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Removal of zinc and cadmium from an aqueous solution using sawdust as a low-cost adsorbent: application of Plackett–Burman design

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ABSTRACT

In this study, the sawdust was used as an abundant and inexpensive material for the removal of two heavy metals simultaneously from an aqueous solution. In order to evaluate the adsorbent potential of the sawdust, the effects of many operating parameters were studied. The metals considered were zinc and cadmium. The experiments were organized according to a well defined window of a statistical design of experiments. Starting from a large number of operating parameters (type, source, size and quantity of sawdust, temperature, pH, contact time, stirring speed, initial concentrations of cadmium, zinc and salt), a Plackett–Burman design was used to identify the most influential factors on the elimination performance of zinc and cadmium simultaneously with a minimum number of experiments. Effects of these factors were deduced from an interesting statistical treatment of experimental responses. For Zn sorption, the most important factors are mass of sawdust, initial concentration of zinc and time; while for Cd sorption, the most important factors are initial concentrations of zinc and cadmium, pH, mass, type and size of sawdust. The presence of cadmium decreased the removal of zinc considerably and the inverse did not happen. These effects were more remarkable for cadmium (sorption varied from 0 to 80%) than for zinc (sorption varied from 0 to 50%). These results allowed to choose the most important parameters which could be optimized using another designs of experiments, such as Box Behnken or full factorial, and response surface methodology to obtain the best performance of metals sorption.

Keywords: Sawdust; Heavy metals; Adsorption; Design of experiments

1. Introduction

The contamination of water by heavy metals due to industrial waste is causing serious toxicological impacts on the environment [1–4]. Heavy metals often used as basic chemicals or catalysts are present in wastewater streams of many industries such as mining and metallurgical engineering, electroplating, galvanizing, chromium electrolysis, nuclear power operations, semiconductor, aerospace, battery manufacturing, etc. [5,6]. Their toxic effects for living organisms are well documented [6]. The volume of wastewater generated from these processes contains high pollutants concentrations. Hence, it is important to remove toxic heavy metals from wastewater before it is discharged. The elimination of these pollutants from wastewater has always been of interest to researchers [7–9]. The most widely used industrial methods for removing pollutants are coagulations and

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precipitations [10]. For example, heavy metals can be precipitated as insoluble hydroxides at high pH or sometimes as sulphides, but a major problem with these types of treatment is the disposal of the precipitated waste [11]. To remove pollutants from water, the ion exchange which gives a good efficiency does not appear to be practical to waste water treatment because of its high cost [12]. The adsorption with activated carbon can also be highly efficient but its large-scale use as adsorbent is not viable for the same reason mentioned just above. Accordingly, the focus of researchers turned to the use of unconventional methods and materials, such as low-cost adsorbents. Sawdust is one of the most appealing materials for removing pollutants such as dyes, salts and heavy metals from water and wastewater. Sawdust is a by-product generated by the wood industry. It is currently being investigated as an adsorbent to remove contaminants from water because it is abundant, inexpensive and renewable. The value of this material is a topic which is taking more and more importance in the field of applied research [13–27]. It is a waste industrial and artisan biomaterial, it appears as a great efficacy to the removal of some toxic metals [28–30]. Ajmal et al. showed that the removal of copper from river water using sawdust was achieved with 63% efficiency [31]. The effects of contact time, pH concentration, temperature, dose, particle size of sawdust and salinity were also studied. Raji and Anirudhan reported that an adsorption of 100% of chromium (VI) by carbon of sawdust could be achieved under optimized conditions [32].

Zinc is one of the most common elements in the earth's crust. It is found in air, in soil and in water. It is present in all foods. It is also an essential element in our diet. Without enough zinc in the diet, people may experience loss of appetite, a decreased sense of taste and smell, a decreased immune function, a slow wound healing and skin sores. Too little zinc in the diet may also cause sex organs poorly developed and retarded growth in young men. If a pregnant woman does not get enough zinc, her babies may have birth defects. On the other hand, a low concentration of zinc above normal can cause some problems but too much zinc is harmful; large doses taken by mouth even for a short time can cause stomach cramps, nausea and vomiting. If taken longer, it can cause anaemia and decrease the levels of good cholesterol [33]. Zinc in untreated waste water can find its way into the water supply system at levels which are toxic to fish and potentially to humans. It can accumulate in aquatic organisms and can be toxic to species that feed on Ref. [4]. Removing zinc from wastewater is an objective of many researches in chemistry of environment [34–40].

