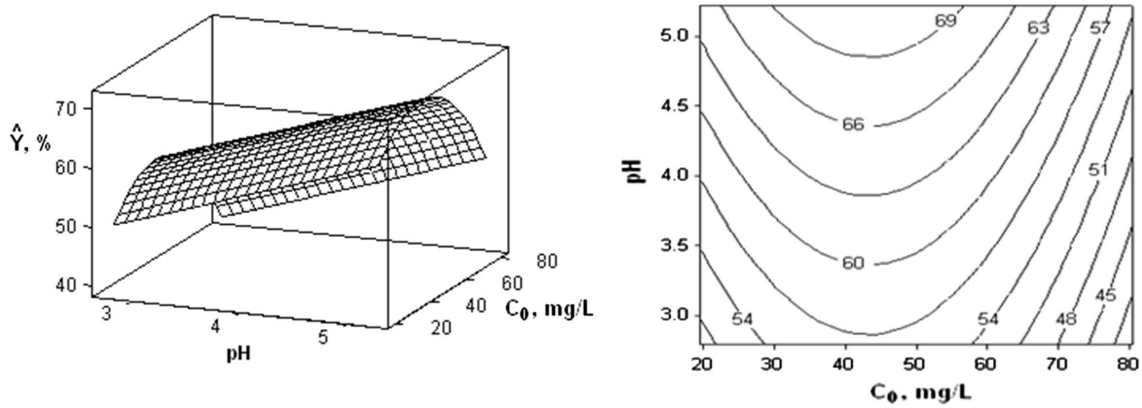

Fig. 3 Response surface plot and *contour-lines* map depending on variables pH and C_0, holding the third variable at its center level $D = 1.85$ % (w/v)

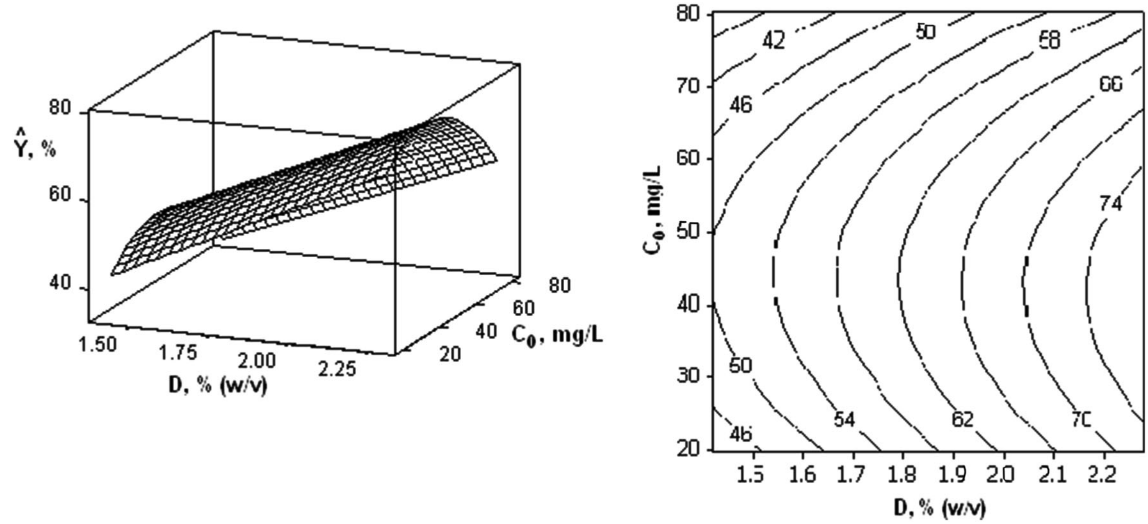

Fig. 4 Response surface plot and *contour-lines* map depending on variables D and C_0, holding the third variable at its center level pH = 4

response with reaching a maximum value followed by a decreasing tendency. The sorbent dosage factor, D has a constant positive influence on the response, within the dose range tested, 1.50–2.20 % w/v, while the contribution of the C_0 interaction is less visible.

The parameter solution pH is also an important factor and the increase in pH from 3 to 5 leads to a visible linear increase in removal efficiency. According to the response surface model, the interaction effects between factors are considered to be insignificant in the presented case study with the exception of interactions between the initial copper concentration and sorbent dose.

