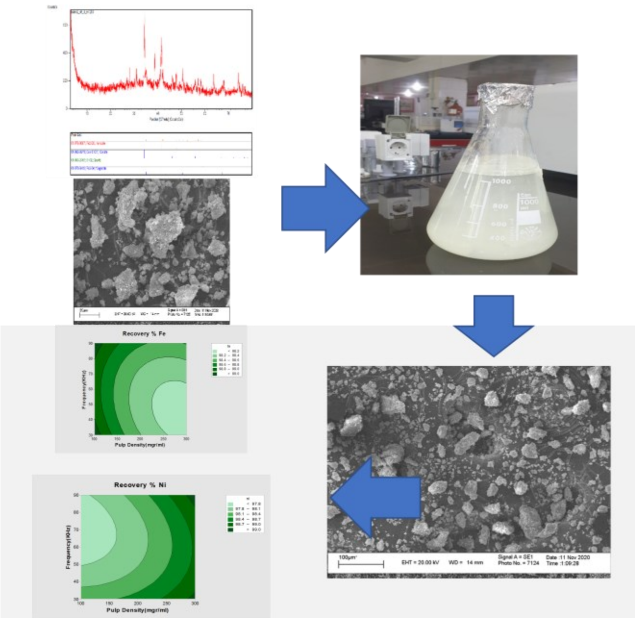
Global NEST Journal, Vol 26, No 2, 05417

Improving heavy metal removal efficiency from steel sludge: Application of the coupled ultrasonic-bioleaching treatment

Mateen Hosseinzadeh[1], Roya Mafigholami[1]* and Ebrahim Rajabzadeh Ghatromi[2]
[1]Department of Water and Wastewater Environment, West Tehran Branch, Islamic Azad University, Tehran, Iran
[2]Department of Marine Biology, Faculty of Marine Sciences, Maritime Science and Technology University, Khorramshahr, Iran
Received: 01/10/2023, Accepted: 12/11/2023, Available online: 28/11/2023
*to whom all correspondence should be addressed: e-mail: r.mafigholami@wtiau.ac.ir
https://doi.org/10.30955/gnj.005417

Graphical abstract



Abstract

This study assessed the efficiency of Fe, Al, Ni and Sr removal from the steel sludge using the coupled bioleaching with *Thiobacillus thiooxidans* and ultrasonic waves. Growth conditions were optimized using the surface response method. The bacterium was adapted successively to three heavy metal-containing solutions with different concentrations of 100, 200, and 300 mg/ml. Samples were exposed to ultrasonic waves at frequencies of 30, 60 and 90 kHz and durations of 20, 30 and 40 min for two weeks. The highest Fe removal efficiency of 98.45% was obtained using the *T. thiooxidation*, wave frequency of 30 kHz for 40 min, and pulp density of 100 mg/ml. The maximum removal efficiency was found to be 99.74% for Al under a wave frequency of 90 kHz for 20 min and a pulp density of 300 mg/ml, approximately 100% for Ni under a wave frequency of 30 kHz for 20 min and a pulp density of 300 mg/ml, and 98.45% for Sr under a wave frequency of 90 kHz for 20 min and a pulp density of 300 mg/mL. Results showed that the removal efficiency of Ni and Al bioleaching improved significantly ($P < 0.05$) under the ultrasonic irradiation while the removal efficiency of Fe and Sr remained statistically unchanged ($P > 0.05$) with and without the application of ultrasonic waves.

Keywords: Bioleaching, heavy metals, *Thiobacillus thiooxidans*, ultrasonic waves, steel sludge

1. Introduction

Sludge management is increasingly recognized as a critical environmental issue due to the large-scale expansion and improvement of wastewater treatment plants with strict effluent requirements around the world. Particularly, large quantities of sludge are produced during the industrial wastewater treatment whose toxicity and concentration of toxic compounds are higher than the original untreated wastewater, thus posing more difficult disposal problems (Hocheng *et al.* 2014; Hobson *et al.* 2017).

Bioleaching is a hydrometallurgical process relying on the ability of bacteria and fungi in transforming solid compounds into the soluble phase and valorization of recoverable elements (Reed *et al.* 2016). Bioleaching has several convincing advantages such as low energy, cost and skill requirements (Rastegar *et al.* 2015; Gomes *et al.* 2018). This technique has attracted increasing attention in recent years as a promising way of treating alkaline wastewaters from mining operations and reuse and valorization of heavy metals (HMs) (MafiGholami *et al.* 2012; Chiang *et al.* 2013). In treating steel slag, bioleaching is also considered as a low energy-consumptive and safe eco-friendly method of metal recovery (MafIGholami *et al.* 2010; Hocheng *et al.* 2014; Murugesan *et al.* 2020).

