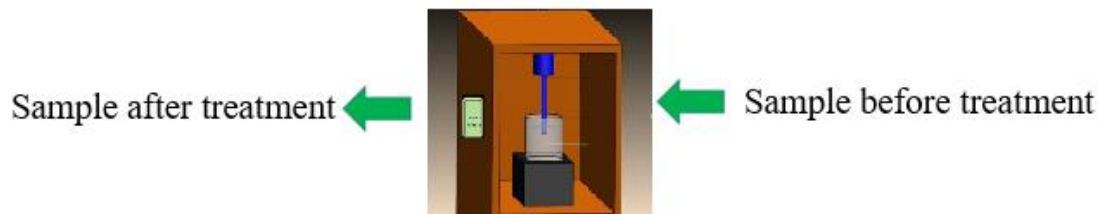


Removal of phosphorus and chemical oxygen demand from excess sludge supernatant using of ultrasound waves

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GRAPHICAL ABSTRACT



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ABSTRACT

The use of ultrasound is one of the most studied methods in treatment of water and wastewater. This study was going to remove pollutants from the supernatant of excess sludge by using of ultrasound. Initial raw supernatant with COD equal to 1600 mg/L and phosphorous equal to 80 mg/L was exposed to ultrasound. The experimental design was used to determine the experiments with variables including time (1.5-9.5 h), ultrasonic power (40-360 w), and the volume of sample (20-180 mL). COD and phosphorous were the responses, those were investigated in this research. Based on the Response Surface Methodology (RSM), a model for COD and phosphorous removal was obtained with a 95 % confidence interval. The optimized removal of COD (97.39 %) and phosphorous (98.73 %) was observed. According to the results, ultrasonic waves is a good way to remove COD and phosphorus from sludge. This method can be used in wastewater treatment plants for treatment of supernatant of excess sludge.

1. Introduction

Activated sludge is used as one of the common methods in the treatment of sewage, in which a large amount of biological sludge (0.4-0.6 g VSS/g COD) is produced, and contains a high amount of water (Dewila et al. 2006; Babanezhad et al. 2017). Recently, the advanced oxidation processes have been used for solving environmental problems, widely (Tavakoli Moghadam and Qaderi. 2019).

Sludge dewatering is the best method to reduce the sludge volume, through which the transportation and disposal of sludge is facilitated and the cost of sludge treatment decreased (Meng et al. 2018). Poor sludge dewater ability is improvable using methods such as ultrasonic, thermal, alkali, and chemical oxidation procedures. These methods facilitating the removal of water through destroying cells and sludge flakes and dissolving intracellular materials affect the viscosity and filterability of sewage (Dewila et al. 2006). Sludge dewatering supernatant contains a high level of organic materials, contaminant, and odor, which are usually returned to the primary sedimentation tank in sewage treatment plants (Uludag-demirer and Othman. 2009). Returning supernatant to the sewage system is of great concern, due to the increased organic load in the sedimentation tank and other parts, the bulking phenomenon in the activated sludge, and the elevated wastewater odor and pollution (Kappe 1958). On the other hand, discharge of sewage into the environment leads to the pollution of water

resources (Lin. 2012). Thus, the treatment of sewage is effective to reduce these problems. The use of ultrasound is an efficient method for mechanical disintegration of sludge. Advantages of this wave are high degradation of sewage (95%), improved biodegradability, no need for chemicals (Mao et al. 2004) and short time and easy operation (Kavitha et al. 2016; Saha et al. 2011).

Ultrasonic waves degrade organic materials and reduce particle size (Kavitha et al.), through the formation of cavitation bubbles in the liquid. As the acoustic cavitation is forming, the temperature, pressure, reach above 5000 k, 500 bar, and radial velocity reaches near the speed of sound, respectively, in the bubble bursting location. As a result, free radicals such as hydroxyl radicals are formed. Moreover, the excessive amount of hydrodynamic shear forces are generated in the solution and react with organic matter (Kavitha et al. 2016; Le et al. 2015). Ultrasound has been used to improve the degradability (Khanal et al. 2007; Zhao et al. 2016), biogas production (Onyeche et al. 2002), odor control (Liu et al. 2016), organic matter solubility (Gronroos et al. 2005), dewater ability and microbial activity (Huan et al. 2009) in sludge.

Moreover, ultrasound treatment combined with other processes such as Fenton and ozone treatment has been used for textile wastewater (Lin et al. 2016) and sludge treatment (Xu et al. 2010) respectively. Regarding previous studies, there is a lack of research on the use of ultrasound to remove organic matter and phosphorus from aqueous solutions, especially the supernatant.