As a by-product of mining and refining of zinc, cadmium is also produced from recycled materials and certain residues or intermediates. Approximately, 10–15% of the total production of Western countries comes from recycled products. In 1994, total world production of cadmium was 18,292 tons/year, while consumption was 16,486 tons/year [41,42]. The toxicity of cadmium to the humans and the environment is now well known; long-term effects of Cd(II) poisoning include kidney damage and changes to the constitution of the bones, liver and blood. Short-term effects include nausea, vomiting, diarrhoea and cramps [42]. In USA, the maximum permissible limit of Cd(II) in drinking water has been set at 0.01 mg/L [43]. The World Health Organization (WHO) recommended maximum permissible limit of Cd(II) in drinking water to be 0.005 mg/L [44]. Removal of cadmium from water has been the objective of different works [45–52].

When different heavy metals are present together, their simultaneous removal from aqueous solution or wastewater becomes more complicated because there are effects of each metal on others. The biosorption of some metals in different systems is more or less affected by the presence of other metals [13,53–57].

Statistical methods of experimental design and system optimization, such as factorial design and response surface analysis, have been applied in different systems for the removal of heavy metals from an aqueous solution due to their capacities to extract relevant information from systems requiring a minimum number of experiments [58–64]. It is thus desirable to reduce the number of factors to a small set. Screening experiments are efficient to identify the important factors, in a minimal number of experiments [65,66]. For example, in the Plackett–Burman design containing up to 11 factors, 12 experiments may be used [67].

In this work, sawdust was used for the removal of zinc and cadmium from an aqueous solution simultaneously. The experiments were organized according to a Plackett–Burman statistical design to identify the most influential factors on the elimination performance of metals to generate a primary regression model and to optimize operating conditions for the best performance.

2. Material and methods

2.1. Preparation of sawdust

Sawdust was used directly for the sorption experiments without any chemical pre-treatment. It was cleaned, dried in sunlight to constant weight, crushed, sieved to pass through the sieve with hole between 0.50 and 1.25 mm (small size) and between 1.25 and 2 mm (large size) and stored in vacuum desiccators before use. Some characteristics of this sawdust were determined and reported in a previous work [68].

Two types of sawdust (red and beech) were obtained from local industries and from two sources to have sawdust chips of different forms.

2.2. Experimental process

Batch adsorption experiments were performed to study the removal of zinc and cadmium from water using sawdust as adsorbent. In the light of levels from Table 1 and experimental design of Table 2, each experiment was carried out according to the following procedure: a mass of sawdust was added into 250 ml flask containing 100 ml of an aqueous solution at a known metal concentration. The aqueous solutions of cadmium and zinc were prepared in distilled water from $Cd(NO_3)_2$ and $ZnSO_4$, analytical grade from Merck. The temperature was controlled, the pH was adjusted by NaOH and H_2SO_4 and the agitation was carried out by a mechanical stirrer.

The removal quantity of zinc and cadmium by sawdust corresponds to the decrease of their concentration in the aqueous solution. The removal quantity Y (%) was evaluated by Eq. (1):

$$Y\ (\%) = 100 \times \frac{C_0 - C}{C_0} \tag{1}$$

where C and C_0 are the measured and the initial concentrations, respectively.

The metals concentrations were evaluated by analysis of filtered sample by using a flame atomic absorption spectrophotometer “Shimadzu AA 6200” at a wavelength of 300 and 270 nm for zinc and cadmium, respectively.