Studies on HM removal via bioleaching are limited. In this case, Pathak *et al.* (2019) assessed the feasibility of nickel (Ni), vanadium, molybdenum, and aluminum (Al) bioleaching with the aid of *Acidithiobacillus thiooxidans.* Copper was also bioleached efficiently by Murugesan *et al.* (2020) from printed circuit boards. Vestola *et al.* (2010) assessed iron (Fe) bioleaching characteristics of steel slag using a mixture of *cidithiobacillus spp*. and *Leptospirillum spp*. cultured in a sulfide-rich condition. Gomes *et al.* (2018) used bioleaching with *Acidithiobacillus thiooxidans* and *A.*

ferrooxidans to retreat Al, chrome and vanadium from the steel-plant wastewater.

Advanced oxidation processes (AOPs) involving ultrasound have proven to be highly effective in wastewater treatment. Ultrasonics are mechanical waves with a frequency exceeding the human auditory capacity (20 to 40 kHz) which offer high antibacterial and pollutant degradation potentials (Wang *et al.* 2016). Through the cavitation process, ultrasonic impulses form cavities or micro-cavities that elevate the water pressure and temperature to about 1000 atm and 500 K, respectively. In this condition, hydroxyl radicals are formed and break down organic matters (Sanmadi *et al.* 2017; Kamani *et al.* 2019). The effectiveness of this method has been demonstrated by prior studies such as Murugesan *et al.* (2020) in bacterial bioleaching of copper using *A. thioxidans* and Box–Behnken and Ma *et al.* (2020) in using ultrasonics to remove chrome from the leather industry wastewater. The high potential of biological methods and ultrasonic waves with optimized bacterial concentration, time and ultrasonic radiation highlight their combined application in sludge pollution reduction. Therefore, this study aimed to investigate the efficiency of the coupled bioleaching-ultrasonic treatment in heavy metals reduction from the sludge of the Ahcaz steel wastewater treatment plant.

2. Materials and methods

2.1. Bacteria used in bioleaching

T. thiooxidans (PTCC1717) was obtained from the Iranian Research Organization for Science and Technology. The bacteria were cultured by inoculating 10% of the pure bacterial cells in a specific acidic culture medium (Table 1) at 28 ° C and refrigerated at 4 ° C (MafiGholami *et al.* 2011). Sulfur was considered as the source of energy required by this bacterium. The pH of the culture medium was adjusted to pH 3.5 using 1 N sulfuric acid. The culture medium was autoclaved at 121 ° C for 15 min to prevent the growth of contaminating microorganisms.

Table 1. Specific acidic culture medium of *T. thiooxidans*

Gram amount in 1000 ml	Substance
2	$(NH_4)_2SO_4$
0/25	$MgSo_4.7H_2O$
0/1	K_2HPO_4
0/1	KCl
5	S

2.2. Sludge production in the steel industry

In the Ahvaz Steel Industry, a considerable environmentally-threatening amount of 45-40 t/month sludge is produced and transferred to the Ahvaz waste landfill for burial. The steel sludge production involves chlorination, primary coagulation and flocculation, fat and oil removal by Dissolved Air Flotation (DAF), secondary coagulation and flocculation and clarification in sedimentation ponds equipped with the blade clarification system to enhance the sedimentation performance. The effluent from the sedimentation ponds is finally disinfected with chlorine gas. The sludge from degreasing and clarification units was dewatered using the belt filter press to a moisture level of 25 %.

2.3. Elemental composition

According to the X-ray powder diffractometer (XRD) and inductively coupled plasma optical emission spectrometry (ICP-OES) analyses, the pre-bleached sludge contained levels of Fe, Al, Ni, Sr (Table 2). The most detected phase was calcite (Ca Co3), followed by iron oxide (Fe2O3).

Table 2. ICP-OES results of Fe, Al, Ni, Sr in the pre-bleaching sludge sample

Pre-bleached ICP-OES (%) readings			
Strontium	Nickel	Aluminium	Iron
0/62	0/0035	8/9	6/2

2.4. Sludge characteristics

Figures 1 and 2 illustrate the pre-bleached sludge characteristics obtained by Scanning Electron Microscopy (SEM- Model: XL30, Philips, Holland) and the wavelength dispersive X-Ray Fluorescence (XRF) technique (PW2404, Philips). As shown in Figure 1, some particles are seen as sedimentary masses on the surface of the sludge.