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In the old optimization method, the optimal parameter was obtained by changing one variable and fixing other variables. This method is time-consuming and has limitations in experiments with several independent and dependent variables. These problems can be solved using the response surface methodology (RSM) in which a model is obtained and variables are optimized. Moreover, individual and simultaneous effects of parameters is evaluated, as well as the interactive effects between parameters (Pham et al. 2009).

Regarding the importance of supernatant treatment using the low-cost and green ultrasound-assisted method, the present study was going to treat the supernatant obtained from excess sludge dewatering in the municipal wastewater treatment plant. Moreover, the experimental design was used to optimize phosphorus and COD removal from supernatant and to evaluate simultaneous and individual effects of independent parameters, as well as the interactive effects between parameters. Although the removal efficiency of phosphorus and COD was modeled.

2. Materials and methods

2.1. Sample

The supernatant used in this study had pH 7.5, 1600 mg/L COD, 80 mg/L total phosphorus and 300 mg/L TS.

2.2. Materials, equipment, and experiment

Ultrasonic Probe Sonicator with the frequency of 20 khz (Topsound Co., Iran) was used. The initial COD was 1600 mg/L and initial total phosphorus of the supernatant was 80 mg/L. The COD and phosphorus were measured according to the standard method with three replications (APHA 1998; Sheikholeslami et al. 2020; Khalegh and Qaderi. 2019). All the materials (like as H₂SO₄, HgSO₄, AgSO₄) used to measure COD and phosphorus were purchased from the Merck Company (Germany).

2.3. The used pilot

According to Fig. 1, a beaker containing sludge inside an ultrasonicator was used as the pilot.

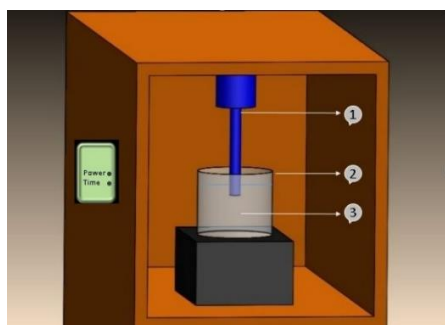


Fig. 1. Schematic view of pilot; 1: ultrasonic probe 2: beaker 3: supernatant.

2.4. Design of experiments by RSM

In this research the response surface methodology was used to determine the experiments. According to the results of experiments, the quadratic model was the best model. Like as the previous researches; accuracy of the used model was determined by the analysis of variance (Pham et al. 2009). According to the design of experiments, each independent variable were examined at 5 levels (-α, -1, 0, +1, +α). The variables in this experiment were ultrasonic power, the wave exposure time, and the sample volume, which are given in Table 1. Twenty experiments were designed using the central composite design (CCD) in RSM, and COD and phosphorus values were measured after each experiment.

Table 1. The levels of Independent variables.

Variables	Unit	-α	-1	0	+1	+α
Time	h	1.5	3	5.5	8	9.5
Ultrasonic power	Watt	40	100	200	300	360
Volume	mL	20	50	100	150	180

3. Results and discussion

Table 2 shows designed experiments and their results.

Table 2. Experiments and the results.

Run	Time, h	Ultrasonic power, w	Volume, ml	COD removal, %	Phosphorus removal, %
1	1.5	200	100	39	50.3
2	8	100	150	76	79.8
3	8	300	150	88	91.3
4	5.5	200	100	65.3	70
5	5.5	40	100	43.2	54
6	8	300	50	92	95
7	5.5	200	100	65.3	70
8	8	100	50	80	83
9	5.5	200	100	65.3	70
10	3	100	50	46	56
11	5.5	200	20	70	72
12	3	100	150	42	53.1
13	5.5	200	100	65.3	70
14	5.5	200	180	60	66
15	3	300	150	54	61
16	9.5	200	100	94.7	98.2
17	5.5	200	100	65.3	70
18	5.5	200	100	65.3	70
19	5.5	360	100	74	77
20	3	300	50	58	64

3.1. The suggestion of the model and analysis of variance

This section provides a model to predict phosphorus and COD removal efficiency of the supernatant based on the independent variables by the ultrasonic process using the response surface methodology.

