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Removal of heavy metals from wastewater using cost effective method: determining optimal strategic conditions and system modeling using response surface methodology

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ABSTRACT

Lead and cadmium are among the heavy metals that result in the highest environmental hazards because of their widespread use, toxicity and distribution. These metals can cause complications such as poisoning and short- term and long term genetic effects. This study aimed to evaluate the removal efficiency of heavy metals of lead and cadmium from wastewater using stabilization ponds. Since such refining systems are important in economical and efficiency terms in developing countries, in this experimental study, anaerobic, facultative and maturation 60-L stabilization ponds were applied at retention times of 1–3 d in anaerobic pond and 3–9 d in the facultative and maturation pond with 1–50 mg/L initial concentration of lead and cadmium to remove chemical oxygen demand (COD), biochemical oxygen demand (BOD5), lead and cadmium on three levels in response surface methodology. Heavy metals were measured using atomic absorption spectrometers. According to results, maximum removal efficiency of COD, BOD5, lead and cadmium were 52.88, 65.5, 83.78 and 90.83%, respectively, in anaerobic stabilization pond. Carbon removal efficiency was directly attributed to hydraulic retention time and was inversely related to the initial concentrations of lead and cadmium. The efficiency of anaerobic stabilization pond was higher compared to that of facultative and maturation ponds. This system can be used instead of expensive and complex systems such as active sludge system and so on, due to its good features such as flexibility, ease of implementation, easy operation and fairly good performance in order to treat industrial wastewater containing heavy metals.

Keywords: Heavy metal; Wastewater; Cost effective method; RSM

1. Introduction

The development of urbanization and industry produces high volumes of sewage containing large amounts of pollutants. A large amount of these pollutants enters the environment due to lack of environmental requirements. Meanwhile, sewage is of high importance. Since in addition to polluting soil and as a result affecting the food chain of animals and humans, it has double negative effects on the quality of receiving waters [1]. Heavy metals are among the pollutants in the waste-waters of the industrial units having destructive effects on humans and environment. The ten-

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dency of heavy metals to survive, circulate and aggregate in the food chain is among the most important factors that increase their importance [2]. Metal pollutants can be transferred to a distance away by water because of their high stability. Solutions from metal compounds enter surface and underground waters and any pollution of surface flows in the upstream areas has many destructive effects on the downstream side [3]. Cadmium is used in plastic, paper, metal melting, photography and paint industrial units and in semi-conductors as well. Metals do have pollution threshold, that is, the maximum allowed is not desirable for them [4]. Despite the higher toxicity of lead compared to cadmium, the rules determine maximum allowed lead concentration above the maximum allowed concentration of cadmium in the soil, since cadmium has more transferability in food chain compared to that of lead [5]. The health effects of lead on the BOD5 are due to the binding of Sulfidryl groups with enzymes and impairing the function of enzymes. Also, when humans are exposed to higher amounts of lead in inhalation, breathing or skin absorptions, they are affected by a lot of physical complications such as skeletal problems, leukemia, encephalitis, heart and neurological problems, etc [6]. Attempts have been made to develop cheaper methods to control and remove pollutions caused by heavy metals. The use of physical, chemical and biological methods is common in treating polluted waste-waters. The efficiency and economical aspects play an important part in selecting each method. In most studies, these two issues have pushed the researchers to search for cheaper and effective methods for sewage treatment [7]. Given the fact that physical methods cannot treat waste waters at acceptable environmental standard levels and that chemical treatment methods require high costs; the use of biological methods has attracted the attention of human communities. Among the most important biological methods used to treat wastewater in addition to active sludge and dripping filter, are the stabilization ponds that can be acceptable as an effective choice or as a solution to environmental pollution caused by heavy metals given the low cost of land in Iran, low cost and ease of implementing this biological method [8,9].

Stabilization ponds are cheap natural systems with good efficiency. If these systems are implemented properly, their efficiency will be high. This method has been accepted thanks to its low implementation and investment costs and maintenance and flexibility against organic and hydraulic loads [10]. It is necessary to optimize the process variables in order to achieve the maximum removal efficiency. The conventional methods for designing experiments require some experiments to achieve the objective and this is rather difficult in terms of economy and time. This limitation can largely be eliminated by using the statistical design of the experiments. Statistical design reduces the frequency of experiments and presents an appropriate model to optimize the process [11]. Response surface methodology (RSM) is an effective widely used method for analyzing and modeling the effects of different variables on the response [12]. The purpose of this study was to evaluate the efficiency of removing heavy metals of lead and cadmium in industrial sewage using stabilization ponds since such treatment systems are important in terms of economics and efficiency in developing countries.

The main objectives of the present study are as follows: investigating the efficiency of anaerobic, facultative and maturation stabilization pond to build up the equation of carbon and heavy metal removal efficiency from stabilized pond with respect to operational conditions (i.e., contact time, and heavy metal concentration), using response surface methodology and central composite design and determining the optimum operational conditions to evaluate suitable models describing the efficiency determination of optimal conditions of the system.

2. Method and materials

2.1. Type of wastewater

The wastewater used in this study was provided from wastewater treatment plant of Kermanshah, Iran. Given the uniform position in wastewater harvesting, all samples were of comparable quality.