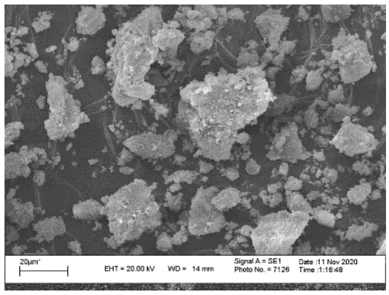


Figure 1. Surface characteristics of pre-bleached sludge obtained by the Scanning Electron Microscopy

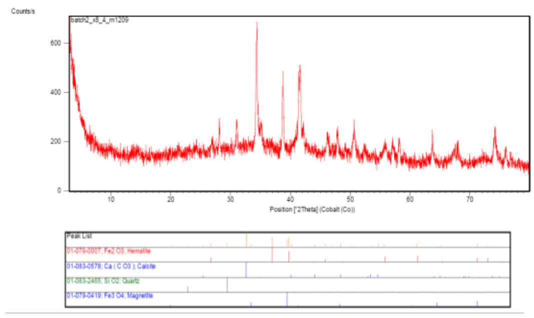


Figure 2. X-Ray Fluorescence spectrum of the pre-bleaching sludge

2.5. Inoculation and adaptation of T. thiooxidans

Inoculation was a 10% volumetric percentage of bacteria with a population of $4*10^7$ bacterial number/ml per Erlenmeyer. The culture was performed at 28 ° C and 150 rpm. The adaptability of bacteria against Fe, Al, Ni and Sr content of the treated wastewater was conducted from the concentration of 100 to 300 mg/L with an increase of 100 mg/ml in each step. In all stages, 500 mg of sulfur was used to allow the bacteria to recover energy. Deionized water was also used to compensate for the water lost from the environment during evaporation. The bacterial adaptation period was considered two weeks (MafiGholami *et al.* 2011).

2.6. Experimental design

The experiments were optimized using Minitab18 software and designing Box–Behnken response curve to achieve the highest bioleaching efficiency. A 3-variable 3-level full factorial experimental design with 3 central points was used and 15 experiments were performed to investigate the parameters affecting the process of heavy metals reduction (Tables 3 and 4).

Table 3. Levels and values of independent variables

Independent variables	High level (-1)	Moderate level (0)	Low level (-1)	Symbol
Pulp Density	300	200	100	A
Frequency	90	60	30	B
Time	40	30	20	C

Table 4. Box- Behnken design for HM bioleaching from the sludge by combining ultrasonic radiation

Run	A: Pulp density (mqr/ml)	B: Frequency (KHZ)	C:Time (min)	Recovery (%)			
				Sr	Al	Ni	Fe
1	100	30	30	98/30	99/65	98/28	99/39
2	300	20	60	98/25	99/55	99/25	99
3	100	30	90	98/31	99/70	97/74	99/10
4	100	40	60	98/29	99/68	98/40	99/70
5	200	20	90	98/43	99/72	98/86	99/10
6	300	30	90	98/31	99/63	99/20	98/35
7	200	20	30	98/23	99/56	99/49	98/45
8	300	40	60	98/19	99/53	99/05	98/20
9	200	30	60	98/22	99/53	98	98/30
10	300	30	30	98/23	99/51	99/09	98/18
11	200	40	90	98/32	99/58	98/50	99/08
12	100	20	60	98/18	99/59	97/80	98/50
13	200	40	30	98/39	99/58	98/45	98/70
14	200	30	60	98/22	99/53	98	98/30
15	200	30	60	98/22	99/53	98	98/30

2.7. Performing the experiment

The experiment environment consisted of fifteen 500 mL Erlenmeyer flasks, each filled with 90 ml of the culture medium inoculated by a 10% volume of adapted bacteria with dewatered sludge powder and 500 mg of sulfur. Except for the control Erlenmeyer flask, pulp densities of 100, 200 and 300 mg were exposed to three levels of ultrasonic waves including 30, 60 and 90 kHz and durations of 20, 30 and 40 min for two weeks (Ultrasonic Power Cleaner 3MS Products from Fabulustre, USA) (Ting and Vyas, 2017). In every bioleaching step, 1 N sulfuric acid (Metrohm, Germany) was used to maintain the pH of the environment. After two weeks, all Erlenmeyers were centrifuged (Hettich Mikro, Germany) at 9000 rpm for 10 min. Cell mass and supernatant were collected by filter paper and sent to Iran Mineral Processing Research Center for SEM and ICP tests to investigate the efficiency of metal bioleaching by bacteria.

2.8. Particle size distribution

The particle size distribution was determined using a particle size analyzer (Scatteroscope, Qudix, South Korean). This device has several logarithmically distributed (log-spaced) size bins ranging from 0.01 to 3000 µm and uses light scattering to determine the size of particles in each channel.

2.9. Special surface area

The specific surface area, total pore volume and mean diameter of the pre- and post-bleached sludge were measured using a high-speed gas adsorption analyzer (Nova 3000, Version 6.07, Quantachrome Corporation). A certain weight of the sample between 0.05 to 0.1 g was deaerated at 80 ° C for one day with the help of nitrogen and immersed in liquid nitrogen at a pressure of 770 mm Hg and a temperature of 77.4 Kelvin. The specific surface area was measured using the Brunauer–Emmett–Teller method.

2.10. Data analysis

Data analysis was performed using the MiniTAB18 statistical software and Box-Behnken design model.

