Available online at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Original Article

Removal of Uranium from Uranium Plant Wastewater Using Zero-Valent Iron in an Ultrasonic Field

Jing Li [a,b,c,d,e], *Libo Zhang* [a,b,c,d,e,*], *Jinhui Peng* [a,b,c,e], *Jinming Hu* [f], *Lifeng Yang* [f], *Aiyuan Ma* [a,b,c,d,e], *Hongying Xia* [a,b,c,d,e], *Wenqian Guo* [a,b,c,d,e], and *Xia Yu* [a,b,c,d,e]

[a] *Yunnan Provincial Key Laboratory of Intensification Metallurgy, Kunming, Yunnan 650093, China*
[b] *Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming 650093, China*
[c] *National Local Joint Laboratory of Engineering, Application of Microwave Energy and Equipment Technology, Kunming, Yunnan 650093, China*
[d] *Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093, China*
[e] *State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, Yunnan 650093, China*
[f] *Nuclear Group Two Seven Two Uranium Industry Limited Liability Company, Hengyang, Hunan 421000, China*

ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form
4 December 2015
Accepted 20 January 2016
Available online 17 March 2016

Keywords:
Iron
Ultrasonic
Uranium Plant Wastewater
Water

ABSTRACT

Uranium removal from uranium plant wastewater using zero-valent iron in an ultrasonic field was investigated. Batch experiments designed by the response surface methodology (RSM) were conducted to study the effects of pH, ultrasonic reaction time, and dosage of zero-valent iron on uranium removal efficiency. From the experimental data obtained in this work, it was found that the ultrasonic method employing zero-valent iron powder effectively removes uranium from uranium plant wastewater with a uranium concentration of 2,772.23 μg/L. The pH ranges widely from 3 to 7 in the ultrasonic field, and the prediction model obtained by the RSM has good agreement with the experimental results.

* *Corresponding author.*
E-mail address: libozhang77@163.com (L. Zhang).
http://dx.doi.org/10.1016/j.net.2016.01.021

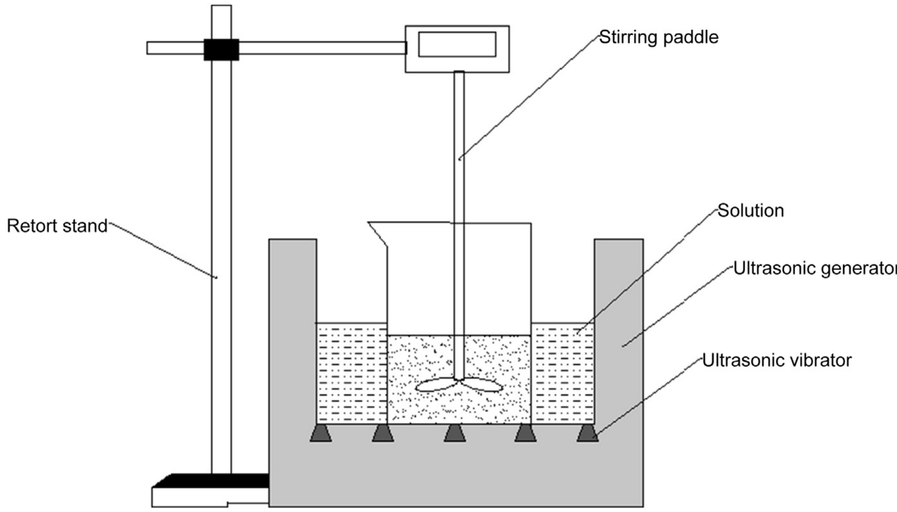

Fig. 1 – The experimental device.

1. Introduction

Uranium and its compounds are threats to human health and the ecological balance because of their radioactivity and heavy-metal toxicity [1]. Elevated levels of uranium have been found in agricultural irrigation drainage water and industrial wastewater [2,3]. The toxic nature of uranium(VI) ions, even at trace levels, has been a public health problem for many years [4]. Therefore, research on uranium removal from wastewater is important.

Uranium in industrial water is usually found in the environment in the quadrivalent uranium [U(IV)] and hexavalent uranium [U(VI)] forms, which coexist with other metal compounds or oxides. Uranium(IV) could be removed in the form of precipitation because it easily forms stable complex-shaped precipitation. Uranium(VI) usually exists in the form of uranium dioxide (UO_2^{2+}), which has good solubility and is difficult to remove. Therefore, the removal of uranium from wastewater generally refers to the removal of U(VI) and its compounds.