2.2. Specifications of the stabilization ponds

In this experimental study, a series of stabilization ponds were built of fiberglass with thickness of six-millimeters at pilot scale. Anaerobic stabilization pond consists of a 60-L feeding tank and plate tap to adjust the flow. It should be noted that the stabilization pond in the form of a rectangular cube was launched in three anaerobic sequences of anaerobic (APS) (1×0.5×2.5 m), facultative (FPS) (1×1.5×1.85 m) and maturation (MPS) (1.1×1.5×5.5 m) stabilization pond. The sewage system initially entered the anaerobic stabilization pond, then the waste from this stage was imported into FPS and subsequently into MPS. The anaerobic stabilization pond was completely sealed to prevent from entering oxygen. The system was run discontinuously [13].

2.3. Sampling and analytical methods

In this study, combined sampling was carried out round the clock, with two-hour intervals. Samples were immediately transferred to the laboratory and were kept at refrigerator temperature of 2–4ºC in order to maintain microbial and chemical properties. Measurement of chemical oxygen demand (COD) was carried out using reflux closed method (5220 C) by spectrophotometer (USA, Jenwaym Hach, 5000), biochemical oxygen demand (BOD 5) with the help of titration procedure (Method 5210 B) and lead and cadmium using atomic absorption spectrometry (Agilent Technology, AA240, USA). All stages of sampling, sample transferring and laboratory analyses were carried out according to standard methods for water and wastewater treatment [14]. pH meter (Digimed Model DM-20. Brazil) was used to measure pH. Also all chemicals and reagents with basic laboratory quality and with purity rate of 99.99% were bought from Merck Co., Germany. Twice distilled water provided in the laboratory was used to prepare standard solutions. Oxidation reduction potential (ORP) was carried out continuously to exploit the ponds using portable ORP meter (Kent, 7020) and sulfate concentration to ensure the conditions dominating the ponds during exploitation. Efficiency of the system was calculated after measuring the desired parameters. In total, 117 samples were taken. To reveal part of the removal mechanism for heavy metals, at the end of each stage, the amount of lead and cadmium in the sludge of the feeding tank and anaerobic pond was measured.

2.4. Designing experiments

Design of statistical tests and data analysis using response surface methodology and under the title of central composite design (CCD) were used to study two factors of (A) hydraulic retention time (HRT) and (B) initial concentration of the lead and cadmium [13]. The initial concentration of lead and cadmium was selected 1–50 mg/L; and hydraulic retention time of 1–3 d for anaerobic pond and 3–9 d for facultative and maturation ponds. The responses of the processes including COD, BOD5, lead and cadmium removal efficiency during 13 experiments including four variable points, 4 axial points, 1 central point and 4 repeated points in the center were studied at three minimum (–1), average (0) and maximum (+1) levels (Tables 1 and 2). Laboratory data obtained were used to determine variance analysis test, polynomial regression equations, the optimal point, validation of experiments and to draw three dimensional diagrams.

3. Results and discussion

3.1. Statistical analysis

CCD was designed to find the relationship between the responses of the process variables. Laboratory results obtained for 4 responses (Y1–Y4), have been presented in Tables 1 and 2. Table.1. Experimental conditions and results (anaerobic)

Table 1
Experimental conditions and results in anaerobic pond

Run	HRT, day (A)	Cd and Pb. Conc. mg/L (B)	Rem. COD, %	Rem. BOD5, %	Rem. Cd, %	Rem. Pb, %
1	3	50	45.87	34.89	83.78	90.83
2	1	25.5	25.4	31.9	55.71	62.3
3	2	25.5	38.44	42.12	63.45	75.5
4	2	1	43.98	52.8	59.68	56.78
5	1	1	36.41	44.02	50.14	48.9
6	2	50	31.32	24.89	72.78	84.26
7	3	25.5	49.6	55.38	76.23	81.11
8	2	25.5	38.1	39.98	62.87	75
9	3	1	52.88	65.6	67.58	67.12
10	2	25.5	39.08	43.38	65.11	76.12
11	2	25.5	39.24	42.98	64.11	76.09
12	1	50	17	15.02	63.16	79.8
13	2	25.5	37.56	41.46	63.04	74.79

Table 2
Experimental conditions and results in facultative and maturation pond

Run	HRT, day	Initial Cd and Pb. Conc. mg/L	Facultative pond				Maturation pond			
			Rem. COD, %	Rem. BOD5, %	Rem. Cd, %	Rem. Pb, %	Rem. COD, %	Rem. BOD55, %	Rem. Cd, %	Rem. Pb, %
1	9	50	41.25	38.31	93.05	91.26	16.17	17.14	29.98	38.09
2	6	50	40.42	37.27	90.04	91.23	12.34	13.12	28.1	33.52
3	3	50	29.67	26.11	78.24	77.31	10.09	10.02	21.78	29.98
4	6	25.5	49.01	43.11	84.8	86.96	15.96	16.32	24.89	30.87
5	6	25.5	47.2	41.65	82.34	83.67	15	15.98	26.3	28.67
6	6	25.5	49.36	43.73	84.49	86.34	14.98	16.57	26.1	31.4
7	6	25.5	47	41	82.47	84.16	15.34	16	25	29
8	9	1	58.78	52.34	82.12	84.43	22.14	21.3	25.7	30.44
9	3	25.5	34.23	31.54	74.4	75.2	13.47	12.15	19.43	25.32
10	3	1	41.47	38.51	71.3	69.89	17.11	15.34	17.98	23.11
11	6	25.5	48.12	42.33	83.71	85.36	15.23	16.25	25.5	29.86
12	9	25.5	50.22	47.36	87.14	86.89	18.41	19.46	27.2	34.12
13	6	1	57.03	49.12	78.24	79.98	19.89	18.46	23	27.14

According to the response surface methodology, that is indicative of the relationship among anaerobic stabilization ponds, facultative and maturation ponds efficiency and dependent variables, it was well documented with laboratory results. Table 3 presents the modified coded models with model significance and the results of variance analysis (ANOVA) for responses.