3. Results and discussion

The ICP-derived values of the heavy metals measured from the post-bleached sludge in 15 treatments are shown in Table 5. The lowest percentage of heavy metals was observed in treatment 16 with Fe, Al, Ni and Sr values of 0.0002, 0.055, 0.00002 and 0.00061%, respectively. The highest percentage of Fe of 0.097, Al of 0.098 And Sr of 0.00086 was measured in treatment 15. Ni reached the highest percentage in treatment 9 (0.000084).

3.1. The catalyst specific surface area

Table 6 shows the surface area of the pre- and post-bleached sludge. The surface area of the fresh sludge was 0.93 m^2/gr before bio-bleaching and increased to 1.31 m^2/gr after the coupled ultrasonic-biobleaching treatment. The coupled treatment procedure increased the specific surface area of the sludge by about 40.5%. When a solution is exposed to ultrasonic waves, the water vapor in cavitation bubbles can take the form of H + or OH. As a result, ultrasonic waves produce radicals that oxidize organic matter (Safari *et al.* 2015). Bacterial attack on sludge and washing with acidic water are some other reasons improving the heavy metal removal efficiency (MafiGholami *et al.* 2011).

Table 5. Mean of Fe, Al, Ni and Sr values (%) measured in the post-bleached sludge using ICP-OES

Treatment	Metal value in percentage			
	Sr	Ni	Al	Fe
1	0/00077	0/00006	0/074	0/0377
2	0/000763	0/000026	0/082	0/074
3	0/00073	0/000079	0/071	0/023
4	0/00076	0/0000558	0/074	0/069
5	0/000675	0/0000398	0/069	0/017
6	0/00073	0/0000278	0/078	0/071
7	0/000795	0/000034	0/084	0/084
8	0/000827	0/0000267	0/086	0/078
9	0/00082	0/000084	0/084	0/087
10	0/00078	0/000031	0/088	0/077
11	0/00072	0/000035	0/071	0/006
12	0/0008	0/000076	0/079	0/054
13	0/00067	0/000041	0/071	0/050
14	0/00068	0/000033	0/075	0/037
15	0/00086	0/000045	0/098	0/097
16	0/00061	0/00002	0/055	0/002

Table 6. Surface area of the fresh and post bio-bleached sludge

Sludge	Surface area (m^2/gr)
Fresh sludge	0.93
Post-bleached sludge	1.31

Figures 3 and 4 represent micrographs of the pre and post bio-bleached sludge taken by electron microscopy. The broken microparticles in Figure 4 can be attributed to bioleaching. A similar finding using the same bacterium (*T. thiooxidans* together with *A. ferrooxidans*) was also found by MafiGholami *et al.* (2011) in bioleaching of cobalt and Ni from the steel sludge.

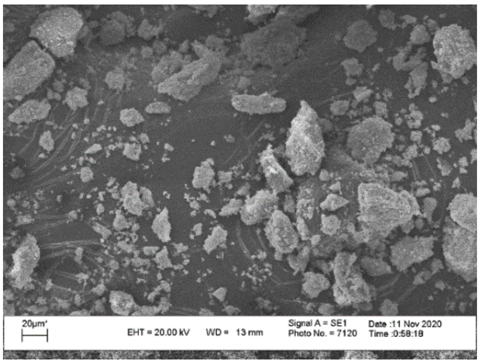


Figure 3. Micrograph of the pre bio-bleached sludge

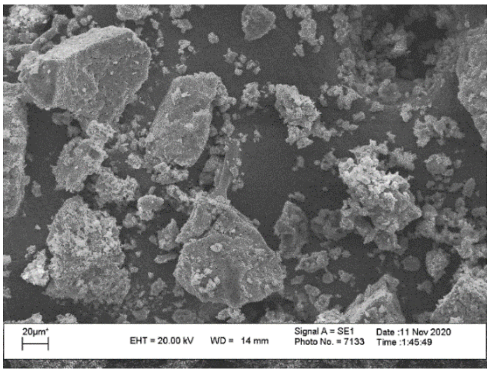


Figure 4. Micrograph of the post bio-bleached sludge

3.2. Selection of suitable models

The following equations were obtained from 15 stages of discontinuous scale experiment and Box- Behnken surface response method. The quadratic model was more consistent with the laboratory data. Coefficients with a probable error greater than 0.05 were not significant and excluded ($P < 0.05$). The Fe removal efficiency equation showed that pulp density and radiation time had a negative and linear effect on the bioleaching efficiency. It seems that above optimal ultrasonic radiation causes excessive breakdown of sludge cells and production of very small particles with a high negative surface charge (Equation 1) (Mahvi *et al.* 2014).

