Removal of Cd and Pb ions from model solutions using natural sorbent

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Abstract

Introduction. One of the limitations of chemical absorbents as a simple and effective method for removal the contamination due to surface absorption mechanism was their exorbitant costs. Therefore, the study of the potential of cheap and accessible natural adsorbents in the removal of heavy metals from industrial waste can be interesting.

Materials and Methods. For the study of absorbent quantity, pH and temperature effectiveness on absorption capacity of cherry core, first the artificial solution was supplied in 1000 mg/lit concentration and was mixed by certain amount of absorbent at certain temperature and pH for 60 minutes. The solutions filtered by filter paper and the contents of each ion in initial and filtered solution were determinate by atomic absorption spectrometry. Effect of absorbent quantity (0.2–2 g/100 ml), pH (3–7) and temperature (30–70 °C) on absorption rate of Lead and Cadmium investigated in Response Surface Methodology (RSM).

Results and Discussion. Increasing temperature improved the absorption rate of cadmium due to decrease of viscosity and accelerate mass transfer. Increasing of temperature limits the formation of boundary layer around the absorbent due to reduce of solution viscosity. So, ion absorption is intensified. Also, Increasing of absorbent quantity raises the surface contact and as results the chance of collision ions is improved with absorbent particles. In the other words, high quantity of absorbent increases the required cites to attach ions. Cadmium elimination at high value of pH was decreased due to conversion of ionic structure to molecular structure. Cadmium absorption rate was also increased by enlarging of absorbent; because of exist the more cites for absorption. Increasing the pH to 5 led to increase the Lead ions absorption, but rise of pH to 7 reduced absorption of Lead. The reason of this pneumonia is due to change of Lead ion structure to molecular state in alkaline pH. While in lower pH, competition hydrogen ions with cations decrease the absorption of metal ions.

Conclusion. The best experimental parameters for maximum absorption ions were determined at the following conditions: temperature 70 °C, pH 5 and concentration of absorbent 2 g/100ml. By applying these conditions, Lead and Cadmium ions were decreased 79.18 and 76.56% respectively from artificial solutions. Also, optimal conditions were tested on sugar industry wastewater, which results indicated the rate of absorption for Lead and Cadmium was obtained 98.98 and 76.1% respectively.

Introduction

Industrial contamination is one of the most important factors that pollute the water sources and spread infection to humans and animals. Household wastes, industrial wastes and agriculture drainage are a major contributor to pollutions. Limitation of water sources, lack of rain and water crisis on one hand and increase the contamination of surface and ground water by heavy metals on the other has caused that finding an effective method is necessary to removal the pollutants specially heavy metals as Cd, Pb, Ni [3].

Mechanism of heavy metal toxicity in biochemical is due to intense inclination of metals Cations to reaction with sulfur molecules. These binding were caused the inactivation of enzymes and lead to the bio failure and death [9–10].

Cadmium is a very toxic metal that its destructive effects have been proven on the lungs, kidneys and bones. Including serious damage of cadmium can be noted to a disease named Itai-Itai (Rheumatism bone pain). Cadmium through the contamination of sediment erosion left over the industries and agriculture slurry and manure is entered to aquatic ecosystems [4].

Also, Lead damages to nervous connections and leads blood and brain diseases. As far as, the 5 micrograms of Lead per deciliter of blood decrease the IQ and impair the focus and aggression in children [14].

Nowadays, various methods exist for reduction the contamination and heavy metals from water sources including membrane technology, exchanges ions resins, electrolysis and surface absorption. Among these methods, absorption processes has been applied widely due to existence of absorbent divers as carbon active, zeolite, silica and clay [10].

Absorption process as an economic and efficient method can be replacing to costly procedures like Revers osmose membrane process for removal heavy metals [2].

In recent years, waste of agriculture and industrial byproducts like threes leaf, peels of fruits, core of fruits even sawdust as natural absorbents have been used to removal the heavy metals in oil, chemical and textile industry, effectively. Application of solid agriculture wastes is growing as effectiveness absorbent because of abundance, low costs and their naturalness [1&8].