Zero-valent iron was used as the medium in the ultrasonic field to remove uranium from uranium plant wastewater in this study. Iron is an active metal with strong reducibility. It can reduce a variety of pollutants, including uranium. When there is sufficient zero-valent iron and corrosion (i.e., iron hydroxide) in the system, UO_2^{2+} is reduced as quadrivalent U(IV) deposited on the iron surface, which could allow complete removal of uranium.

Acoustic cavitation, thermal effect, and chemistry effect have tremendous positive effects; therefore, many researchers have focused much attention on applying ultrasonic technology [5–7]. Studies have indicated that ultrasonic mixing is efficient, timesaving, and economically functional, and it offers many advantages over the classical procedure [6,7]. Therefore, an ultrasonic field was employed in the uranium removal in uranium plant wastewater research.

In this paper, the effect of pH, ultrasonic reaction time, and dosage of zero-valent iron rates on uranium removal efficiency were evaluated in an ultrasonic field by using response surface methodology (RSM). In addition, the uranium content of the solution, which was treated by zero-valent iron in an ultrasonic field, was detected by inductively coupled plasma mass spectrometry (ICP-MS). The relative standard deviation is less than 5%, and the detection range is between 10^{-9} ng/mL and 1 mg/L.

2. Materials and methods

2.1. Experimental procedure

Uranium plant wastewater with a uranium concentration of 2,772.23 μg/L and pH value of 8.69 was obtained from purification processing. All experiments in the ultrasonic field were performed using 500-mL flat-bottomed glass beakers (diameter, 9 cm) containing 200 mL of uranium plant wastewater. The uranium plant wastewater was stirred by mechanical agitation with a stirring speed of 55 r/min. The wastewater was pretreated by pH adjustment using extraction raffinate with the uranium concentration of the raffinate of 2,984.1 μg/L and pH value of 0.12. A certain amount of zero-valent iron powder was then added to the wastewater after pH adjustment had been finished. An ultrasonic reactor with 500 W power was started.

After a period of time, the reaction was finished. The reaction mixture was pumped through a filter. The uranium removal efficiency was calculated by the uranium concentration of the filtrate detected by ICP-MS. The experimental device is shown in Fig. 1.

2.2. Experimental design

To optimize and analyze the effects of solution pH, ultrasonic reaction time, and dosage of zero-valent iron (per 200 mL of

Table 1 – The uranium removal experimental design used in response surface methodology studies by using three independent variables showing the observed values of uranium removal efficiency.

Run	Variables			Response
	pH A	Ultrasonic reaction time (min) B	Dosage of zero-valent iron powder (g per 200 mL uranium plant wastewater) C	Uranium removal efficiency (%) Y
1	7	60	0.4	99.72
2	5	70.23	0.3	99.77
3	1.64	45	0.3	92.28
4	8.36	45	0.3	98.60
5	3	60	0.2	98.40
6	5	19.77	0.3	99.66
7	3	30	0.4	99.38
8	3	30	0.2	98.84
9	5	45	0.13	99.40
10	5	45	0.3	99.77
11	7	30	0.4	99.59
12	5	45	0.3	99.69
13	3	60	0.4	99.34
14	5	45	0.3	99.65
15	5	45	0.3	99.74
16	5	45	0.3	99.67
17	5	45	0.47	99.83
18	7	60	0.2	99.52
19	7	30	0.2	99.55
20	5	45	0.3	99.67

uranium plant wastewater) on uranium removal efficiency, a statistically designed experiment with minimal experimental runs is greatly desired. To date, many researchers have tried to enhance the uranium removal efficiency from uranium plant wastewater and underground water through a statistical approach [8,9]. Statistical approaches such as the RSM are successful in calculating the complex interaction between the independent process factors [10]. Statistical approaches such as RSM consume minimal resources and time, compared to conventional experimental work, and provide information-rich data and analysis with minimal experimental runs [11].

The RSM is an effective statistical technique for developing, improving, and optimizing complex processes [12,13]. The RSM is a collection of statistical and mathematical techniques that are useful for analyzing the effects of several independent variables on a response [14]. This process usually employs a low-order polynomial equation in a predetermined region of the independent variables, which is later analyzed to locate the optimum values of the independent variables for the best response [15]. The RSM defines the effect of the independent variables—alone or in combination—in the processes. In addition to analyzing the effects of the independent variables, this experimental methodology also generates mathematical models [14].