$$\text{Recovery } \% - \text{Fe} = 98.3 - 0.3702(A) - 0.5\,(AC) \qquad (1)$$

In the Al removal efficiency equation (2), pulp density had a negative linear effect while wave frequency exhibited a linear effect and a quadratic positive effect on Al removal. The positive effect of wave frequency on the heavy metal bioleaching from sludge was also reported by Ma *et al.* (2020) and was ascribed to the effect of wave frequency on the release of organic matters from the sludge. On the other hand, the efficiency of Al removal was also associated with the negative interplay of wave frequency and time. In assessing the effect of ultrasonic waves on Ni and Cobalt removal from aqueous solutions with the help of carboxylated nanoporous grapheme particles, Khaligh *et al.* (2017) found an increase and then a constant heavy metal removal efficiency with increasing radiation time. As shown in Equation 2, the maximum Al removal efficiency can be achieved by increasing wave frequency while decreasing pulp density. However, the negative interaction between the radiation time and frequency was minimal.

$$\text{Recovery \%} - \text{Al} = 99.53 - 0.05\,(\text{A}) + 0.0412\,(\text{B}) + 0.0575\,(\text{B2}) - 0.04\,(\text{BC}) \quad (2)$$

The Ni removal efficiency had a positive linear relationship with pulp density as well as a positive quadratic relationship with radiation frequency and time (Equation 3).

$$\text{Recovery \%} - \text{Ni} = 98 + 0.547\,(\text{A}) + 0.389\,(\text{B2}) + 0.432\,(\text{C2}) \quad (3)$$

The Sr removal efficiency (Equation 4) had a positive linear relationship with radiation frequency and time while a negative linear one with pulp density. Moreover, the pulp density had a negative quadratic whereas radiation frequency and time had a negative quadratic association with the Sr removal efficiency. Ultrasonic waves greatly improve the bacteria access efficiency to the particles (Lisa *et al.* 2015) by breaking and separating the sludge metal molecules and entering them into the liquid phase (Xuejiang Wan *et al.* 2015). Hence, the Sr-bioleaching efficiency increased with increasing duration of bacterial activity. There was a positive interaction between pulp density and wave frequency whereas negative interactions among pulp density, frequency and time in the Sr removal efficiency model (Equation 4).

$$\text{Recovery \%} - \text{Sr} = 98.22 - 0.0125\,(\text{A}) + 0.0275\,(\text{B}) + 0.0125\,(\text{C}) - 0.02375\,(\text{A2}) + 0.09125\,(\text{B2}) + 0.03125(\text{C2}) + 0.0175\,(\text{AB}) - 0.425\,(\text{AC}) - 0.0675(\text{BC}) \quad (4)$$

The R2 value of the models designed for Fe, Al, Ni and Sr removal (equations 1-4) was 91.25%, 93.04%, 91.26% and 99.45%, respectively.

3.3. Contour plots and response surfaces

The three-dimensional response levels of metal recovery as well as contour plots of the relationships between various parameters are shown in Figures 5 and 6. Given that the interactions between the model parameters had a significant effect on the response, the diagrams are presented in the form of confrontational expressions, i.e: simultaneous effect of several parameters on the removal efficiency.

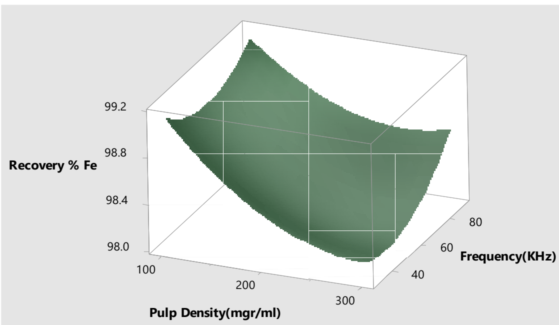


Figure 5. Three-dimensional response surface of Fe after bioleaching with the interaction of bacterial and ultrasonic waves

According to Figures 5 and 6, the combined *T. thiooxidans* and ultrasonic waves had a high Fe removal efficiency (%) at low sludge concentrations and a constant time of 30 min. The effect of radiation frequency was negligible in the Fe bioleaching such that the Fe removal efficiency at the presence of *T. thiooxidans* remained constant with and without the application of ultrasonic waves.

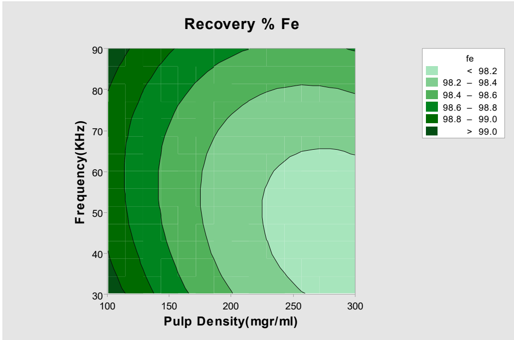


Figure 6. Contour plot of Fe after bioleaching with the interaction of bacterial and ultrasonic waves

According to Figures 7 and 8, the Al removal efficiency increased with increasing radiation frequency and decreasing pulp density. Increasing Al removal efficiency was directly related to increasing radiation frequency and decreasing pulp density. In previous studies such as Das *et al.* (2018) and Veligo *et al.* (1997), increasing pulp density was found to reduce the Al removal efficiency because bacteria are not exposed to properly the required oxygen and nutrients. Moreover, pulp density has an effective influence on the growth of microbes. As the pulp density increases, the interaction between bacteria and metal particles increases and heat production arises due to friction. Therefore, bacterial growth requires a suitable pulp density to surface area ratio (Das *et al.* 2018).