Process responses were studied using different linear, two degrees and 2FI models proportional to data. Expressions in the model were achieved after omitting meaningless variables and their interactions. The values obtained from ANOVA analysis determined the degree of significance of the model. F-value and P-value were calculated for each response to determine the significance of the model. The amount of P-value for all presented models for responses studied was equal to 0.0001. High F-value and low P-values are indicative of model significance. Amounts of P- value <0.0001 in all modified models of the process are indicative of high significance of the models. In other words, it is only 0.01% likely that the significance of the models be due to error. Also, P-values <0.05 show that the expressions of resulted models are significant. In this case, all tested models are of great significance (P-value<0.05). In Table 3 (ASP), F-value for removal models of COD, BOD5, lead and cadmium were 205.699, 352.08, 188.66 and 108.51, respectively. The F-values for facultative and maturation ponds for removing COD, BOD5, lead and cadmium were 153.17 and 169.38; 102.14 and 296.6; 198.24 and 164.23; 183.32 and 121.44, respectively. Given the results, lack of fit was not significant for all models ($p < 0.05$). Lack of fit indicates good prediction capability of the model. Also, the fit of resulting models was confirmed by correlation coefficient of R^2, adjusted R^2 and predicted R^2, between laboratory values and predicted values of the models in a way that correlation coefficients of adjusted R^2, R^2 and predicted R^2 were close to each other, being approximately 1. Coefficient R^2 has been defined as the proportion of explained variable to total variation and measurement of the fitness degree of the model that was logically high in all models ($R^2 > 0.98$). In other words, around 98% of changes for the removal of COD, BOD5, lead and cadmium has been well explained by the dependent variable and only 2% of the changes has not been presented in the models. Three-dimensional Figs. 1–3 indicate the effect of the initial concentration of heavy metals and hydraulic retention time on the removal of studied parameters.

In RSM, accuracy determines the error in experiments. If this error is greater than 4, the accuracy of the models is reported desirable [15]. In general, this proportion varied in all responses in anaerobic stabilization, facultative and maturation ponds between 66.45–35.96, 41.56–29.59 and 57.82–37.39, respectively. In addition, low standard deviation (SD) and variance coefficient (CV) for APS, FPS and MPS is indicative of significant accuracy and high performance results [16]. It should be noted that the coefficients of these equations and their mathematical symbols (-/+) indicate the extent and direction of the effect of independent parameters on the efficiency of the anaerobic stabilization pond.

3.2. Process performance

To ensure conditions in anaerobic system in the pond, the parameters of oxidation reduction potential and sulfate concentration were continuously evaluated. ORP < –246 and sulfate concentration lower than 70 confirmed the optimal conditions for anaerobic treatment.

3.2.1. Effect of variables on organic carbon removal

The effect of different initial concentrations of lead, cadmium and HRT on the responses in the form of removal efficiency of COD and BOD5 has been shown by experimental models in Table s 1 and 2. Figs. 1–3 show that the removal efficiency of above-mentioned parameters increased significantly with reducing the initial concentration of the lead and cadmium and raising HRT. The effect of HRT on the removal efficiency of COD in anaerobic pond was higher than that of the initial concentration of the lead and cadmium whereas in facultative and maturation ponds the initial concentration effect of lead and cadmium on removal efficiency was evident. In relation with the removal efficiency of BOD5, it should be noted that the effect of initial concentration of heavy metals on removal efficiency was more evident in FPS and MPS. The maximum removal efficiency of COD was obtained in APS (58.78%), FPS (58.78%) and MPS (22.14%), in maximum HRT and at 1 mg/L of concentration of heavy metals. Also, the minimum removal efficiency of BOD5 was achieved in APS (15.02), FPS (26.11%) and MPS (10.02%) in minimum hydraulic retention time and 50 mg/L concentration of heavy metals. In general, carbon removal efficiency rose with raising retention time in a way that with increasing HRT from 1 to 3 d in APS, the amounts of COD and BOD5 removal in the initial concentration of the heavy metals of 25.5 mg/L increased 24.21 and 23.48%, respectively. With raising HRT from 3 to 9 d in the facultative and maturation ponds (initial concentration of 1 mg/L), the increase in COD, was 17.31% and 5.03%, respectively. Under the same conditions, we witnessed the increase in BOD5 up to 13.83 % and 5.96% in FPS and MPS, respectively. Results revealed that the presence of heavy metals has an adverse effect on the efficiency of carbon removal. But its adverse effect can be reduced by raising HRT. The order of the carbon removal efficiency was as follows: APS > FPS > MPS. Results obtained during low hydraulic retention time demonstrated that the maturation pond had lower efficiency compared to those of facultative and aerobic ponds and this could be attributed to some intervening external materials that have been provided by the high organic load of the process. High removal mechanism of COD and BOD5 consists of deposition of solids followed by anaerobic digestion in the sludge layer. In anaerobic digestion stage, some methane will be produced of which around 30–50% of input BOD5 will escape or emit in the form of methane gas. The rest of the material which is not deposited is oxidized by heterotrophic bacteria such as *Pseudomonas aeruginosa* [17]. In this study, 52.34% of BOD5 removal in the facultative pond is indicative of anaerobic stage performance of the pond. Faleschini et al. found that the COD removal efficiency of facultative stabilization pond was 41%. Growth

Table 3
ANOVA results for the equations of the Design Expert 6.0.6 for studied responses

