ULTRASOUND ASSISTED ELECTROCOAGULATION REMOVAL OF HEAVY METALS FROM WATER

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1 Abstract

In this paper, ultrasonic treatment, electrocoagulation and the combinations of these treatments were compared for the removal of manganese, nickel, cobalt, cadmium and chromium from a synthetic solution. Experiments were conducted using aluminium electrodes in a modified ultrasonic bath. The experimental design approach (DOE) and multi-level categoric design were used to design the experiments and optimize the results. The results show that ultrasound largely affects the EC heavy metals removal process and leads to higher efficiencies than EC alone.

Keywords: electrocoagulation, ultrasound, water treatment, heavy metals, sonoelectrocoagulation, DOE

2 Introduction

Heavy metal pollution of drinking water is a current problem with potentially serious consequences. Due to their toxic, biodegradable, and persistent nature, heavy metals pose a serious threat to aquatic ecosystems, as well as to human health [1,2]. In response to the challenge of reducing the concentration of heavy metals in water, various technologies have been developed. Conventional methods include physicochemical processes such as chemical precipitation, ion exchange, adsorption on various materials, electrochemical processes such as electrocoagulation, electroflotation and electrodeposition, and membrane filtration processes[3–5].

Electrocoagulation (EC) is characterized by the formation of coagulants in situ by oxidation of the metal anode due to the application of electric current. The process consists of dissolution of the sacrificial anode, formation of hydroxide ions and hydrogen at the cathode, electrolyte reactions at the electrode surface, adsorption of coagulants on colloidal contaminants and removal of the resulting flocs by precipitation or flotation [6–9]. Parameters effecting the efficiency of the EC in removing heavy metals from water are: electrode material, solution pH, current density, treatment time, electrode potential, pollutant concentration, concentration of anions, and temperature[10].

Ultrasound is a longitudinal wave with a frequency range between sonic and mega sonic region (20-600 kHz) [11]. Ultrasonic waves transmit energy through the vibration of molecules in the environment in which the wave is being spread [12]. Most commonly, ultrasonic waves are generated by the piezoelectric effect. Piezoelectric crystals are used to convert high frequency electrical energy to mechanical vibrations. The vibrating part can be made in different forms and different ultrasonic devices are commercially available. Ultrasonic devices, usually, operate at frequencies from 20k Hz to 10 MHz. High power ultrasound at low frequencies (<100 kHz) has the ability to cause cavitation [13]. Cavitation is a rapid physical phenomenon caused by sudden drop in pressure. It starts with formation of small vapour bubbles inside a liquid medium [14]. Pressure changes cause bubble propagation and eventually a violent collapse. The energy released from the bubble collapse causes extreme local increases in temperature and pressure. “Hot spots” with temperatures over 1000 K can form in the centre of the

collapsing bubble, leading to formation of highly reactive hydroxyl radicals [15]. In ultrasonic baths, transducers are attached to the side or bottom of the tank and this cavitation is considered low intensity due to the large surface area through which the energy is transmitted. In ultrasonic baths, sometimes the bubbles do not actually collapse, but oscillate for many sonic cycles. This means that the extreme conditions caused by bubble collapse do not happen, but micro eddies occur causing shear stress. This type of cavitation is named "stable cavitation" and cavitation with bubble collapse is called "transient cavitation" [16].

Electrocoagulation is an effective method for removing heavy metals and has many advantages. However, the main disadvantage of the EC process is the polarization and passivation of the electrodes [10]. Passivation is the formation of a passive film forming on the electrode surface over time, which results in diminishing of the process efficiency [10]. Polarization can be caused also by gas accumulation near to the electrode surface and as a result depletion of pollutant in the electrode's boundary layer [17]. To overcome that drawback, it is possible to couple the treatment with ultrasound. Ultrasonic waves break up the deposits formed at the electrode surface. In addition, ultrasound can generate radical species through the cavitation phenomenon, resulting in better contaminant removal and making sono-electrocoagulation a promising technology for water and wastewater treatment [18].