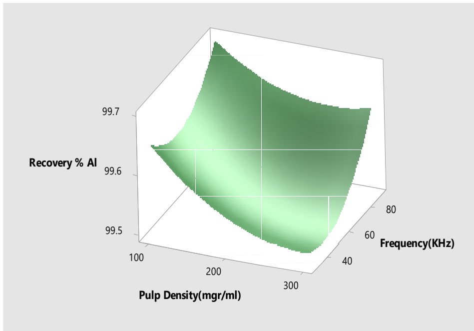


Figure 7. Three-dimensional response surface of Al after bioleaching with the interaction of bacterial and ultrasonic waves

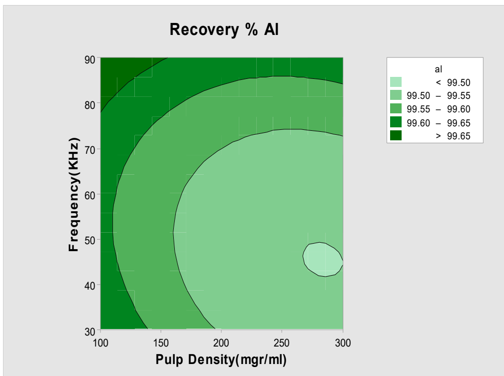


Figure 8. Contour plot of Al after bioleaching with the interaction of bacterial and ultrasonic waves

The Ni removal efficiency (Figures 9 and 10) increased with simultaneous increase of pulp density and radiation frequency, indicating that increasing radiation time had a positive impact on removal efficiency.

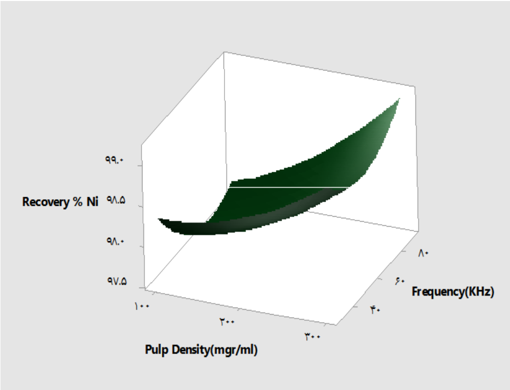


Figure 9. Three-dimensional response surface of Ni after bioleaching with the interaction of bacterial and ultrasonic waves

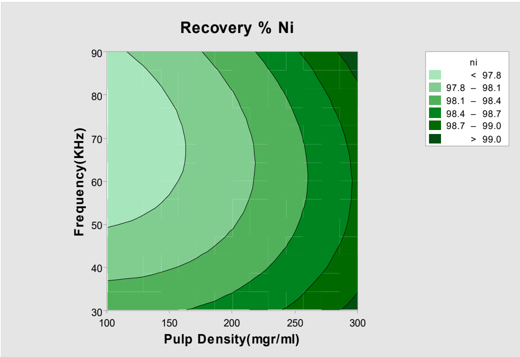


Figure 10. Contour plot of Ni after bioleaching with the interaction of bacterial and ultrasonic waves

The Sr removal efficiency remained constant with increasing pulp density between the radiation frequencies of 50 and 70 kHz which indicates the insignificant effect of pulp density on the Sr removal efficiency. It seems that the Sr removal efficiency is dependent upon the radiation frequency. With increasing pulp density and radiation frequency, the Sr removal efficiency decreased at frequencies between 30 and 45 kHz but increased at frequencies between 70 and 90 kHz. These results indicate that the Sr removal efficiency is strongly dependent on the interaction between pulp density and frequency (Figures 11 and 12).

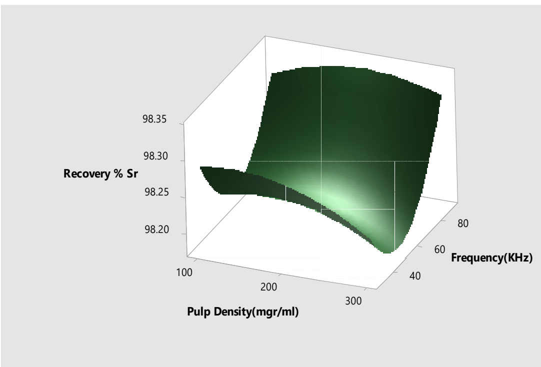


Figure 11. Three-dimensional response surface of Sr after bioleaching with the interaction of bacterial and ultrasonic waves