3.1.1. COD removal efficiency

The Quadratic model was the best model for COD removal efficiency. The coefficient of determination 0.92, which is presented in Eq. 1.

$$Eq. 1: COD\ Removal = 37.63 + 8.05 \times A + 0.16 \times B - 0.44 \times C + 6.8 \times 10^{-5} \times A \times B - 0.014 \times A \times C - 4.25 \times 10^{-5} \times B \times C - 0.42 \times A^2 - 1.86 \times 10^{-4} \times B^2 + 1.6 \times 10^{-4} \times C^2$$

where, A is time; B is volume and C is power.

Regarding this model, the retention time caused to the highest increasing in the COD removal efficiency. Also, among simultaneous independent parameters effect, the ultrasonic power and retention time simultaneous effects caused to the highest increasing in the COD removal efficiency.

Analysis of variance (ANOVA) test of results is shown in Table 3.

Table 3. ANOVA of the COD removal efficiencies.

Source	Sum of Squares	df	Mean Square	F Value	p-value	
Model	4692.17	9	521.35	104.66	< 0.0001	Significant
A-time	986.73	1	986.73	198.08	< 0.0001	Significant
B:power	1943.91	1	1943.91	390.24	< 0.0001	Significant
C-volume	1370.64	1	1370.64	275.15	< 0.0001	Significant
AB	23.46	1	23.46	4.71	0.06	
AC	23.46	1	23.46	4.71	0.06	
BC	0.36	1	0.36	0.073	0.8	
A2	84.16	1	84.16	16.90	0.002	Significant
B2	42.99	1	42.99	8.63	0.015	Significant
C2	199.06	1	199.06	39.96	< 0.0001	Significant
Residual	49.81	10	4.98			
Lack of Fit	49.81	5	9.96			
Pure Error	0.000	5	0.000			
Core Total	4741.99	19				

The results of this test showed that the model is significant within a 95 % safety factor. The model used for prediction of COD removal efficiency is significant. The retention time, ultrasonic power and sample volume had P value <0.0001, that shows the significant effect of these parameters in the model.

3.1.2. A predictive model for phosphorus removal efficiency and the analysis of results

Eq. 2 shows the predictive model of phosphorous removal efficiency based on independent variables. The most appropriate model

for the prediction was the Quadratic model. Coefficient of determination was 0.88. Based on this model, the retention time had the highest effect on phosphorus removal efficiency.

$$\text{Eq 2: Phosphorus Removal} = 49.72 + 5.36 \times T + 0.13 \times P - 0.33 \times V + 6.85 \times [10]^{(-3)} \times T \times P - 0.012 \times T \times V - 2.33 \times [10]^{(-4)} \times P \times V - 0.25 \times T^2 - 1.07 \times [10]^{(-4)} \times P^2 + 1.34 \times [10]^{(-3)} \times V^2$$

where, T is time; V is volume; and P is power.

ANOVA test (for phosphorus removal) is shown in Table 4. This test showed that the model is significant within a 95% confidence interval. The phosphorous removal efficiency model is significant at P value <0.0001. The retention time, ultrasonic power and sample volume had P value <0.0001.

Table 4 ANOVA of phosphorus removal efficiencies.

Source	Sum of Squares	Df	Mean Square	F Value	p-value	
Model	3149.03	9	349.89	68.29	< 0.0001	significant
A-time	672.04	1	672.04	131.16	< 0.0001	significant
B-power	1292.47	1	1292.47	252.25	< 0.0001	significant
C-volume	940.79	1	940.79	183.61	< 0.0001	significant
AB	23.46	1	23.46	4.58	0.06	
AC	17.11	1	17.11	3.34	0.1	
BC	10.81	1	10.81	2.11	0.18	
A2	29.34	1	29.34	5.73	0.04	
B2	14.17	1	14.17	2.76	0.13	
C2	139.33	1	139.33	27.19	0.0004	significant
Residual	51.24	10	5.12			
Lack of Fit	51.24	5	10.25			
Pure Error	0.000	5	0.000			
Core Total	3200.27	19				

3.2. The individual effect of independent variables

The individual effects of each of the independent variables on dependent variables are discussed in this part.

3.2.1. Retention time

Increasing the retention time enhances the time of pollutant exposure to ultrasound, the production of hydroxyl radical, and the degradation and oxidation of pollutants (Fig. 2).

As shown in Fig. 2, both COD and phosphorous removal efficiencies enhanced with increasing retention time. Moreover, with ultrasonic power of 200 w and the volume of 100 mL, maximum removal efficiency for COD (70.6 %) and phosphorous (76.8 %) were obtained at 8 h retention time. The result of the research of Zhang et al. (2008) showed that increasing ultrasonic exposure time enhances its efficiency, due to increasing the ultrasonic specific energy and the dose of ultrasonic energy, leading to stronger cavitation, more free radical formation, and increased thermal energy (Zhang et al. 2008a).