Type of pond	Response, %	Modified equations in terms of code factors	Type of Model	F Value	Adeq Precision	R^2	Adj. R^2	Pred. R^2	S.D	C.V	PRESS	Probability for lack of fit
Anaerobic	Rem. COD	Y= +37.84+11.59A-6.51B+3.1AB	2FI	205.69	48.912	0.985	0.984	0.983	1.33	3.53	22.75	0.993
	Rem. BOD5	Y = +42.46+10.82A-14.6B-2.92B^2	Quadratic	352.08	66.45	0.979	0.988	0.982	1.38	3.36	34.74	0.48
	Rem. Cd	Y = +64.36 + 9.76A+7.05B+1.83B2	Quadratic	188.66	47.55	0.991	0.978	0.963	1.28	1.96	32.55	0.178
	Rem. Pb	Y = +74.42+8.01A+13.68B-3.13B2	Quadratic	108.51	35.96	0.973	0.964	0.928	2.17	2.98	113.45	0.24
Facultative	Rem. COD	Y = +48.31+7.47A-7.66B-5.69A2	Quadratic	153.17	41.56	0.98	0.974	0.942	1.31	2.87	46.36	0.261
	Rem. BOD5	Y = +42.17+6.97A-5.88B-3.14A2	Quadratic	102.14	35.2	0.971	0.962	0.932	1.32	3.23	36.68	0.293
	Rem. Cd	Y = +83.73+6.39A+4.94B-2.69A2+1AB	Quadratic	98.24	35.39	0.98	0.97	0.935	1.3	1.25	27.79	0.644
	Rem. Pb	Y = +85.39+6.7A+4.25B-4.56A2	Quadratic	83.32	29.59	.965	0.953	0.927	1.33	1.6	33.27	0.582
Maturation	Rem. COD	Y = +15.48+2.67A-3.43B+0.8B2	Quadratic	169.38	46.146	0.982	0.976	0.96	0.48	3.01	4.6	0.298
	Rem. BOD5	Y = +15.93+3.4A- 2.47B	Linear	296.6	57.82	0.983	0.981	0.972	0.42	2.65	3.01	0.785
	Rem. Cd	Y = +25.56+3.95A+2.2B-1.88 A2	Quadratic	164.23	42.5	0.982	0.976	0.966	0.52	2.11	4.59	0.817
	Rem. Pb	Y = +30.11+4.04A+3.48B	Linear	121.44	37.39	0.96	0.952	0.944	0.84	2.78	9.95	0.954