Response surface optimization

The aim of the process optimization is to figure out the optimal values of the factors inside of the region of experimentation in order to maximize the removal efficiency. To accomplish this goal, the polynomial regression equation Eq. (15) has been used as the objective function for numerical simulations and process optimization. Thus, the optimization problem may be presented as given:

$$\max_{x}\left\{\hat{Y}(x_1, x_2, x_3,)\right\}$$
$$\text{subjected to}: x_j \in \text{Surf}, j = \overline{1,3} \qquad (15)$$

In order to solve the given optimization problem, a method based on Monte-Carlo simulations (Redhe et al. 2004) was used. The stochastic simulations were carried out with using a multistage zooming-in approach in order to figure out the optimal solution value more accurately. The results of optimization are summarized in Table 4, where both the coded levels and the actual optimal values of the factors are given. In addition, a validation experiment was carried out in order to confirm experimentally the computed optimal solution.

The removal efficiency obtained experimentally under the optimal conditions (Table 4.) has the maximum value of 79.56 %. This is the best experimental value found within the region of experimentation. The disagreement between the response given by the empirical model and the experimental data is slightly higher than the value of the maximum residual error calculated above, but still it is in agreement with the accepted residual error of about 5 % in practice.

The results for Cu(II) removal from aqueous solutions are presented in Fig. 6 for both raw sorbent materials (FA, SW) and for the mixture (SWFA).

The results shown in Fig. 6 reveal that the removal efficiency of SWFA sorbent increases in comparision with the unmodified FA sorbent, however, it slowly decreases in comparison with the performance of the unmodified SW

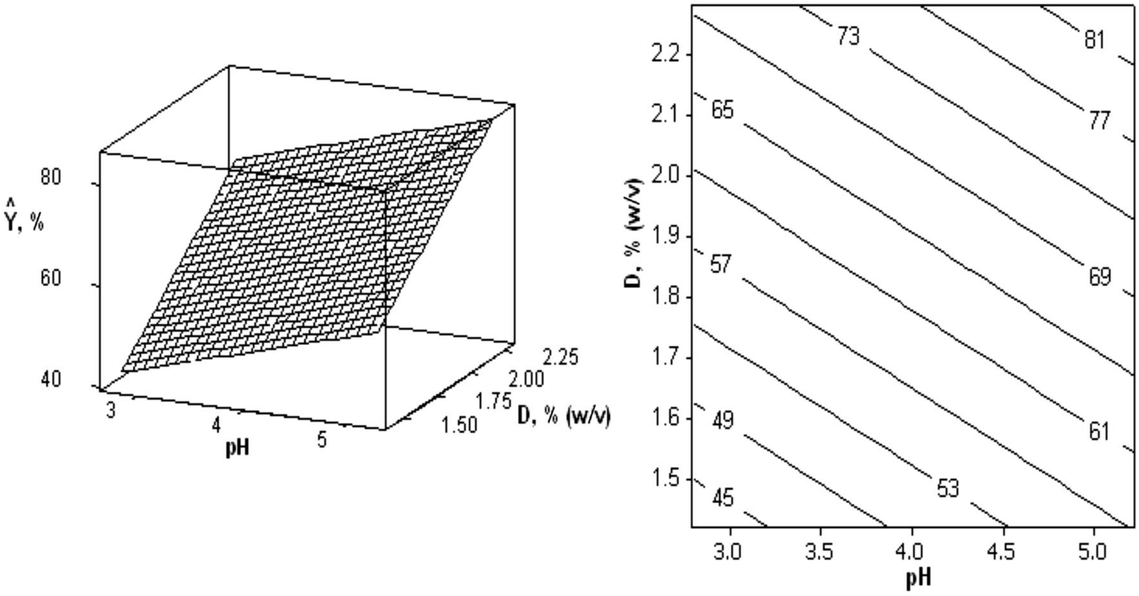

Fig. 5 Response surface plot and *contour-lines* map depending on variables pH and D, holding the third variable at its center level $C_0 = 50$ mg/L

Table 4 Optimal values of the factors into the region of experimentation for maximum removal efficiency

Initial concentration of Cu(II) in aqueous solutions		pH of solution		Sorbent dose		Y (%) experimental value	$\hat{Y}$ (%) model-based value
x_1	C_0 * (mg/L)	x_2	pH*	x_3	D* (% w/v)		
−0.34	41.54	1.22	5.22	1.22	2.28	79.56	84.99