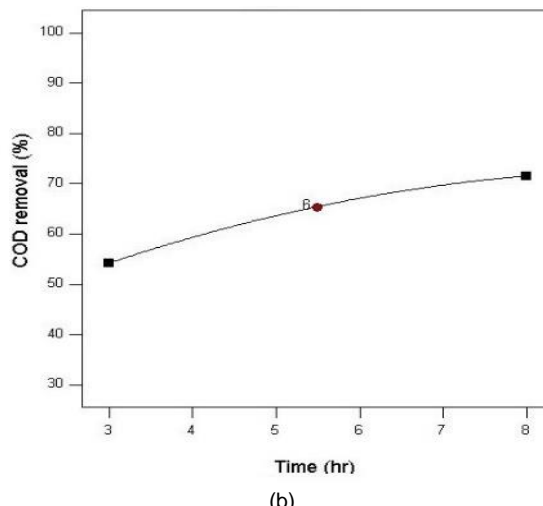
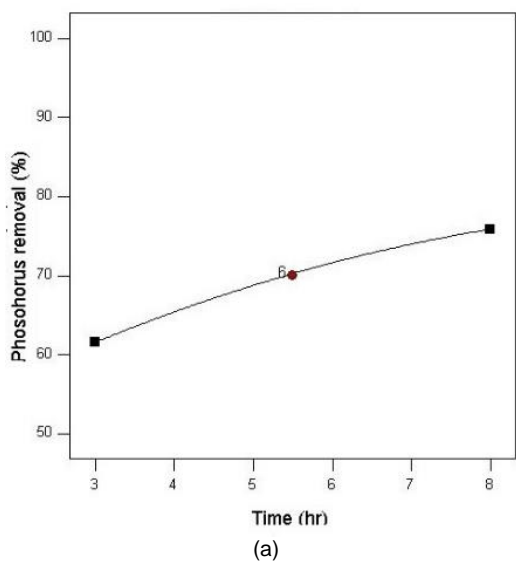


Fig. 2. Retention time effect on dependent variables as (a) phosphorus removal, (b) COD removal.

3.2.2. Ultrasonic power

The phosphorous and COD removal efficiency increased with enhancing ultrasonic power (Fig. 3).

This result is due to increasing the ultrasonic specific energy at higher ultrasonic power and the bubble formation at high pressure and temperature, namely, more acoustic cavitation. This results in the formation of large amounts of H⁺ and hydroxyl radicals, which oxidize the sample. This has also been observed in the research carried out by Zhang et al. (2008b).

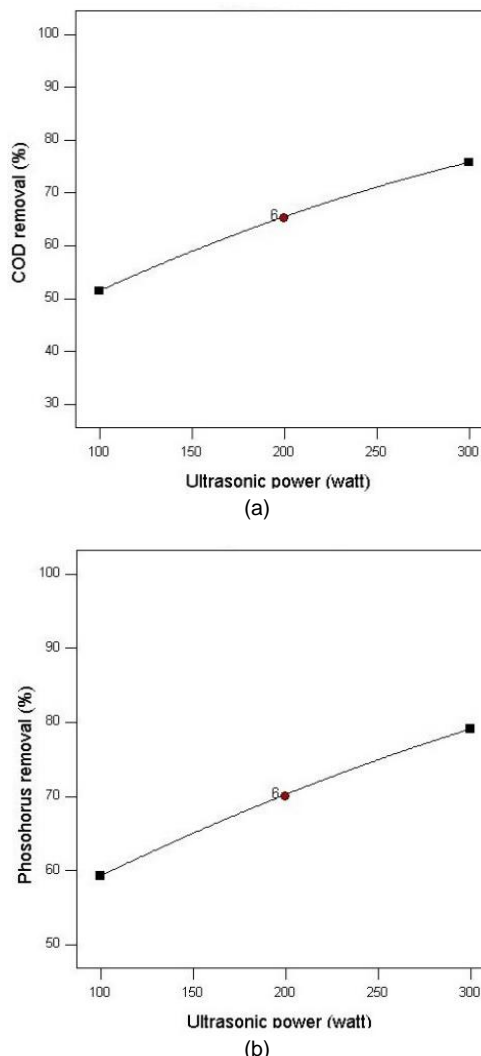


Fig. 3. Ultrasonic power effect on dependent variables as (a) COD removal, (b) phosphorus removal.