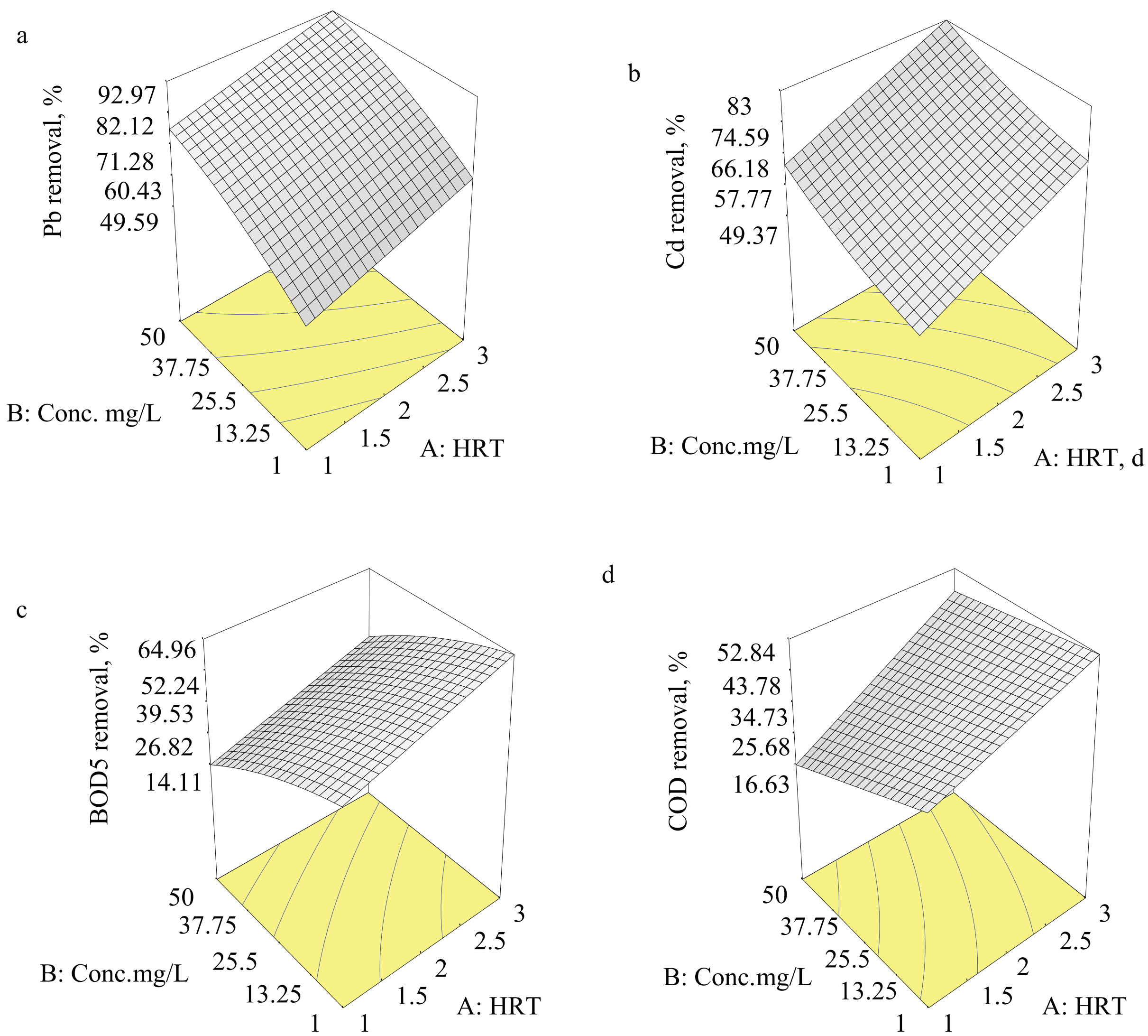

Fig. 1. Response surface plot for anaerobic stabilization pond (a) Pb removal (b) Cd removal (c) BOD5 removal and (d) COD removal.

in the removal of BOD5 is due to the rapid growth of algae [18]. According to studies conducted in stabilization ponds, removal of BOD5 can reach up to 92% in anaerobic pond [19], and 96% in facultative pond [20]. Although a large part of biodegradable material is removed in anaerobic hydrolysis, most organic suspended solids during the hydrolysis process in anaerobic pond turn into intermediate compounds with low biodegradability [21]. Also, the efficiency of anaerobic and facultative stabilization ponds with varying concentration of heavy metals was higher on the input compared with the result of the study by Abdel-Aatty et al. [22]. They showed that the efficiency of COD and BOD5 removal by anaerobic pond system was 18.89%. 22.21%, respectively [22].

3.2.2. *Effect of variables on heavy metal removal*

Given that biological treatment process transfers the waste into the ultimate products, the use of this method is increasing nowadays [23]. The 3-dimensional diagram response surface methodology for treated lead and cadmium in the series of stabilization ponds has been shown in Figs. 1–3. These figures demonstrate the interactive effects of the initial concentration of lead and cadmium and HRT on the removal of heavy metals. As it is seen, with increasing HRT and the initial concentration of lead and cadmium, the efficiency of heavy metals' removal rises. For example, in the same HRT in the facultative pond (9 days), it reveals an increase in the initial concentration of the lead from 1 to 50 mg/L, resulting in 6.83% increase in system performance. The efficiency of lead removal in ASP, FSP and MSP was respectively in the range of 48.9–90.83, 71.3–93.05 and 23.11–38.09%. Also, the efficiency of cadmium removal in ASP, FSP and MSP was respectively in the range of 83.78–50.14, 93.05–71.3 and 29.98–17.98%. The highest efficiency of lead and cadmium removal was achieved at initial concentration of 50 mg/L and HRT of