3 Methods

3.1 Experimental design

In this work, the Design of Experiment approach was used for experiment design and statistical analysis. For this purpose, Design Expert 12 software from Stat-Ease was used. The multi-level categoric design was selected. The factors studied and their characteristics are presented in Table 1. There were 4 treatment options included in the design (US, US/EC, EC/US, sono-EC). US frequency was tested at 2 levels (25 and 45 kHz) and US intensity at 3 levels (10, 50, 100%). The efficiencies of the process for each heavy metal were treated as responses. The efficiency of the process was evaluated by measuring the change in heavy metals concentrations at the end of the process. It was calculated according to Eq(1), where C_0 is the initial concentration of the metal and C_t is the concentration of the metal measured at time t.

$$\eta(\%)=(C_0-C_t)/C_0 *100 \quad (1)$$

Table 1. Selected parameters for multilevel categoric design

Factor	Name	Units	Type	SubType	Minimum	Maximum	Levels
A	frequency	kHz	Categoric	Nominal	25	45	2
B	intensity	%	Categoric	Nominal	10	100	3
C	treatment		Categoric	Nominal	US	EC/US	4

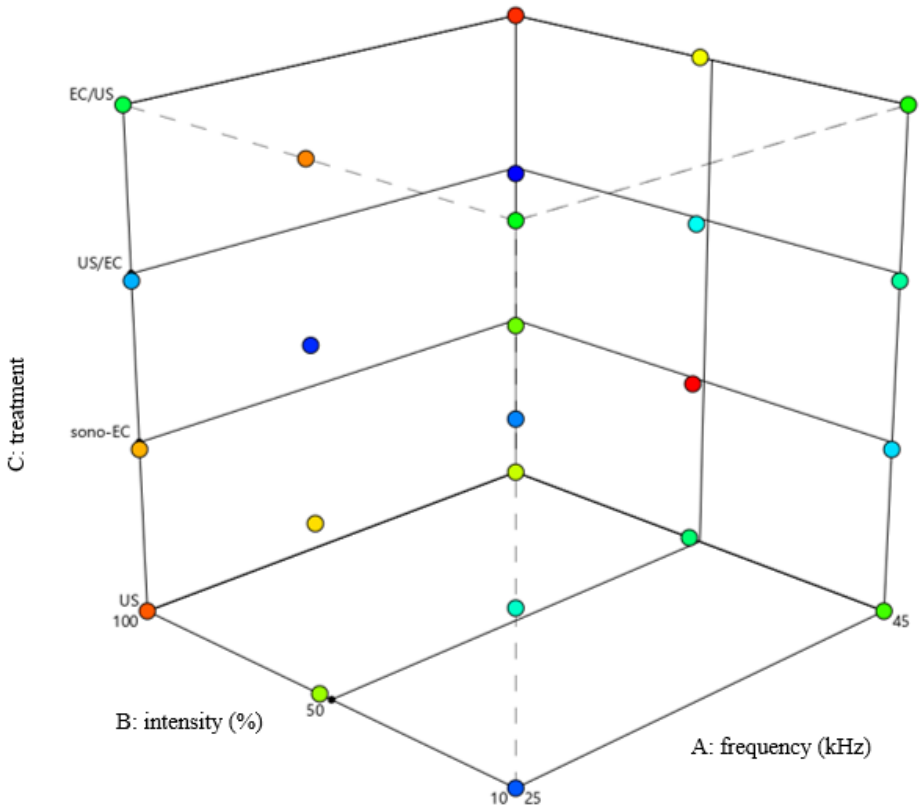

Figure 1. Scatterplot of three-level categorical design used in this study

3.2 Experimental method

The experiments were carried out in a modified ultrasonic bath (Elma Ultrasonics TI-H 10 MF2) with 2 frequency settings (25/45 kHz) and adjustable intensity (10-100%). The mixing of the treated solution was achieved by recirculation using a peristaltic pump set to 0.5l /s flow rate. For electrocoagulation treatment, 4 aluminium electrodes connected to the laboratory power supply were used. Electrodes were arranged as follows: anode/cathode/anode/cathode with the interelectrode distance of 1 cm. The electrodes were completely submerged with active surface area of 91.32 cm^2. The power supply was set to 60 V voltage and kept constant. An aqueous solution containing 1 ppm of Ni, Cd, Cr and Co and Mn was used as a model solution. pH value, temperature and conductivity of the solution was not altered.
5 different types of treatments were tested: EC as a standalone treatment for 2 minutes, US as a standalone treatment for 2 minutes, 2 minutes of simultaneous EC and US treatment (sono-EC), 1 minute of US followed by 1 minute of EC and 1 minute of EC followed by 1 minute of US. The frequency and intensity of ultrasound were varied according to the experimental plan in the experiments including US treatment.