3.2.3. The volume of the sample

According to Fig. 4, increasing the volume disperses contaminants in the beaker and increases the distance from the wave source, leading to reducing the probability of the particle being exposed to the waves, the ultrasonic specific energy, the sample oxidation with the hydroxyl radical, and the removal efficiency.

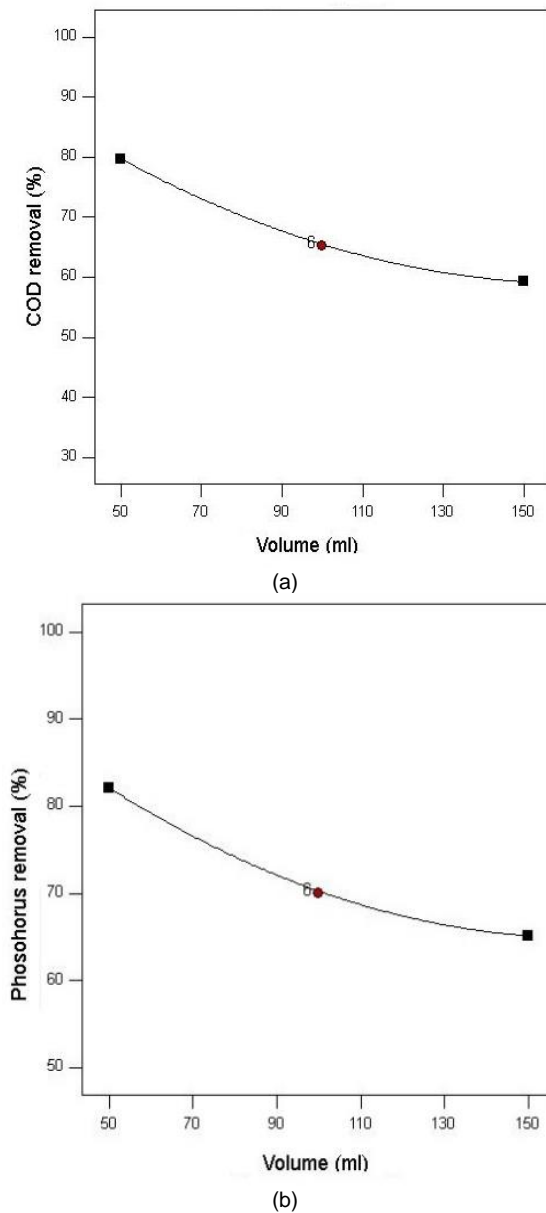


Fig. 4. Sample volume effect on dependent variables as (a) COD removal, (b) phosphorus removal.

3.3. Simultaneous effect of independent variables

The independent variables simultaneous effect (two variables for each test) on dependent variables is presented here.

3.3.1. Simultaneous effect of ultrasonic power and retention time

As shown in Fig. 5, more removal efficiency of COD and phosphorous was observed by increasing the ultrasonic power and the retention time at a constant volume (100 mL), due to higher hydroxyl radical formation and COD and phosphorus oxidation.