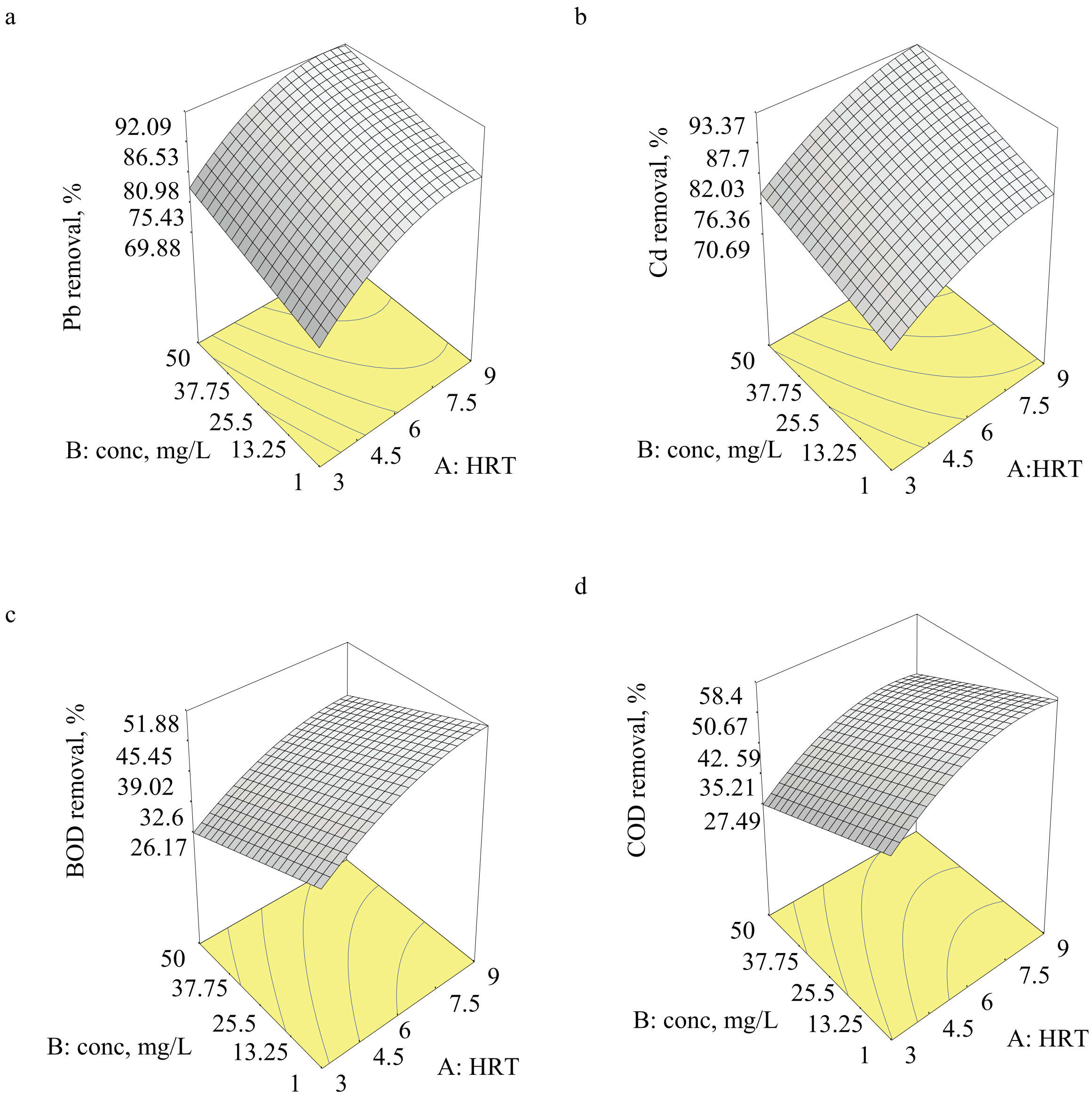

Fig. 2. Response surface plot for facultative stabilization pond (a) Pb removal (b) Cd removal (c) BOD5 removal and (d) COD removal.

3 d in anaerobic pond and 9 d in facultative and maturation ponds. According to the polynomial equations of lead and cadmium removal, the effect of the initial concentration of lead and cadmium on the efficiency of the process is more than that of HRT in anaerobic pond while in facultative and maturation ponds, HRT has more effect on the process. The efficiency of stabilization pond was higher than those of facultative and maturation ponds and the efficiency of maturation pond was lower than that of facultative one in the removal of heavy metals from wastewater. The effect of HRT in anaerobic pond on removing heavy metals was significant. It could be stated that it is more likely that the existence of variable algae population in facultative pond will lead to bi-absorption of heavy metals that accounts for this biological phenomenon [24]. Also, given the alkaline pH in this type of pond (pH = 8 ± 0.9), alkalinity can be another reason leading to bicarbonates' combination with metal cations and their treatment [25]. Results indicate that the mean removal of lead in the anaerobic and maturation ponds is more than that of cadmium whereas in facultative pond the results are close to each other. In the study by Lim et al. in Ethiopia in 2017, on the removal of heavy metals using stabilization pond, it was concluded that the concentration of outgoing heavy metals of chrome, lead and cadmium from pond system was measured lower than 20 mg/L. And this is not consistent with results of this study [26]. According to results, the effect of HRT is greater in anaerobic pond compared to that facultative pond.

Considering that the removal mechanisms in the pond are carried out physically, chemically and biologically, physical removal, that is, deposition of lead and cadmium cations along with propellant or disposable