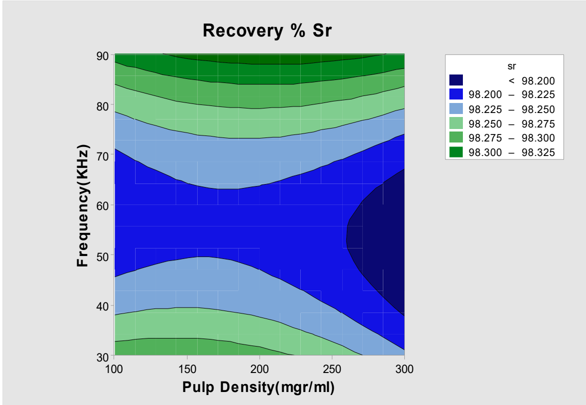


Figure 12. Contour plot of Sr after bioleaching with the interaction of bacterial and ultrasonic waves

3.4. Determining the optimal conditions

The following equations were obtained from 15 stages of discontinuous scale experiment and Box- Behnken surface response method. The quadratic model was more consistent with the laboratory data. Coefficients with a probable.

Table 7. Optimal conditions for maximum removal efficiency of Fe, Al, Ni and Sr

	Target	Pulp Density	Frequency	T	% Recovery
Fe	Maximize	100	30	40	98/45
Al	Maximize	100	90	20	99/74
Ni	Maximize	300	30	20	100
Sr	Maximize	300	90	20	98/45

The optimal conditions for the maximum Fe, Al, Ni, and Sr removal efficiency are given in Table 7. Under optimal conditions, the highest Fe removal efficiency of 98.45% was obtained using the acidic T. thiooxidation, a radiation frequency of 30 kHz for 40 min and a pulp density of 100 mg/ml. However, the Fe removal efficiency decreased to 99.96% without the assistance of ultrasonic radiation. The maximum removal efficiency was found to be 99.74% for Al under a wave frequency of 90 kHz for 20 min and a pulp density of 300 mg/ml, approximately 100% for Ni under a wave frequency of 30 kHz for 20 min and a pulp density of 300 mg/ml, and 98.45% for Sr under a wave frequency of 90 kHz for 20 min and a pulp density of 300 mg/mL. The removal efficiency of Al and Ni decreased to 99.38% and 99.42%, respectively, without the use of ultrasonic radiation. For Sr, however, the removal efficiency was bar far better (99.01%) in the absence of ultrasonic radiation. In a study by Pathak *et al.* (2019), a significant improvement was reported in Ni bioleaching using the acidic bacterium of *T. thioxidation* (in comparison with vanadium, molybdenum, and Al) which can be attributed to its relatively weaker binding with sludge particles than other heavy metals (Garg and Singh, 2016; Pathak *et al.* 2018). Hence, Fe, Al and Sr should either be in a more acidic condition or have a longer bioleaching duration (especially for iron) to achieve higher removal efficiencies (Srichandan *et al.* 2015). Increasing time improves the adaptability of bacteria to high metal concentrations as well as the efficiency of sulfur oxidation and formation of metal sulfides. Drawing from previous studies, different bacteria perform differently in metal bioleaching and according to the findings of Gholami *et al.* (2011), *A. ferrooxidans* has a higher Ni bioleaching efficiency compared to *A. thiooxidans*.

3.5. Conclusion

The results of this study highlight the efficiency of the coupled ultrasonic- bioleaching with *A. thiooxidans* in removing Fe, Ni, Al and Sr from the steel sludge. The maximum bioleaching efficiency for Fe, Ni, Al and Sr was found to be 98.45%, 99.74%, 100% and 98.45%, respectively. The removal efficiency of Ni and Al bioleaching improved significantly ($P < 0.05$) under the ultrasonic irradiation while the removal efficiency of Fe and Sr remained statistically unchanged ($P > 0.05$) with and without the application of ultrasonic waves.

References

Das A.P. and Ghosh S. (2018). Bioleaching of Manganese from mining waste materials, Materials Today: *Proceedings*, **5**, 2381–2390.

Garg J. and Singh K. (2016). Slag recycling in submerged arc welding and its effects on the quality of stainless steel claddings, *Material Desigen*, **108**, 689–698

Gomes H., Funari V., Mayes W., Rogerson M. and Prior T. (2018). Recovery of Al, Cr and V from steel slag by bioleaching: Batch and column experiments, *Journal of Environmental Management*, **222**, 30–36.

Hobson A.J., Stewart D.I., Bray A.W., Mortimer R.J.G., Mayes W.M., Rogerson, M. and Burke I.T. (2017). Mechanism of vanadium leaching during surface weathering of basic oxygen furnace steel slag blocks: a microfocus X-ray absorption spectroscopy and electron microscopy study, *Environmental Science Technology,* **51**, 7823–7830.

ocheng H., Su C. and Jadhav U.U. (2014), Bioleaching of metals from steel slag by Acidithiobacillus thiooxidans culture supernatant, *Chemosphere*, **117**, 652–657.