2.3. Experimental results

Effects of the 11 parameters on the elimination of zinc and cadmium by sawdust are followed by the removal quantities as responses which are determined from the diminution of metals concentration in the aqueous solution. The removal efficiencies of zinc and cadmium, simultaneously, are determined by Eq. (1) and presented in Table 2.

3. Discussion

Some factors may be important and others may have little or may not affect the response.

3.1. Important factors

Using Minitab, a Pareto chart of effects was used for identifying important factors (Figs. 1 and 2). The chart shows the main effect estimates plotted against the horizontal axis and includes a vertical line to indicate the $p = 0.05$ threshold for statistical significance [69].

The Pareto chart of effects shows that the initial concentration of zinc and the sawdust mass are the most important factors influencing zinc removal efficiency (Fig. 1). It is very probable that the site number of sorption is high relatively when the sawdust mass

Table 1
Levels and units of the 11 studied factors

	Factor	Name	Unit	Level	
				Low (−1)	High (+1)
A	Sawdust type	Type	–	Red	Beech
B	Sawdust source	Source	–	Source 1	Source 2
C	Sawdust size	Size	–	Small	Large
D	Sawdust mass	Mass	g	0.5	2
E	Initial Cd concentration	$[Cd]_0$	mg/L	10	30
F	Initial Zn concentration	$[Zn]_0$	mg/L	10	30
G	Contact time	Time	min	5	30
H	Temperature	Temps	℃	25	40
I	Stirring speed	ss	rpm	150	300
J	Initial pH	pH	–	3	6
K	Initial salt concentration	Salt	mg/L	0	30

Table 2
Plackett–Burman experiment design and results

N°	A	B	C	D	E	F	G	H	I	J	K	*Y* (%) (Zn)	*Y* (%) (Cd)
1	1	1	−1	1	−1	−1	−1	1	1	1	−1	45.4	77.7
2	1	1	−1	1	1	−1	1	−1	−1	−1	1	42.1	51.3
3	−1	−1	1	1	1	−1	1	1	−1	1	−1	49.8	55.1
4	−1	1	−1	−1	−1	1	1	1	−1	1	1	12.97	21
5	1	1	−1	1	1	−1	1	−1	−1	−1	1	38.1	51.3
6	−1	1	1	1	−1	1	1	−1	1	−1	−1	32	14.9
7	1	−1	−1	−1	1	1	1	−1	1	1	−1	17.83	17.77
8	1	−1	1	−1	−1	−1	1	1	1	−1	1	29.9	25.9
9	1	1	1	−1	1	1	−1	1	−1	−1	−1	2	7.23
10	1	−1	1	−1	−1	−1	1	1	1	−1	1	26.9	24.9
11	−1	1	−1	−1	−1	1	1	1	−1	1	1	16.43	15.3
12	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	25.8	21.6
13	−1	1	1	−1	1	−1	−1	−1	1	1	1	23.6	1.17
14	−1	−1	−1	1	1	1	−1	1	1	−1	1	24.33	12.17
15	1	−1	−1	−1	1	1	1	−1	1	1	−1	14.73	17.77
16	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	25.8	18.4
17	1	−1	1	1	−1	1	−1	−1	−1	1	1	14.93	33.8
18	1	1	−1	1	−1	−1	−1	1	1	1	−1	46.5	79.4
19	−1	−1	−1	1	1	1	−1	1	1	−1	1	26.17	7.33
20	−1	1	1	−1	1	−1	−1	−1	1	1	1	21.9	4.03
21	1	1	1	−1	1	1	−1	1	−1	−1	−1	0	0
22	−1	−1	1	1	1	−1	1	1	−1	1	−1	48.7	52.43
23	−1	1	1	1	−1	1	1	−1	1	−1	−1	32.4	20.6
24	1	−1	1	1	−1	1	−1	−1	−1	1	1	16.07	34.5