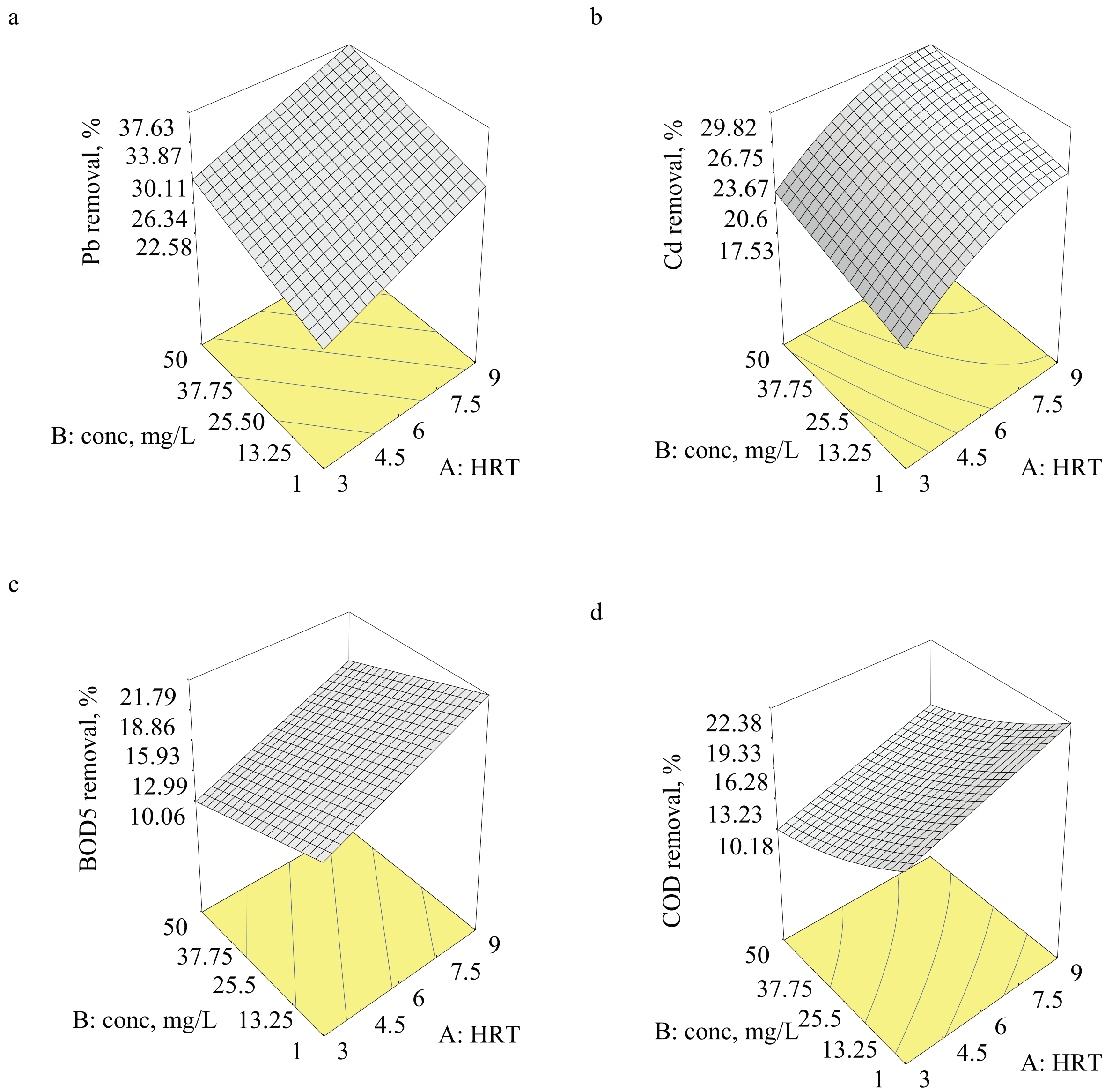

Fig 3. Response surface plot for maturation stabilization pond (a) Pb removal (b) Cd removal (c) BOD5 removal and (d) COD removal.

material mainly happens in the bottom of the pond in anaerobic ponds [27]. Results obtained after each stage of experiment and their comparison with feeding tank and the sludge from startup period that were at the same level, confirms the superiority of the treatment mechanism. Since in the sludge accumulated, the amount of lead was 76 times higher than the feeding tank and the amount of cadmium was 9 times higher than Pb, chemical combination of Pb^{+2} and Cd^{+2} cations with S^{-2} leads to formation of Pb and Cd that deposit in the pond. It is necessary to explain that sulfate turns into S^{-2} in anaerobic ponds and its considerably high tendency to be combined with cations, leads to formation of sulfur. This mechanism is the product of the activity of Sulfate reducing bacteria that is provided with very good conditions by anaerobic pond environment. The superiority of the anaerobic stabilization pond is attributed to this reason compared to facultative and maturation ponds [28]. Results show the removal of heavy metals of lead and cadmium and that the efficiency of this type of pond is lower compared to anaerobic stabilization pond. This could be attributed to the low concentration of heavy metals at the entrance of this type of pond. On the other hand, the microbial consortium and its biological conditions differ in terms of the formation of deposit-able metal complexes from anaerobic ponds [29]. But the existence of variable algae population provides the conditions for bi-absorption of some part of lead and cadmium removed by bacteria and algae and it is carried out by bi-absorption and bi-leaching phenomena in facultative pond [30]. The important point in this study is the positive effect of inlet heavy metal in raising the efficiency of anaerobic pond. It could be said that its performance depends on the physical and biological absorption and treatment phenomena [31]. Results of this