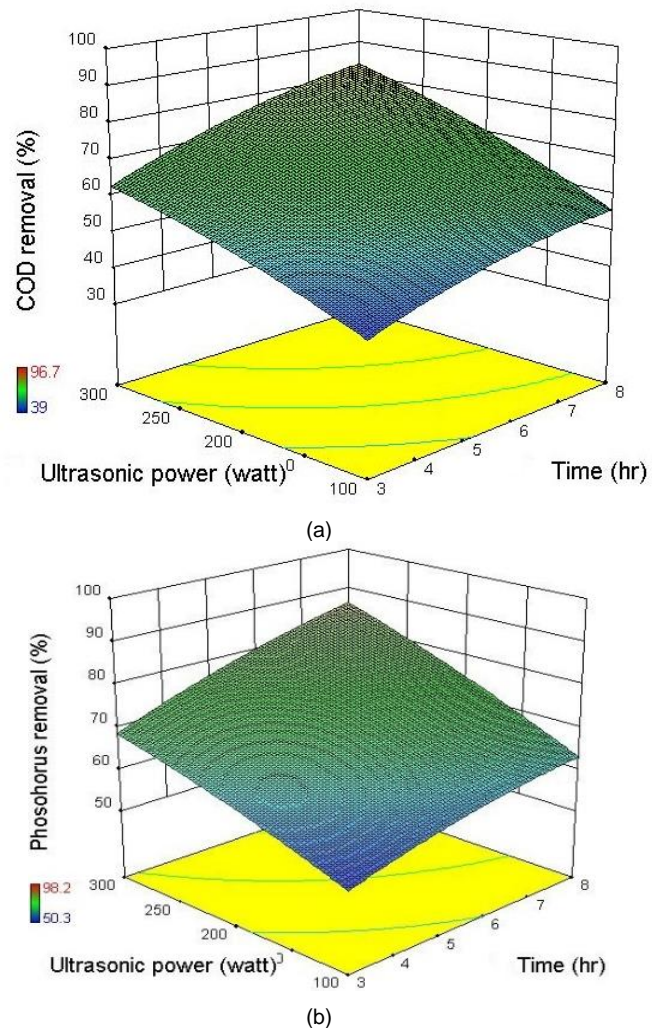
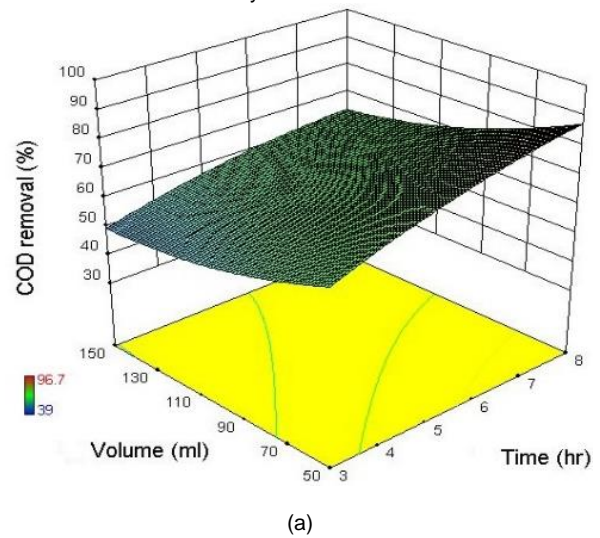


Fig. 5. Simultaneous effect of ultrasonic power and Time on dependent variables a: COD removal, b: phosphorus removal

3.3.2. Retention time and sample volume simultaneous effect

Based on the Fig. 6, more retention time and less sample volume increase the removal efficiency.



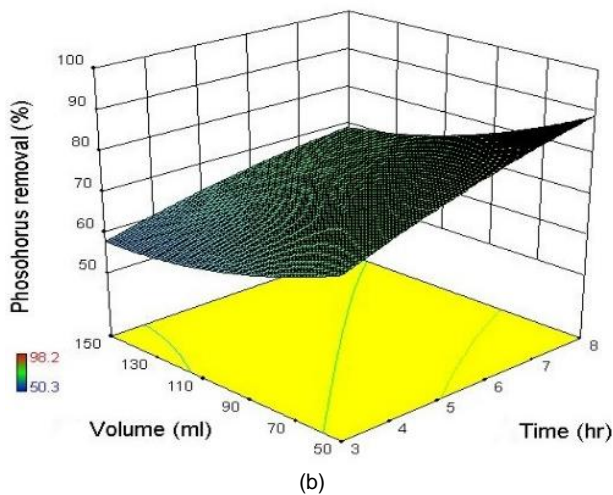
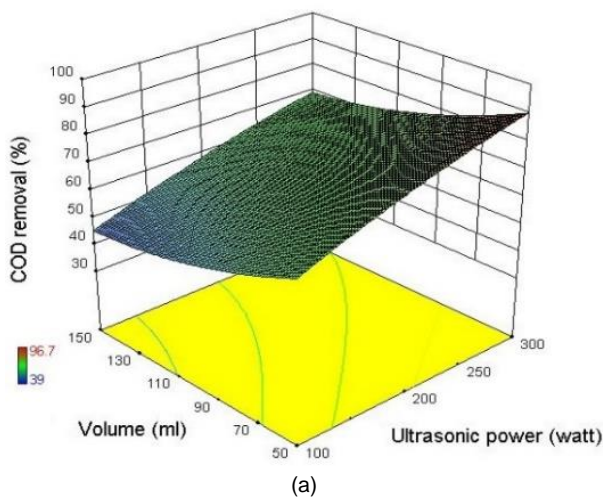