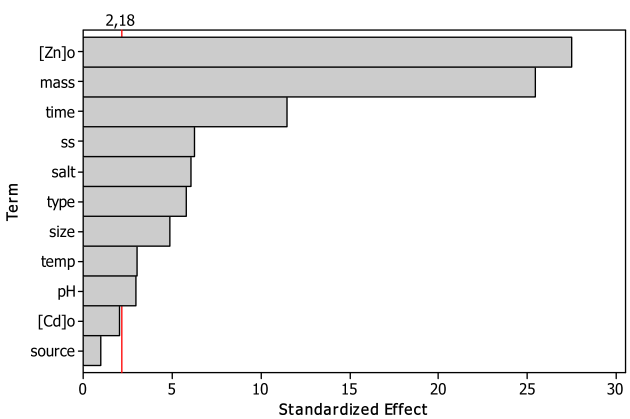

Fig. 1. Pareto chart of standardized effects of factors on the removal quantity of Zn ($\alpha = 0.05$).

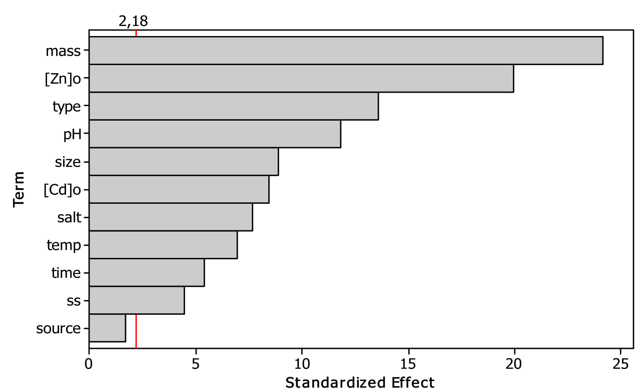

Fig. 2. Pareto chart of standardized effects of factors on the removal quantity of Cd ($\alpha = 0.05$).

increases or the initial concentration of metal ions decreases. In both cases, the removal of zinc is higher. The contact time is the third important factor. Kinetically, this implies a slow phenomenon. The source and the presence of cadmium in the solution have no effect on the removal of zinc. The other parameters have small effects.

On the other hand the removal of cadmium is more affected by the presence of zinc in the solution than the initial concentration of cadmium (Fig. 2). Type, pH and size become more important in this case comparatively to results for zinc. Time is not very important, which indicates that the phenomenon may have rapid kinetic process. The other parameters have the same effects in both cases.

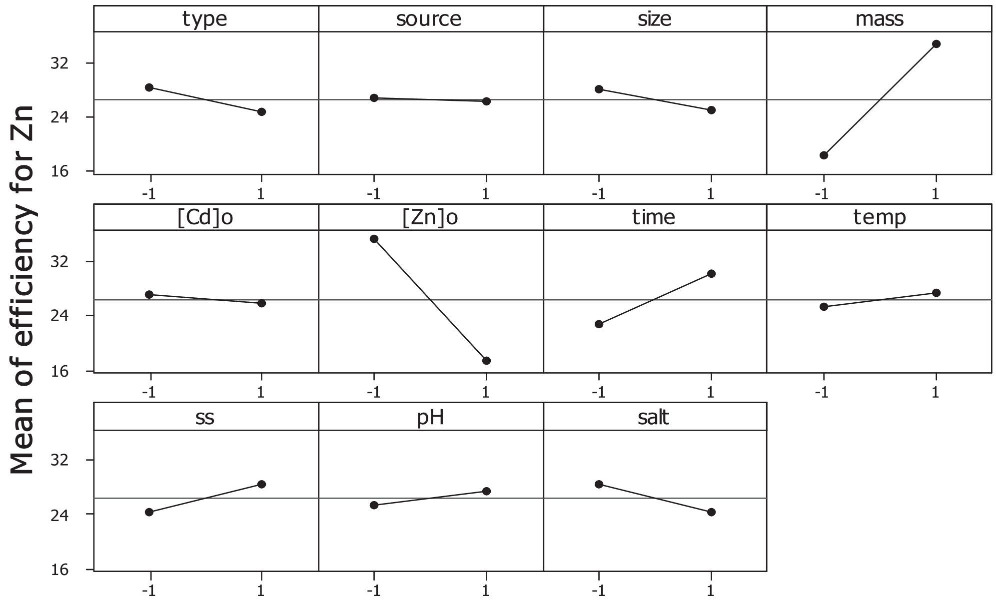

Fig. 3. Main effects plot for the removal quantity of Zn.