In 2007 Kamitz et al., reported that bagasse modified with succinic anhydride can be considered as useful natural absorbent for cu, Pb and Cd. This absorbent could remove the copper, lead and cadmium until 114, 196 and 189 mg/g, respectively.

Kelly-Vargas (2012) compared the adsorb capacity of lemon and banana peels to removal Copper, Lead and Cadmium ions. Results indicated that the lemon peels was more successful in absorbing Copper and Lead than other, but Cadmium absorption was better by banana peels (82%).

In similar study by Saka et al (2012) was shown that date fruit core in compare to onion peel was better in absorbing of Lead ions.

So, in this study, the potential of cherry core to removal the Lead and Cadmium ions from industrial wastewater was assessed and conditions of operation were optimized, too.

Materials and methods

Preparation of natural absorbent

First, cores of cherry were washed by distilled water several times to elimination their surface impurities and were dried in oven (Unitherm Model, Germany) at 103 °C for 2

hours. Then, due to increasing the capacity of contact surface, the cores were grinded and sifted (screen shaker, Retsch AS200, Germany) in sieve mesh > 35 and < 60. Dusty particles of cherry core maybe come in a hunch shape due to mixed in solutions, while shaper particles have a lower contact surface (area to volume ratio). Finally, cherry core powders were put to desiccator to prevent the absorption of moisture [7].

Preparation of artificial wastewater

By dissolving the Lead nitrate and Cadmium nitrate (Merck, Germany), the synthetic solutions was supplied in concentration of 1000 mg/lit. Also, sulfuric acid and NaOH solution (0.1 M) were used to adjusting the pH [7].

Experiment method

For the study of absorbent quantity, pH and temperature effectiveness as experimental variables on absorption capacity of cherry core, first the artificial solution was mixed by certain amount of absorbent at certain temperature and pH for 60 minutes that has been determined by statistical design (Table 1). pH and temperature adjusted by pH meter (Metrohm Model Germany) and magnetic stirrer equipped by heater (IKA Model, Germany) and finally, after 60 minutes, the solutions filtered by filter paper (Whatman, 42 micron). For calculation of absorption rate, the ion contents in initial and filtered solution were determinate by atomic absorption spectrometry (Analytik Jena Model, Germany). When the solution is exposed to high temperature, the electrons of atom can be excited due to absorbing energy which is different for each atom by atom [7].

Statistical design

Effect of absorbent quantity (0.2–2 g/100 ml), pH (3–7) and temperature (30–70 °C) on absorption rate investigated in Response Surface Methodology (RSM) statistical design and state of Box-Bhenken subject the full quadratic model (Equation 1) by Minitab Ver.17 software. Also, the best of parameter to elimination of cadmium and lead was optimized by this software.

$$f = b_0 + b_1T + b_2T^2 + b_3P + b_4P^2 + b_5C + b_6C^2 + b_7TP + b_8TC + b_9CP \qquad (1)$$

where: T – Temperature, P – pH and C – Concentration

Table 1

Experimental runs, independent variable levels and replicate runs in RSM (Box-Bhenken method)

Run Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Temp (^oC)	30	70	30	70	30	70	30	70	50	50	50	50	50	50	50
pH	3	3	7	7	5	5	5	5	3	7	3	7	5	5	5
C (g/100mL)	1	1	1	1	0.2	0.2	2	2	0.2	0.2	2	2	1	1	1

Result and discussion

Effect of independent parameter on Lead absorption

According to the Figure 1, increasing the pH to 5 led to increase the Lead ions absorption, but rise of pH to 7 reduced absorption of Lead. The reason of this pneumonia is due to change of Lead ion structure to molecular state in alkaline pH. While in lower pH, competition hydrogen ions with cations decrease the absorption of metal ions [17]. Also, at lower pH, the concentration of hydrogen ion is high and consequently the competition between metal ions and hydrogen ions is great for adsorbing on the absorbent surface. By adsorbing the hydrogen ions on absorbent surface, ionic repulsion is created. On the other hand, in higher value of pH due to increasing of hydroxide ions, the formations of metal hydroxides are increased and as a result the rate of absorption in decreased [11].