Based on the regulations for radiation protection for uranium processing and fuel fabrication facilities (EJ1056-2005) [16], a uranium concentration of 50 μg/L is acceptable for discharge instead of the 300 μg/L mentioned in the Integrated Wastewater Discharge Standard (GB8798-1996) [17]. Therefore, a novel technology with high uranium removal efficiency is in demand. To date, uranium removal from uranium plant wastewater using zero-valent iron and ultrasonic vibration has not been reported. To obtain high uranium removal efficiency to meet the new national policy of a uranium concentration of 50 μg/L, the current study aimed to illustrate the interaction between the operating conditions of uranium removal using zero-valent iron media by ultrasonic method and uranium removal efficiency in diagnostic analysis using the central composite design (CCD) of the RSM. The final regression models obtained from the CCD may predict the highest uranium removal efficiency operating parameters in the uranium removal process from uranium plant wastewater using zero-valent iron media by the ultrasonic method.

3. Results and discussion

The uranium removal experimental design and the observed responses are shown in Table 1. Fitting the data to various models (e.g., linear, two factorial, quadratic, and cubic models) and their subsequent analysis of variance (ANOVA) showed that uranium removal efficiency was most suitably described with a quadratic polynomial model [Eq. (1)]:

Table 2 – The analysis of variance for responses Y [i.e., uranium removal efficiency (%)].

Source	Sum of squares	DF	Mean square	F	Prob > F	
For Y						
Model	39.67	9	4.41	3.58	0.0299	Significant
Residual	12.33	10	1.23			
Lack of fit	12.32	5	2.46	1,131.88	< 0.0001	Significant
Pure error	0.011	5	$2.177E^{-003}$			
$R^2 = 0.7629$						
Pred R = −0.7962						
Adequate precision = 7.747						

DF, degrees of freedom.

$$Y = 99.66 + 0.96A - 0.014B + 0.18C + 0.073AB - 0.15AC + 0.07BC - 1.27A^2 + 0.24B^2 + 0.21C^2 \quad (1)$$

where A refers to the value of pH, B is ultrasonic reaction time, and C is the dosage of zero-valent iron powder.

The statistical significance of the model equation was evaluated by the F-test for the ANOVA. The ANOVA evaluations of this model, shown in Table 2, imply that this model can describe the experiments. In Table 2, the prob > F-values for relative density and bending strength were lower than 0.05, which indicated that the quadratic models were significant [18]. The coefficient of determination (R^2) was 0.7629, which was close to 1, and indicated a correlation between the observed and the predicted values. The "lack-of-fit tests" compare the residual error to the "pure error" from replicated experimental design points. Values of $p > 0.05$ for both responses indicated that the lack of fit for the model was insignificant. Adequate precision measures the signal-to-noise ratio, and a ratio greater than 4 is desirable. The adequate precision for Y was 7.747. This high value of adequate precision demonstrated that the model was significant for the process.

In the model analysis of variance, the correlation coefficient of quadratic regression equations of uranium removal efficiency was $R^2 = 0.7629$, which indicated that the model very well fit the actual situation. The F value of 3.58 implied that the model was significant. There was only a 2.99% chance that a model F value this large could occur because of noise. Values of Prob > F less than 0.0500 indicated that the model terms were significant. In this situation, A and A^2 were significant model terms. A negative Pred R^2 of −0.7962 implied that the overall mean was a better predictor of response than the current model. "Adeq precision" measures the signal-to-noise ratio. A ratio greater than 4 was desirable. The ratio of these uranium removal experiments was 7.747, which indicated an adequate signal. This model can be used to navigate the design space.

The actual and predicted uranium removal efficiency and the response surface plots for relative uranium removal efficiency are plotted in Fig. 2 and Fig. 3, respectively. Fig. 3 depicts the change in uranium removal efficiency due to pH, ultrasonic reaction time, and dosage of zero-valent iron, plotted for the situation in which the ultrasonic power is 500 W.