3.2. Main effects

The main effects plot is most useful when there are several factors (Figs. 3 and 4). Changes in the level means can be compared to deduce which factors influence the response the most. For a factor with two levels the response increases or decreases from the low to the high level. This difference is a main effect.

3.2.1. Significant factors and regression models

The term "significant" is used in its restricted sense of statistical significance. In other words, if an effect is significant, there is a high probability (95, 99 and 99.9%) that means the effect is "real" [70]. Analysis of variance (ANOVA) is an essential tool for determining the significance of an effect or of a mathematical model. The most significant factors can

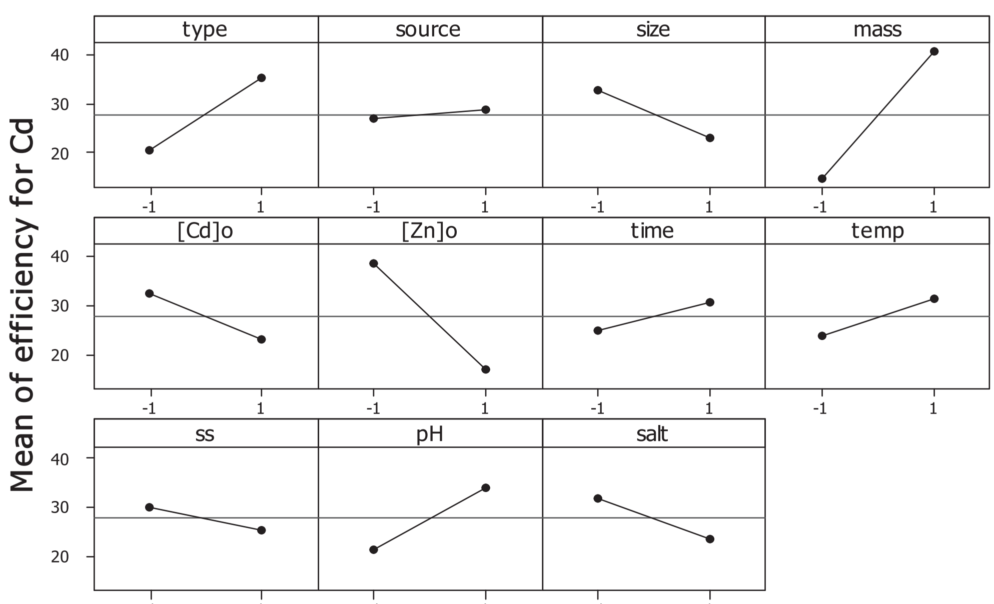

Fig. 4. Main effects plot for the removal quantity of Cd.

Table 3
Effects and coefficients for removal efficiency Y (%) of Zn (coded and uncoded units)

Factor	Effect	Coef. coded	Coef. uncoded	P
Constant	0.00	26.432	15.2675	0.000
Type	−3.786	−1.893	−1.89306	0.000
Source	−0.631	−0.315	−0.315278	0.351
Size	−3.164	−1.582	−1.58194	0.000
Mass	16.553	8.276	11.0352	0.000
$[Cd]_0$	−1.319	−0.660	−0.0659722	0.065
$[Zn]_0$	−17.886	−8.943	−0.894306	0.000
Time	7.447	3.724	0.297889	0.000
Temp	1.986	0.993	0.132407	0.010
ss	4.081	2.040	0.0272037	0.000
pH	1.947	0.974	0.649074	0.011
Salt	−3.964	−1.982	−0.132130	0.000

be determined by using a statistical parameter, which is the P value (Tables 3 and 4). This value was compared with another value Alpha which represents the risk of model. Generally, Alpha is equal to 5% of the risk.