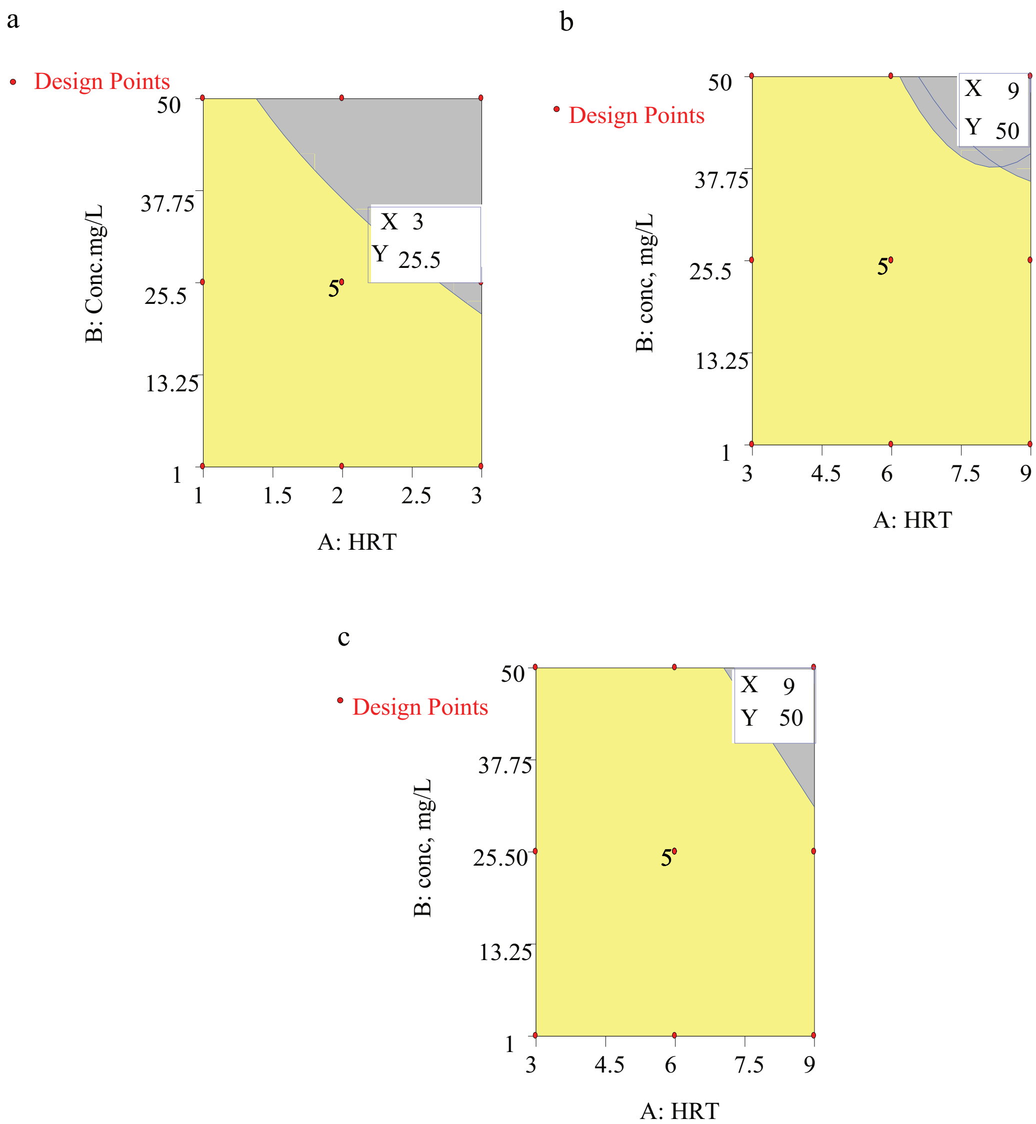

Fig. 4. Overlay plot for optimal region for removal pollutants from a) anaerobic stabilization pond, b) facultative stabilization pond and c) maturation stabilization pond.

study by Almasi et al. on petroleum refining show that the efficiency of anaerobic stabilization pond rises with increasing retention time in terms of removing organic materials [32].

Also, results demonstrated that the accumulation of metals in the bottom of the pond is much higher than that of the feeding tank and this also is directly attributed to increasing concentration. According to analysis of variance, inlet cadmium accumulation in the feeding tank did not show a significant mean difference (P-value > 0.05) but this difference was significant in the pond (P-value < 0.05). The mean of lead and cadmium concentration in the feeding tank was 4.45 and 2.6 mg/L, respectively. But the rate of lead accumulation based on the arrival of 1, 10 and 50 mg/L was measured 1.5, 20 and 76 times, respectively. This amount was twice, 6 times and 9 times of concentration in the feeding tank.

3.3. Process optimization and verification

To determine optimal conditions, experiments were carried out using central composite design (CCD) in response surface methodology (RSM). Two factors of hydraulic retention time and the initial concentration of lead and cadmium were studied to determine the optimal conditions for system efficiency in anaerobic, facultative and maturation ponds. After conducting the experiments according to CCD, we evaluated the laboratory responses and determined optimal conditions in four models based on the four responses of the process obtained from experiments. The optimal area was determined in anaerobic stabilization pond according to carbon removal efficiency of more than 70%, and lead and cadmium more than 90%, in facultative pond, removal efficiency of carbon, Pb and Cd was more than 90% and in maturation pond, carbon

Table 4
Verification experiments at optimum conditions

Type of pond		Conditions	Responses, %			
			COD. Rem	BOD5. Rem	Cd. Rem	Pb. Rem
Anaerobic	Experimental values	HRT: 3 day,	49.6	55.38	76.23	81.11
	Model response (Cl 95% Error)	Initial concentration of	50.92	55.01	75.73	85.16
	Standard Error	heavy metal: 25.5 mg/L	1.49	1.58	1.46	2.49
Facultative	Experimental values	HRT: 9 day,	41.25	38.31	93.05	91.26
	Model response (Cl 95% Error)	Initial concentration of	44.53	42.23	95.44	93.91
	Standard deviation	heavy metal: 50 mg/L	1.61	1.61	1.37	1.63
Maturation	Experimental values	HRT: 9 day,	16.17	17.14	29.98	38.09
	Model response (Cl 95% Error)	Initial concentration of heavy metal: 50 mg/L	16.81	17.46	31.21	38.83
	Standard deviation		0.56	0.5	0.75	1

removal efficiency was more than 30% and that of lead and cadmium was more than 40%.

The dark areas indicate areas where optimization has been made whereas in yellow areas, the design criteria have not been met. To confirm the accuracy of model studied, one point was chosen through the optimal area shown by flag and the real responses were compared with predicted ones. Table. 4 shows the result of this guided experiment through the facultative area. The accuracy of each response was tested using standard deviation. Results showed that the findings were consistent with the model prediction and are in the same direction.

4. Conclusion

The efficiency of anaerobic stabilization pond in removing heavy metals of lead and cadmium is higher than that of facultative pond. The highest efficiency of lead removal (77.64%) is achieved in anaerobic pond at concentration of 50 mg/L and in HRT: 2.5 d, and the highest efficiency in removing cadmium is obtained at concentration of 50 mg/L and HRT of 7.5 d (76.07%). Also, in facultative pond, maximum cadmium removal efficiency is achieved in retention time of 7.5 d (91.06%) and the highest lead removal is achieved in facultative pond in retention time of 6 d (81.55%). Also, in maturation pond maximum cadmium removal is achieved in HRT of 3 d (98.83%) and the highest efficiency of lead removal is obtained in retention time of 7.5 d (86.82%). Also, the removal efficiency of heavy metals is higher in anaerobic ponds compared to facultative pond. Results of present study indicate that with raising the concentration of heavy metals, the efficiency of removal goes up in anaerobic stabilization pond, too. Also, it was revealed that anaerobic pond is of higher efficiency in removing heavy metals. Results showed that the accumulation of lead in the sludge of stabilization pond is 15 times higher than that of cadmium. Given the results of this study, the flexibility and very good performance of stabilization pond in reducing heavy metals under study were confirmed, and selecting this economical biological method for industrial waste waters that are faced with heavy metal problems is justifiable. Considering the good properties of this system such as flexibility, ease of implementation, simplicity of productivity and fairly good efficiency, it could be used instead of expensive and complex.

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