The pH and ultrasonic reaction time had different effects on the response (i.e., uranium removal efficiency). The ultrasonic field showed a high effect for uranium removal, with the maximum uranium removal of 99.77% occurring from 2,772.23 μg/L uranium plant wastewater within the 20–70 minutes reaction time, 0.13–0.47 g dosage of zero-valent of iron powder per 200 mL uranium plant wastewater, and a pH of 3–7. Based on the experimental results, a mildly acidic pH was suitable for uranium removal. In a weak acid, acidic, or nearly neutral solution, uranium exists in the form of UO_2^{2+}, which is more easily reduced by zero-valent iron for better uranium removal in the ultrasonic field. However, in an alkaline solution, uranium primarily exists in the form of complex ions. These complex ions could suppress the reduction and precipitation of uranium by a zero-valent iron, which would lead to a sharp decrease in uranium removal. The effect of uranium removal improves with the ultrasonic reaction time, and after 45 minutes the effect is steady. With a longer reaction time in the ultrasonic field, the chance of contact between U (VI) and zero-valent iron is greater. A greater chance of contact would promote the combination of uranium acyl and the iron hydroxide flocculation body, thereby increasing the uranium removal efficiency. After reaching reaction balance, a longer reaction time has no effect on uranium removal. The zero-valent iron dropped in the water is first oxidized, and then forms an iron hydroxide flocculation body, which ultimately has an adsorption function on the uranium acyl. In the meantime, unreacted iron could provide a surface for sediment adsorption. The higher the dosage of iron powder, the more uranium that is removed. When the uranium content of wastewater is very low, a larger dosage of iron powder has little impact on increasing uranium removal. In this situation, the mass concentration of uranium in wastewater is below 0.04 mg/L, which is below the national discharge standard [19]. Therefore, excessive dosage of iron powder should not work on uranium removal. As shown in Fig. 3, a maximum uranium removal efficiency of 99.83% was obtained at the ultrasonic power of 500 W.

The mathematical model generated during RSM implementation was validated by conducting an experiment at the given optimal medium setting. The process parameters of experimental optimization recommended by RSM are shown in Table 3. The optimized parameters were a pH of 5, ultrasonic reaction time of 45 minutes, and dosage of zero-valent iron of 0.3 g (per 200 mL uranium plant wastewater). As Table 3 shows, the predicted value of uranium removal efficiency was 99.66%. There was only a 0.2% error, compared to the experimental value of 99.86%, which indicated that the value predicted by the RSM was in good agreement with the experimental value of uranium removal efficiency.

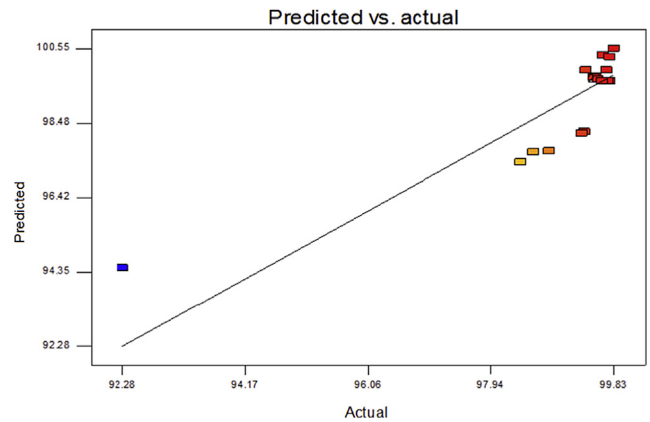

Fig. 2 – The predicted response versus the actual response.