From these results, it was found that the effects of sawdust mass, initial concentration of zinc and contact time are the most important and significant factors for zinc removal efficiency. The other factors are not important and can be considered negligible. Mathematic models of the efficiency according to the coded and uncoded process parameters were determined with the regression coefficients presented in Tables 3 and 4.

Coded parameters:

$$Y_{Zn}\ (\%) = 26.432 + 8.276\times \text{mass} - 8.943\times [Zn]_0 + 3.724\times \text{time} \quad (2)$$

Uncoded parameters:

$$Y_{Zn}\ (\%) = 15.267 + 11.0352\times \text{mass} - 0.894\times [Zn]_0 + 0.298\times \text{time} \quad (3)$$

For cadmium removal efficiency it was more complicated. Indeed, 10 parameters were important. The model of its efficiency according to coded parameters can be given by Eq. (4):

$$Y_{Cd}\ (\%) = 27.73 + 13.14\times \text{mass} - 10.87\times [Zn]_0 + 2.96\times \text{time} + 7.40\times \text{type} - 4.85\times \text{size} + 6.43\times \text{pH} - 4.60\times [Cd]_0 + 3.81\times \text{temp} - 2.43\times \text{ss} - 4.18\times \text{salt} \quad (4)$$

and according to uncoded parameters it can be given by Eq. (5):

Table 4
Effects and coefficients for removal efficiency Y (%) of Cd (coded and uncoded units)

Factor	Effect	Coef. coded	Coef. uncoded	P
Constant	0.00	27.73	8.31130	0.000
Type	14.79	7.40	7.39722	0.000
Source	1.86	0.93	0.927778	0.114
Size	−9.71	−4.85	−4.85278	0.000
Mass	26.29	13.14	17.5259	0.000
$[Cd]_0$	−9.20	−4.60	−0.460000	0.000
$[Zn]_0$	−21.74	−10.87	−1.08694	0.000
Time	5.91	2.96	0.236444	0.000
Temp	7.61	3.81	0.507407	0.000
ss	−4.86	−2.43	−0.0324074	0.001
pH	12.86	6.43	4.28704	0.000
Salt	−8.35	−4.18	−0.278333	0.000

Table 5
Comparison between experimental and modelled efficiencies for Zn and Cd

Run	Efficiency (%)			
	Experimental		Modelled	
	Zn	Cd	Zn	Cd
1	45.4	77.7	45.95	78.55
2	42.1	51.3	40.1	51.3
3	49.8	55.1	49.25	53.765
4	12.97	21	14.7	18.15
5	38.1	51.3	40.1	51.3
6	32	14.9	32.2	17.75
7	17.83	17.77	16.28	17.77
8	29.9	25.9	28.4	25.4
9	2	7.23	1	3.615
10	26.9	24.9	28.4	25.4
11	16.43	15.3	14.7	18.15
12	25.8	21.6	25.8	20
13	23.6	1.17	22.75	2.6
14	24.33	12.17	25.25	9.75
15	14.73	17.77	16.28	17.77
16	25.8	18.4	25.8	20
17	14.93	33.8	15.5	34.15
18	46.5	79.4	45.95	78.55
19	26.17	7.33	25.25	9.75
20	21.9	4.03	22.75	2.6
21	0	0	1	3.615
22	48.7	52.43	49.25	53.765
23	32.4	20.6	32.2	17.75
24	16.07	34.5	15.5	34.15

$$
\begin{aligned}
Y_{\mathrm{Cd}}\ (\%) = {} & 8.31130 + 17.5259\times\text{mass} \\
& - 1.08694\times[\mathrm{Zn}]_0 + 0.236444\times\text{time} \\
& + 7.39722\times\text{type} - 4.85278\times\text{size} \\
& + 4.28704\times\text{pH} - 0.460000\times[\mathrm{Cd}]_0 \\
& + 0.507407\times\text{temp} - 0.0324074\times\text{ss} \\
& - 0.278333\times\text{salt} \qquad (5)
\end{aligned}
$$

To check the performance of the polynomial regressions identified above, the answers given by the theoretical models are compared with the experimental values of removal efficiencies Y (%) for Zn and Cd in Table 5.