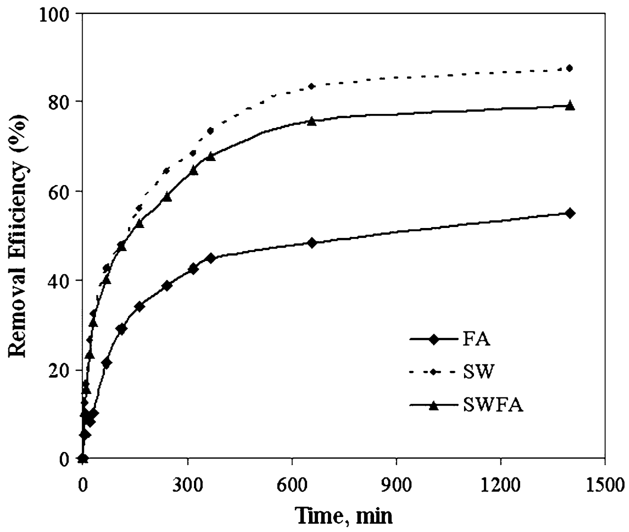

Fig. 6 Removal efficiency of different sorbents for copper removal $T = 293$ K, pH = 5.2, $C_0 = 42$ mg/L

sorbent. The experimental results presented for all three sorption materials are in full concordance with the results obtained under the equilibrium conditions, which were taken into consideration at the modeling and optimization process.

This new type of sorbent material is recommended for wastewater treatment with initial pH over 4, because the FA from the mixture contributes to the increase in pH value (efficiency is maximum at pH 5.2) and for the removal efficiency of about 80 %.

Conclusion

The results obtained in this study show that the mixture of FA and SW in a weight ratio of 1: 4 can be applied as low-cost sorbent for the removal of Cu(II) ions from wastewaters.

Generally, it can be stated that the disadvantage of the low-cost sorbents such as the raw FA is related to the relatively low binding capacity for heavy metals. In this respect, the enhancement of the sorption capacity by mixing the FA with other inexpensive sorbent with higher sorption capacity such as SW was investigated. The mixture of these two low-cost sorbents presents a porosity due to the content of FA, an alkaline character that is able to neutralize the acidic media, as well chelating properties due to ligno-cellulosic structures of SW.

Four different isotherm models (i.e., Freundlich, Langmuir, Sips and Toth) with two and three parameters were used for modeling and evaluation of the equilibrium data. The Sips model was found to be the most suitable equation for describing the experimental data at $T = 293$ K. According to Langmuir and Sips isotherms, the maximum sorption capacity of the novel type material was found to be 3.22–3.29 mg Cu(II)/g at 293 K. The negative value of free energy of $\Delta G = -3.775 \pm 0.231$ kJ/mol underlines the spontaneous nature of sorption process carried out at a solution pH ranged between 4 and 5.

The optimal conditions of sorption determined by RSM and experimental design were as follows: $C_0 = 41.54$ mg/L, pH = 5.22 and $D = 2.28$ % w/v. Under such conditions, the experimental removal efficiency for copper was 79.5 %, which represents the best experimental maximum point for the mixed sorbent.

A comparison between the FA, SW and mixture of those, carried out in a batch system under the same experimental conditions, indicated a multifold increase in the removal rate of Cu(II) ions when novel type of sorbent is used.

This study shows a possible utilization of two waste materials which can be found in significant amounts in Romania. These wastes can be used as efficient sorbents for Cu(II) removal from acidic wastewater streams. According to this study, the use of the mixture of these wastes, usually disposed on landfills, can contribute to the decrease in the ecological footprint of the involved industrial activities. After the sorption process, the used and depleted sorbent can be burnt after drying due to the high organic content of the SW and can be used for heat cogeneration. Such type of application is in full accordance with the pollution prevention principles and has beneficial impacts on both the environmental and human health.

The obtained results suggest the continuation of the study in order to determine the optimum ratio of the SW and FA.

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Nomenclature

calc	Subscript indicating the calculated value
exp	Subscript indicating the experimental value
T	Superscript denoting the transpose matrix
*	Superscript indicating optimal value

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