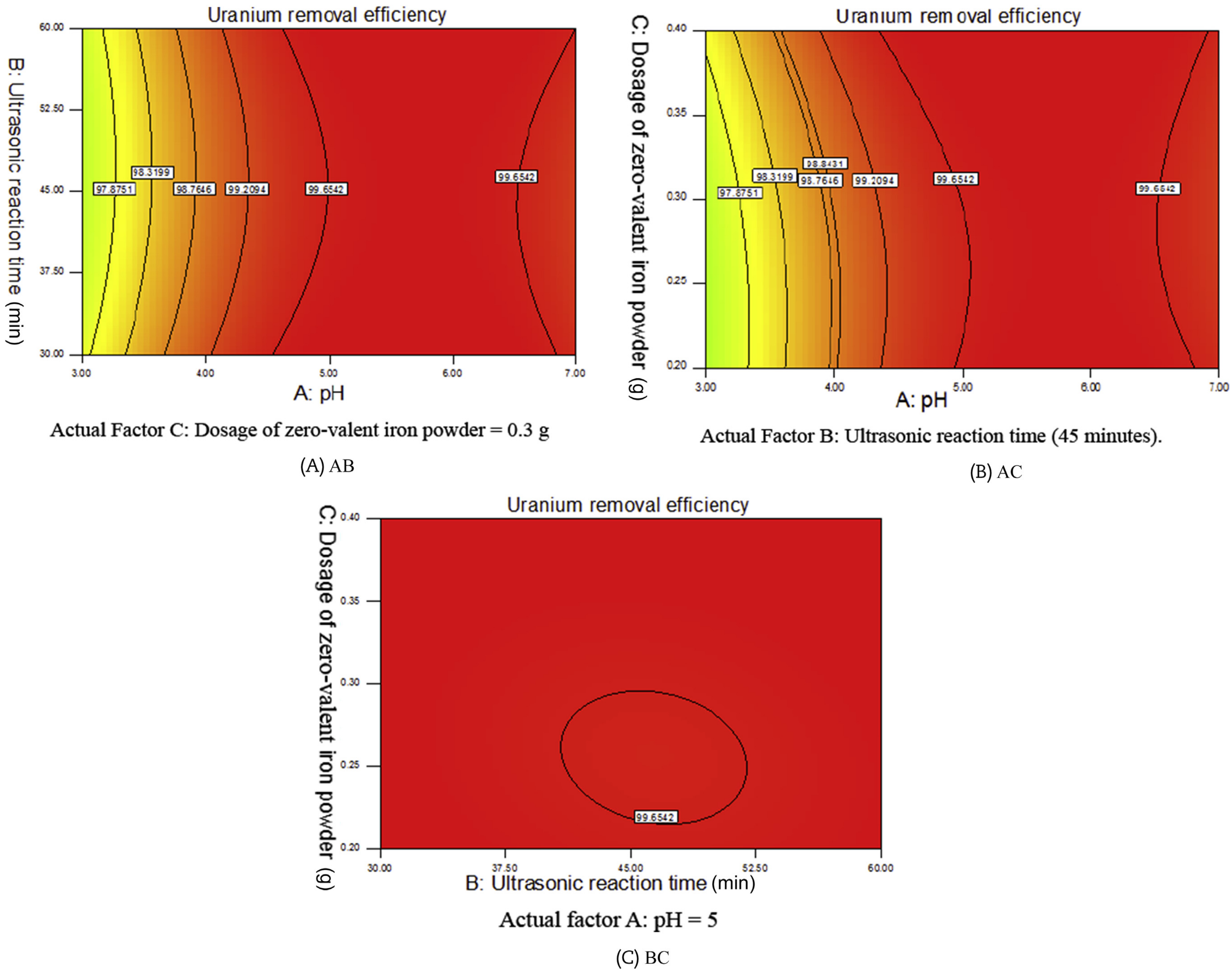

Fig. 3 – The response surface diagrams show the impact of pH, ultrasonic reaction time, and dosage of zero-valent iron powder on uranium removal efficiency. (A) AB. (B) AC. (C) BC.

Table 3 – Predicted value and the validation experiment value of uranium removal efficiency in the optimal technological condition.

pH A	Ultrasonic reaction time (min) B	Dosage of zero-valent of iron (g per 200 mL uranium plant wastewater) C	Uranium removal efficiency (%)	
			Predicted value	Experiment value
5	45	0.3	99.66	99.86

4. Conclusions

Instead of nitric acid or other acid, extraction raffinate obtained from the extraction section in the process of uranium production was used for pH adjustment, which utilized resources comprehensively and was environmentally friendly. The ultrasonic method employing zero-valent powder is effective for uranium removal from uranium plant wastewater. The maximum uranium removal rate could reach approximately 99.77% in 2,772.23 μg/L uranium plant wastewater within a reaction time of 20–70 minutes using 0.13–0.47 g dosage of zero-valent of iron powder per 200 mL uranium plant wastewater with a pH of 3–7.

Optimization by the RSM of the uranium removal from uranium plant wastewater using zero-valent iron in an ultrasonic field shows that all three reaction variables (i.e. pH, ultrasonic reaction time, and dosage of iron powder) affect uranium removal. A pH of 5, ultrasonic reaction time of 45 minutes, and 0.3 g iron powder (per 200 mL uranium plant wastewater) were the optimum conditions to achieve maximum uranium removal from uranium plant wastewater.

The predicted model obtained from RSM fits well with the experimental results. Therefore, the RSM is adequate for predicting the uranium removal rate, which is important when wastewater is derived from various plants with varying properties such as composition or pH. Many time-consuming experimental investigations for every wastewater composition were prevented by using RSM.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgments

The authors are grateful for financial support by the National Natural Science Foundation of China (grant no., 51404115), Kunming Personnel Training Project (grant no., KKSY201352104), The Young and Middle-aged Academic Technology Leader Backup Talent Cultivation Program in Yunnan Province, China (2012HB008), State International Joint Research Center of Advanced Technology for Superhard Materials (grant no., 2013B01038), Yunnan Provincial Science and technology innovation Talents scheme–Technological Leading Talent (grant no., 2013HA002), Kunming Academician Workstation of Advanced Preparation for Superhard Materials Field, and Kunming Academician Workstation of Metallurgical Process Intensification.