Fig. 5 shows a good correlation between experimental and modelled efficiencies. The data are fairly distributed around the regression line and the coefficients R^2 are equal to 0.993 and 0.9926 for Zn and Cd, respectively.

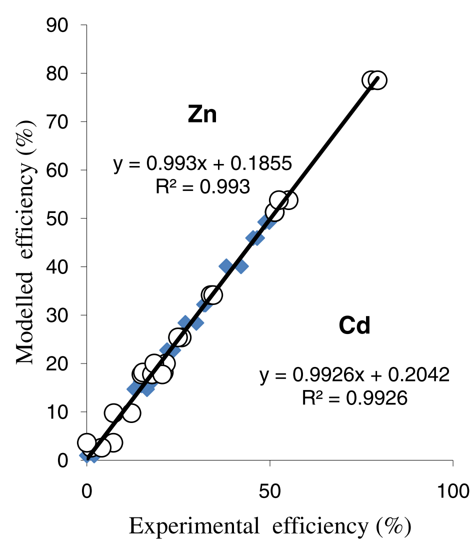

Fig. 5. Correlation between experimental and modelled removal efficiencies for Zn (○) and Cd (■).

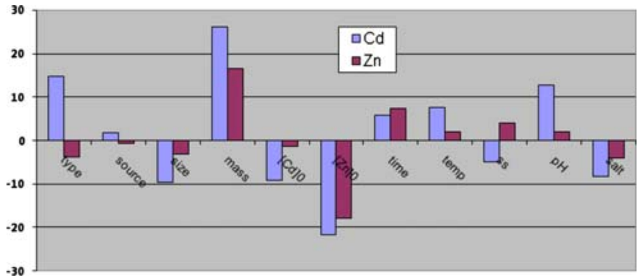

Fig. 6. Main effects for Cd and Zn removal simultaneously.

3.2.2. Comparison of parameters effects on cadmium and zinc removal

Fig. 6 summarizes the effects of various parameters on the sorption of both cadmium and zinc by the sawdust in the following conclusions:

(a) The positive effect of wood type on the removal efficiency of cadmium shows that the beech wood gives better performance, while the red wood is more favourable for the sorption of zinc (Fig. 6). The red wood is more porous than beech wood. Therefore, the red wood has a larger specific surface area, which led to more number of sites. Zinc atoms with smaller size than that of cadmium occupy the pores more easily. Cadmium with larger size can only remain on the outer surface. Furthermore, there is probably a favourable cationic exchange on the surface of beech wood.

(b) The source did not significantly affect the different responses.

(c) The size has significant negative effects on both metals. This result is logical. With the size increasing, the specific and external surfaces decrease, which led to the metal–adsorbent contact decreasing. Compared to Cd, the effect is not very important for zinc. This may be explained by the fact that in addition to their specific adsorption on the surface, zinc atoms diffuse slowly inside the volume which is constant for both different sizes.

(d) The mass of sawdust is a very important parameter for both cadmium and zinc. The effect of the adsorbent mass is positive in both cases, increasing the mass of the adsorbent results in higher efficiency of both metals due to the greater exchange surface, hence a more availability of sorption sites [13].

(e) Generally, the initial concentration of metals has negative effects on their respective sorption. At equilibrium, the mass of sawdust becomes saturated and the surplus of the metal remains in solution. On the other hand as reported in the literature [71–73], it was observed that Zn^{2+} had a negative effect on the Cd^{2+} biosorption, but the interference of Cd^{2+} on the sorption of Zn^{2+} was not very important.

(f) The positive effect of the time shows that zinc removal is slower than cadmium removal. This can be explained by the fact that if cadmium is adsorbed only on the surface of the sawdust, zinc also goes inside the volume which requires more time.

(g) When the temperature increases from 25 to 40˚C, the metals sorption increases, which indicates that the sorption process is endothermic. This result was found by other researchers [13,74].