Increasing of absorbent quantity raises the surface contact and as results the chance of collision ions is improved with absorbent particles. In the other words, high quantity of absorbent increases the required cites to attach ions. Increasing of temperature limits the formation of boundary layer around the absorbent due to reduce of solution viscosity. So, ion absorption is intensified [16].

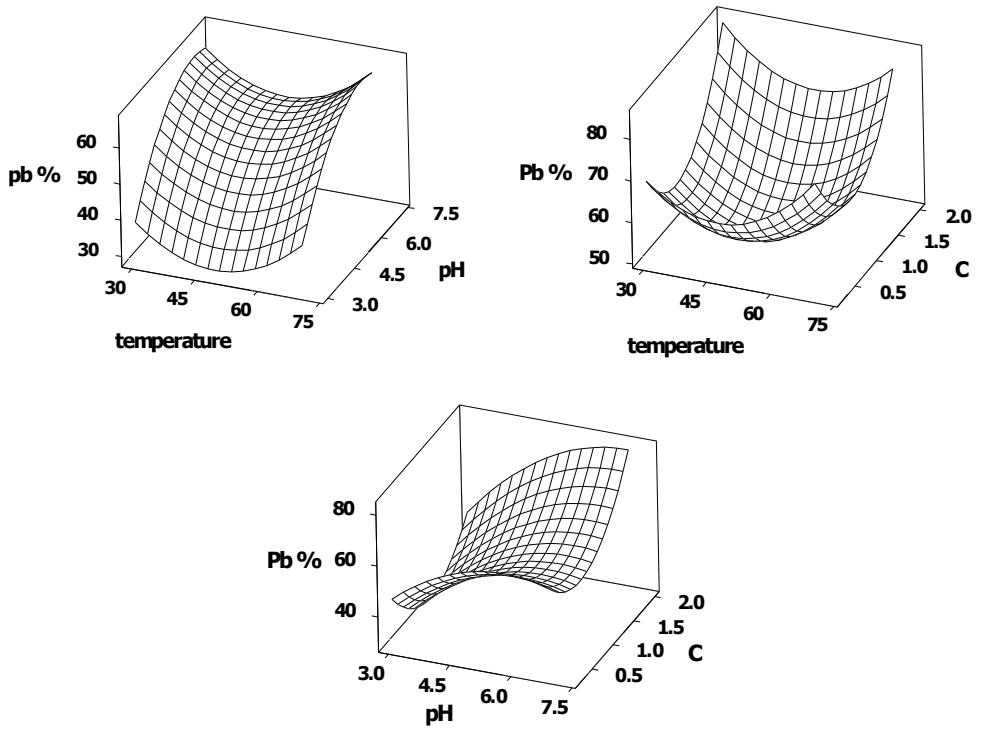

Figure 1. Effect of experimental variable on Lead absorption rate (Hold values are at temperature = 50 ^{o}C, pH 5 and C = 1.1)

Effect of independent parameter on Cadmium absorption

The effect of pH, temperature and absorbent concentration on the Cadmium absorption can be seen in the Figure 2. By increasing pH, Cadmium elimination was decreased due to conversion of ionic structure to molecular structure and formation of metal hydroxide due to exist of hydroxide ions. Cadmium absorption rate was also increased by enlarging of absorbent; because of exist the more cites for absorption [12]. Increasing temperature improved the absorption rate of cadmium due to decrease of viscosity and accelerate mass transfer.