REFERENCES

[1] W.H. Zou, L. Zhao, R.P. Han, Removal of uranium (VI) by fixed bed ion-exchange column using natural zeolite coated with manganese oxide, Chin. J. Chem. Eng. 17 (2009) 585–593.
[2] D.L. Sparks, Environmental Soil Chemistry, Academic Press, San Diego (CA), 1998.
[3] J. Latey, C. Roberts, M. Penberth, C. Vasek, An agricultural dilemma: drainage water and toxics disposal in the San Joaquin Valley, University of California Agricultural Experiment Station, Riverside (CA), 1986.
[4] R. Han, W. Zou, Y. Wang, L. Zhu, Removal of uranium (VI) from aqueous solutions by manganese oxide coated zeolite: discussion of adsorption isotherms and pH effect, J. Environ. Radioact. 93 (2007) 127–143.
[5] J.B. Ji, X.H. Lu, M.Q. Cai, Z.C. Xu, Improvement of leaching process of geniposide with ultrasound, Ultrason. Sonochem. 13 (2006) 455–462.
[6] C. Stavarache, M. Vinatoru, R. Nishmura, Y. Maeda, Fatty acids methyl esters from vegetable oil by means of ultrasonic energy, Ultrason, Sonochem. 12 (2005) 367–372.
[7] J. Ji, J. Wang, Y. Li, Y. Yu, Z. Xu, Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation, Ultrasonics 44 (2006) e411–e414.
[8] L.M. Camacho, S. Deng, R.R. Parra, Uranium removal from groundwater by natural clinoptilolite zeolite: effects of pH and initial feed concentration, J. Hazard. Mater. 175 (2010) 393–398.
[9] M. Dickinson, T.B. Scott, The application of zero-valent iron nanoparticles for the remediation of a uranium-contaminated waste effluent,, J. Hazard Mater. 178 (2010) 171–179.
[10] D.C. Montgomery, United States; Solutions from Montgomery. Design and Analysis of Experiments, John Wiley & Sons, Hoboken (NJ), 2001.
[11] A.L. Ahmad, S.C. Low, S.R. Abd Shukor, A. Ismail, Optimization of membrane performance by thermal-mechanical stretching process using responses surface methodology (RSM), Sep. Purif. Technol. 66 (2009) 177–186.
[12] M. Basri, N.Z. Rahman, A. Ebrahimpour, A.B. Salleh, E.R. Gunawan, B.A. Rahman, Comparison of estimation capabilities of response surface methodology (RSM) with artificial neural network (ANN) in lipase-catalyzed synthesis of palm-based wax ester, BMC Biotechnol. 53 (2007) 1–14.
[13] C.J. Shieh, C.C. Akoh, P.E. Koehler, Four-factor response surface optimization of the enzymatic modification of triolein to structured lipids, J. Am. Oil. Chem. Soc. 72 (1995) 619–623.
[14] B.K. Korbhati, N. Aktas, A. Tanyolac, Optimization of electrochemical treatment of industrial paint wastewater

with response surface methodology, J. Hazard. Mater. 148 (2007) 83–90.
[15] H. Ceylan, S. Kubilay, N. Aktas, N. Sahiner, An approach for prediction of optimum reaction conditions for laccase-catalyzed bio-transformation of 1-naphthol by response surface methodology (RSM), Bioresour. Technol. 99 (2008) 2025–2031.
[16] EJ1056–2005, Regulations for radiation protection for uranium processing and fuel fabrication facility, China Commission of Science Technology and Industry for National Defense, Beijing (China), 2005 [In Chinese].
[17] GB8798–1996, Integrated Wastewater Discharge Standard, National Standard of the People's Republic of China, 1998 [In Chinese].
[18] P. Verma, U.S. Agrawal, A.K. Sharma, B.C. Sarkar, H.K. Sharma, Optimization of process parameters for the development of a cheese analogue from pigeon pea (*Cajanus cajan*) and soy milk using response surface methodology, Int. J. Dairy Technol. 39 (2005) 319–320.
[19] H.S. Wu, G.C. Zhu, X.W. Lu, Application of micro-electrolysis process for the treatment of dyestuff wastewater, Environ. Herald 2 (1999) 18–20 [In Chinese].