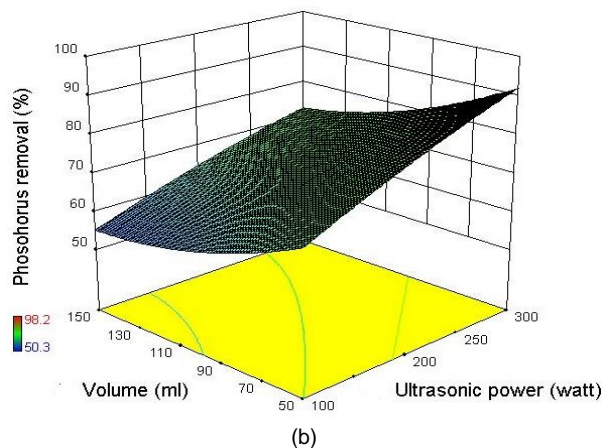
Fig. 6. Simultaneous effect of volume and time on dependent variables as (a) COD removal, and (b) phosphorus removal.

3.3.3. Sample volume and ultrasonic power simultaneous effect

Based on the Fig. 7, More ultrasonic power and less sample volume increase the COD removal efficiency and phosphorous.



(a)



(b)

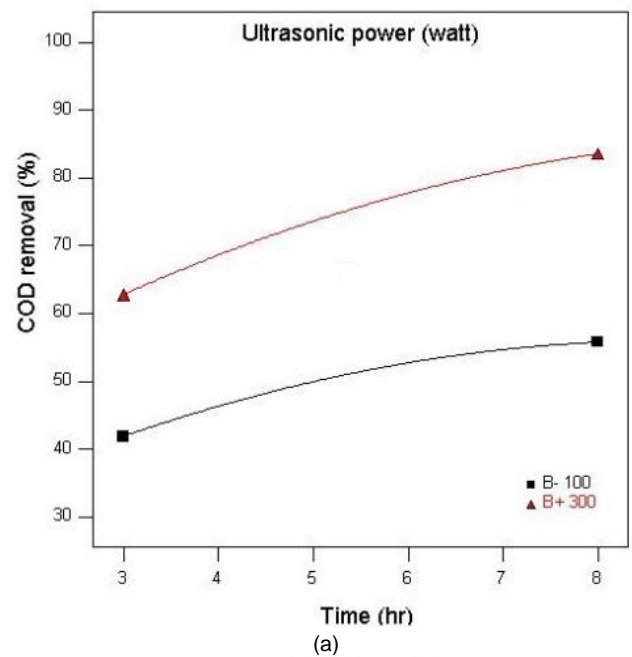
Fig. 7. Volume and ultrasonic power simultaneous effect on dependent variables as (a) COD removal, and (b) phosphorus removal.

3.4. Interaction of independent variables

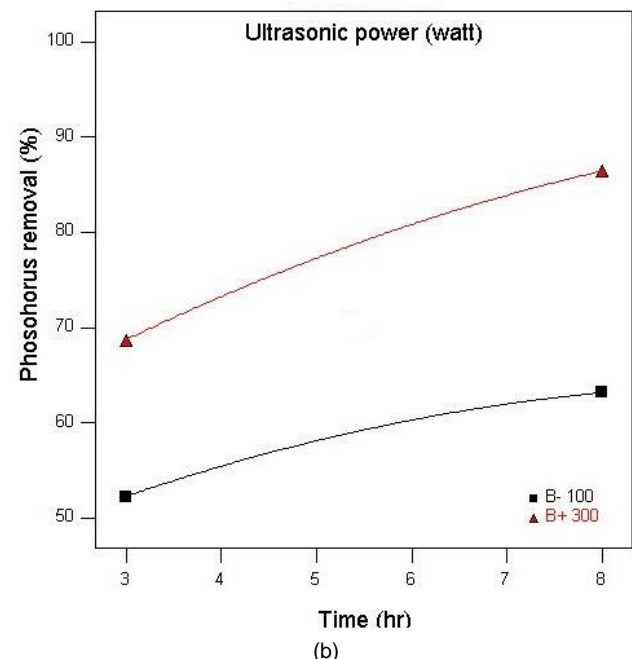
Interaction of independent variables are important in all of the experimental investigations.

3.4.1. The ultrasonic power and retention time

Based on Fig. 8, there is a synergistic effect between retention time and ultrasonic power.



(a)



(b)

Fig. 8. Interaction effect of ultrasonic power and time on dependent variables as (a) COD removal, and (b) phosphorus removal.

3.4.2. The interactive effect of retention time and sample volume

These two parameters have an antagonistic effect on each other (Fig. 9). The interactive effect of time and sample volume on the phosphorus removal efficiency was insignificant based on analysis of variance (Table 4).