(h) Increasing the stirring speed disadvantages, the sorption of cadmium promotes the sorption of zinc. A strong agitation could suppress the sorption of cadmium. On the other hand, the sorption of zinc into sawdust is promoted by agitation. The zinc atoms could replace cadmium atoms which detach from the surface.

(i) The positive effect of initial pH yields the sorption of cadmium and zinc [74–76]. At low pH, the surface of the sawdust could be occupied by H^+ ions which are abundantly present in the solution. This creates an electrostatic repulsion between the surface of the sawdust and the cationic metal.

(j) Na_2SO_4 has a negative effect on the performance of metal removal. In this case, salt ions compete with metals and occupy a part of the active sites of adsorbent reducing the fixation of pollutants on the adsorbent. Ionic strength also has a negative effect on the kinetics of sorption due to a competition between salts and metal ions. Analogue results were reported in other works; as hardness increases the competition with calcium ions strongly reduces the affinity of the biosorbent for zinc [77].

3.2.3. Other notes

The variation in levels of factors has a more remarkable effect on cadmium (Table 3) than on zinc sorption (Table 4). This may be seen from a comparison between the regression coefficients of both metals (Tables 3 and 4). For this reason, the theoretical model for zinc can be expressed according to only some factors, while for cadmium, it is expressed according to several factors. The optimization of operating conditions for simultaneous sorption of zinc and cadmium

Table 6
Selected properties of Cd and Zn ions

Metal ion	Ionic radius (Å)	Hydrated ionic radius (Å)	Pauling's electronegativity
Cd^{2+}	0.95	4.26	1.69
Zn^{2+}	0.74	4.30	1.65

should consider first the optimal conditions of cadmium which can be more affected by the change of several factors.

After studying several papers on the removal of cadmium and zinc from an aqueous solution by adsorption, it was found that the adsorption capacities of these metals varied from one study to another; adsorption capacities were very close to 0.477 $mmolg^{-1}$ for cadmium and 0.505 $mmolg^{-1}$ for zinc ions, respectively, using Crank diffusion model [78]. In other works, adsorption of zinc was more favourable than that of cadmium and was explained by the smaller zinc ionic radius (0.74 Å) compared to cadmium radius (0.83 Å) [9,73,75,79]. Contrary to these results, in this present work and in other ones the adsorbed amount of cadmium is greater than that of zinc [13,80–82]. This phenomenon may be explained as follows:

- The high mass of heavy metals may undergo higher momentum energy. This fact may facilitate the biosorption of heavy metals by increasing the probability of an effective collision between the metal and the solid surface.
- In the ion-exchange process, larger multivalent ions are more effectively removed than smaller ones.
- The sorption of metals is favourable when their hydrated ionic radius is small (Table 6).
- The higher Pauling's electronegativity (Table 6) of the atom makes the ion sorption easier by the biosorbant.
- The global effect will be in function of the combination of all the above cited factors.

4. Conclusion

In this work, the sawdust was used as a low-cost material for the simultaneous removal of zinc and cadmium from an aqueous solution. An experimental design methodology was used to identify factors which have important effects on the metals removal. From 11 studied factors, the most important effects for zinc sorption were its initial concentration, sawdust mass and contact time. A theoretical model was than deduced. For cadmium sorption almost all factors were important and had significant effects. Effects of factors on metals sorption were more remarkable for cadmium than for zinc. The presence of zinc decreased the removal of cadmium and the inverse was not true. The mechanisms of cadmium and zinc sorption may be different. It is an adsorption or a cationic exchange on the surface of sawdust for cadmium and a pseudo-absorption in the volume of sawdust for zinc. The Pauling's electronegativity of heavy metals and their hydrated ionic radius have also some effect on their sorption by sawdust.

To enhance the capability and efficiency of sawdust sorption, pre-treatment of sawdust may be needed. Untreated sawdust does not mean that the sawdust can be used directly without cleaning and size reduction or mechanical preparation.

However, Plackett–Burman model is a primary regression model and it may be used as a first step to determine the most important operating parameters. The interaction effect of parameters and an optimization of these parameters can be carried out using an experimental design of second order.

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