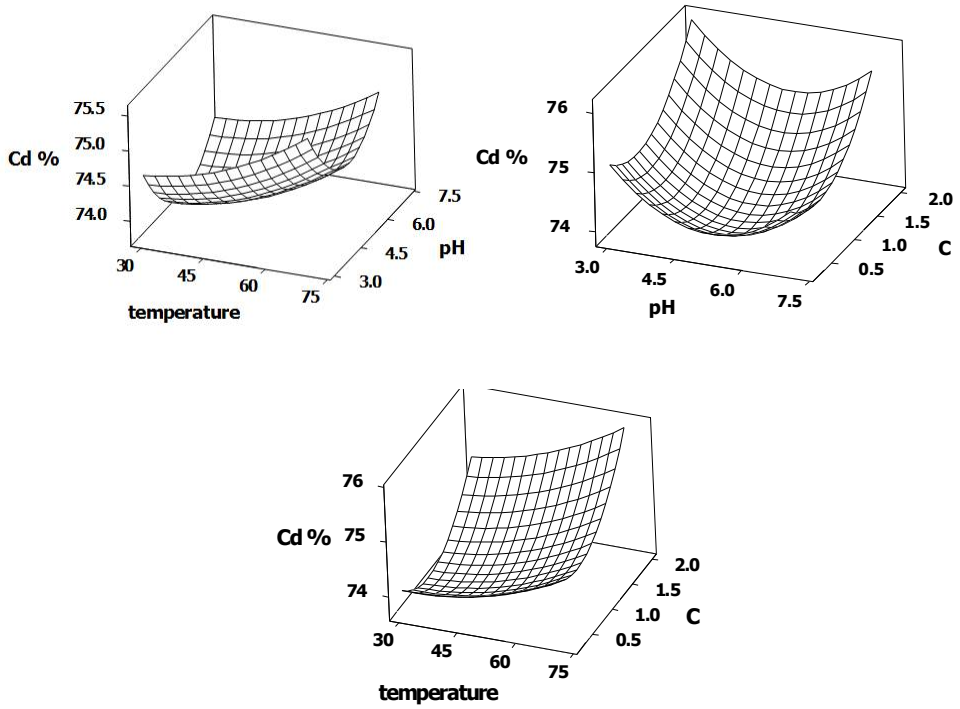

Figure 2. Effect of experimental variable on Cadmium absorption rate (Hold values are at temperature = 50 °C, pH 5 and C = 1.1)

Optimization

Minitab software was applied to optimization of experimental parameter. In setting section of software the goal of study was placed on maximum ions absorption. Also in this stage, must be graded the important of ions elimination. Since the risks of both ions from the point of toxicity and the health are same, the importance value of these indexes was considered equally.

Thus, the best conditions for maximum absorption ions were determined in the following conditions with satisfaction desirability (100%): temperature = 70 °C, pH 5 and concentration of absorbent= 2 g/100 ml (Figure 3). As shown in the Figure 4, in the best condition, Lead and Cadmium removal reached to 90.5 and 76.4%, respectively.