3.4.3. The interactive effect between Volume and ultrasonic power

As shown in table 3 and table 4, these two parameters have not significant interactive effect on dependent variables.

3.5. Optimization and validation of the suggested models

The optimized removal of COD (97.39 %) and phosphorous (98.73 %) was obtained at 7.94 h retention time, 296.19 w ultrasonic power, and 54.52 mL volume. In order to validate the predictive models, the COD and phosphorous removal efficiencies, Fig. 10 is shown. Based on this Fig., the proximity of the actual and the predicted values indicate the high validity of the models.

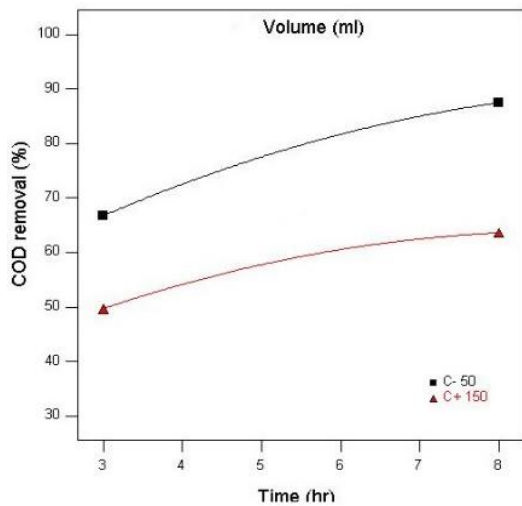
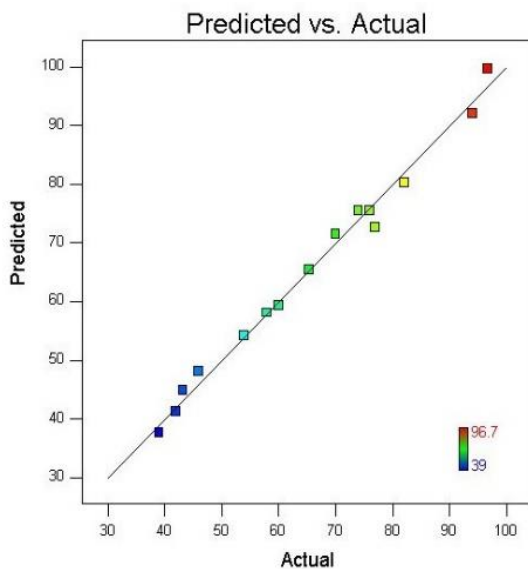
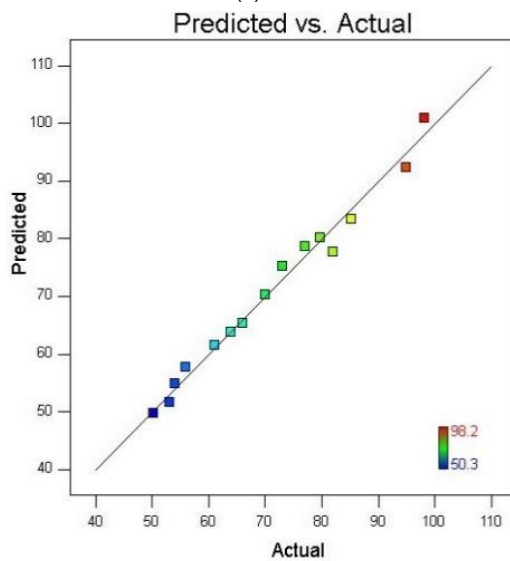


Fig. 9. Interaction effect of volume and time on COD removal efficiency.



(a)



(b)

Fig. 10. The prediction values versus the real values as (a) COD removal, and (b) phosphorus removal.

4. Conclusions

The use of ultrasound in sludge treatment is one of the most efficient methods. Regarding the need for the treatment of supernatant obtained from sludge dewatering, this study evaluated the effect of this process on supernatant of sludge. Results showed that this technology was able to completely remove phosphorus and COD from sludge, in agreement with all the advantages reviewed in the literature. The novelty of this study was the evaluation of the simultaneous and interactive effects of parameters on the treatment of supernatant by ultrasonic waves. In addition, a logic model was suggested to predict results.

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Nomenclature

COD	Chemical Oxygen Demand
RSM	Response Surface Methodology
P	Phosphorus
CCD	Central Composite Design
hr	hour
df	Degree of freedom

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