Kamani H, Hossein Panahi A, Norabadi E. and Abi G. (2019). Performance evaluation of combined Ultrasonic-Persulfate Processes in Organic Matter Reduction of synthetic Dairy Wastewater, *Journal of Birjand University Medical Science*, **26(1)**, 32–43.

Khaligh A., Mousavi H. and Rashidi A. (2017). Ultrasonic assisted removal of Ni(II) and Co(II) ions from aqueous solutions by carboxylated nanoporous grapheme, *Journal of Applied Chemistry*, **11**, 49–58.

Lisa A., Davies AD JRD. and Michael E. (2015). Deary Use of 24 kHz ultrasound to improve sulfate precipitation from wastewater, *Ultrason Sonochem*, **23**, 424-431.

Ma H., Li X., Zhu C., Chen F., Yang Y. and Chen X. (2020). Liberation and recovery of Cr from real tannery sludge by ultrasound-assisted supercritical water oxidation treatment, *Journal of Cleaner production*, **20**, 32111–32119.

MaFigholami R., Borgheri S.M. and Mousavi S.M. (2010). Bacterial leaching of a spent MO-CO-Ni refinery catalyst using *Asidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*, In press Doi: 10.1016/j.hydromet.2010.11.011

MafiGholami R.M., Borghei S.M. and Mousavi S.M. (2011). Bacterial leaching of a spent Mo–Co–Ni refinery catalyst using Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans, Hydrometallurgy, **106**, 26–31.

MafiGholami R., Mousavi S.M. and Borghei S.M. (2012). Process optimization and modeling of heavy metals extraction from a molybdenum rich spent catalyst by Aspergillus niger using response surface methodology, *Journal of Industrial and Engineering Chemistry*, **18**, 218–224.

Mahvi A, Heidari A, Nabizadeh R, Alimohammadi M. and Gholami M. (2014). A survey on the effect of ultrasonic method on dewatering of bio sludge in wastewater treatment plant, *Journal of Sabzevar University Medical Science*, **5**, 424–430

Murugesan M.P., Kannan K. and Selvaganapathy T. (2020). Bioleaching recovery of copper from printed circuit boards and optimization of various parameters using response surface methodology (RSM). Materials Today, *Proceedings* xxx (xxxx) xxx.

Pathak A., Healy M.G. and Morrison L. (2018). Changes in the fractionation profile of Al, Ni, and Mo during bioleaching of spent hydroprocessing catalysts with Acidithiobacillus ferrooxidans, *Journal of Environmental Science and Health*, **53(11)**, 1006–1014

Pathak A., Srichandan H. and Kim D. (2019). Column bioleaching of metals from refinery spent catalyst by Acidithiobacillus thiooxidans: Effect of operational modifications on metal extraction, metal precipitation, and bacterial attachment, *Journal of Environmental Management,* **242**, 372–383

Safari GH, Nasseri S, Mahvi AH, Yaghmaeian K, Nabizadeh R. and Alimohammadi M. (2015). Optimization of sonochemical degradation of tetracycline in aqueous solution using sono-activated persulfate process, Journal of Environmental Health and Science Enginerring, **13**, 76.

Samadi F, Mirbagheri S.A. and Falsafi S.M. (2017). Dairy Industrial Wastewater Treatment Using (UASB) Reactor, *International Research Journal of Scientific and Engineering Research*, **8(9)**, 1005–1009.

Srichandan H., Singh S., Blight K., Pathak A. and Kim D.J. (2015). An integrated sequential biological leaching process for enhanced recovery of metals from decoked spent petroleum refinery catalyst: a comparative study, *International of Journal Minerral Process*, **134**, 66–73

Veglio F. (1996), Process Biochemistry. **31(8)**, 773–785.

Vestola E.A., Kuusenaho M.K., Närhi H.M., Tuovinen O.H., Puhakka J.A., Plumb J.J. and Kaksonen, A.H. (2010), Acid bioleaching of solid waste materials from copper, steel and recycling industries, *Hydrometallurgy*, **103**, 74–79.

Ting S. and Vyas Y. (2019). Effect of ultrasound on boleaching of hydrodesulphurization spent catalyst. *Environmental Technology and Innovation*, **18**, 1–50.

Wang S. and Zhou N. (2016), Removal of carbamazepine from aqueous solution using sono-activated persulfate process, *Ultrason Sonochem*, **29**, 156–162.

Wang X., Chen J., Yan X., Xin W., Zhang J. Huang J. and Zhao J. (2015), Heavy metal chemical extraction from industrial and municipal mixed sludge by ultrasound-assisted citric acid, *Journal of Industrial and Engineering Chemistry*, **27**, 368–372.