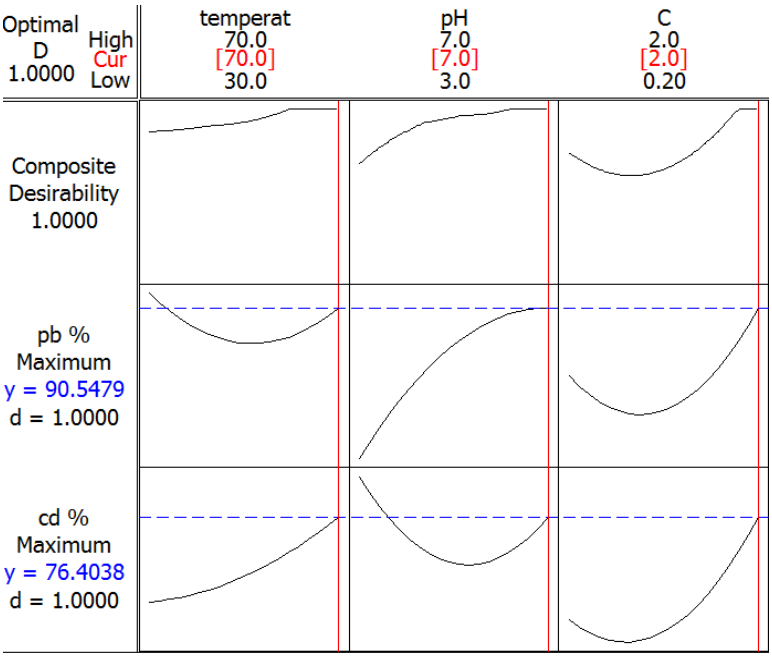

Figure 3. Determination of optimum experimental parameters by Minitab software

Table 2

Analysis of operational parameter and coefficient of full quadratic model

Source	DF	Lead			Cadmium		
		Coefficient	SS	P-Value	Coefficient	SS	P-Value
Model	9		3449.19	0.072		7.47662	0.026
Constant		51.4267		0	73.98		0.000
Linear							
T	1	0.8975	6.44	0.807	-0.4288	1.47061	0.019
P	1	12.7825	1307.14	0.014	-0.5162	2.13211	0.009
C	1	5.4	233.28	0.182	-0.21	0.35280	0.156
Quadratic							
T·T	1	10.2329	353.16	0.103	0.2825	0.25272	0.187
P·P	1	-9.2871	413.20	0.130	0.2525	0.22823	0.231
C·C	1	16.3829	991.02	0.024	0.06	0.01329	0.759
Interaction							
T·P	1	-0.0975	0.04	0.985	0.31	0.38440	0.142
T·C	1	-2.6125	27.30	0.619	-0.7675	2.35623	0.008
P·C	1	5.4225	117.61	0.321	0.2675	0.28623	0.193
Residual	5		485.46			0.63247	
Lack-of-fit	3		482.43	0.009		0.56587	0.154
Pure error	2		3.03			0.06660	
Total	14		3934.65			8.10909	
R^2 (%)		87.66			92.20		

After determination of optimum parameter, the study carried out at optimal conditions again. By applying these conditions, Lead and Cadmium ions were decreased 79.18 and 76.56% respectively from artificial solutions. Also, optimal conditions were tested on sugar industry wastewater, which results indicated the rate of absorption for Lead and Cadmium was obtained 98.98 and 76.1% respectively.

Conclusion

In this research the potential of Lead and Cadmium absorption was investigated by cherry core under the influence of different levels of temperature, pH and absorbent quantity variables with Response Surface Methodology statistical design. Results shown that, increasing temperature improved the absorption rate of cadmium due to decrease of viscosity and accelerate mass transfer. Increasing of temperature limits the formation of boundary layer around the absorbent due to reduce of solution viscosity. So, ion absorption is intensified. Also, Increasing of absorbent quantity raises the surface contact and as results the chance of collision ions is improved with absorbent particles. In the other words, high quantity of absorbent increases the required cites to attach ions. Cadmium elimination at high value of pH was decreased due to conversion of ionic structure to molecular structure. Cadmium absorption rate was also increased by enlarging of absorbent; because of exist the more cites for absorption. Increasing the pH to 5 led to increase the Lead ions absorption, but rise of pH to 7 reduced absorption of Lead. The reason of this pneumonia is due to change of Lead ion structure to molecular state in alkaline pH. While in lower pH, competition hydrogen ions with cations decrease the absorption of metal ions. The results showed, at optimal condition (T=70, pH 5 and C=2 g/100ml) the absorption rate for Lead and Cadmium reached to 79.18 and 76.56 % in artificial solution and 98.98 and 76.1% in sugar industrial wastewater respectively. The operational parameters in this research were effective on the variations of Temperature, pH and quantity of absorbent with appropriate R^2. Analysis of operational parameters effectiveness subject the full quadratic model summarized in the Table 2.

According to the Table 2, the full quadratic equations for adsorption rate of Lead and Cadmium were summarized as follows:

$$f_{Lead} = 51.4267 + 0.8975T + 10.2329T^2 + 12.7825P - 9.2871P^2 + 5.4C + 16.3829C^2 - 0.0975TP - 2.6125TC + 5.4225PC$$

$$f_{Cadmium} = 73.98 - 0.4288T + 0.2825T^2 - 0.5162P + 0.2525P^2 - 0.21C + 0.06C^2 + 0.31TP - 0.7675TC + 0.2675PC$$

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