Figure 2. Modified ultrasonic bath with recirculation, laboratory power supply and aluminium electrodes

The samples were taken at the beginning and the end of every experiment, using a syringe. They were filtered using a 45 µm PES filter and acidified before analysis. The concentration of heavy metals was measured using ICP-OES analysis. All chemicals used were of analytical grade, and sample containers were previously soaked in 10% nitric acid for 24 hours. The electrodes and the reactor were thoroughly rinsed between experiments.

4 Results and discussion

The electrocoagulation experiments carried out in this experimental setup resulted in the removal of 84.41 % Cd, 71.84% Co, 93.60 % Cr, 52.47 % Ni and 38.80 % Mn in a treatment time of 2 minutes. The results of the other treatments (1 minute of US treatment followed by 1 minute of EC, 1 minute of EC followed by 1 minute of of US, 2 minutes of simultaneous US-EC treatment, and 2 minutes of US treatment) are presented in Table 2.

Table 2. The experimental matrix with factors and responses

		Factor 1	Factor 2	Factor 3	Response 1	Response 2	Response 3	Response 4	Response 5
Std	**Run**	**A:freq. kHz**	**B:inten. %**	**C:treatm.**	**Mn %**	**Ni %**	**Cd %**	**Cr %**	**Co %**
18	**1**	45	100	US/EC	39.47	55.79	79.92	96.38	72.73
15	**2**	25	50	US/ EC	35.09	53.42	88.00	98.34	70.55
1	**3**	25	10	US	0.49	9.11	20.76	36.29	10.38
13	**4**	25	10	US/ EC	24.18	38.42	79.75	98.94	55.34
17	**5**	25	100	US/ EC	30.69	44.75	81.55	94.42	63.44
8	**6**	45	10	sono-EC	46.46	64.62	77.23	85.53	68.37
16	**7**	45	50	US/ EC	29.52	48.07	80.63	98.24	67.06
7	**8**	25	10	sono-EC	32.85	49.73	88.59	73.33	67.43
14	**9**	45	10	US/ EC	31.98	52.01	87.00	99.59	68.21
4	**10**	45	50	US	0.00	6.66	48.77	89.74	9.30
23	**11**	25	100	EC/US	27.80	47.60	82.01	94.66	63.02
19	**12**	25	10	EC/US	24.56	40.60	76.27	88.00	56.07
20	**13**	45	10	EC/US	26.22	42.33	79.42	95.56	59.09
2	**14**	45	10	US	0.68	1.28	9.77	56.70	1.37
12	**15**	45	100	sono-EC	23.13	40.63	78.73	98.50	60.56
3	**16**	25	50	US	0.00	3.74	35.06	72.26	6.25
6	**17**	45	100	US	0.52	8.20	27.95	75.83	11.19
22	**18**	45	50	EC/US	21.10	36.89	74.70	96.90	52.41
9	**19**	25	50	sono-EC	27.45	47.64	80.81	99.21	69.24
11	**20**	25	100	sono-EC	29.18	46.27	83.97	99.08	62.51
21	**21**	25	50	EC/US	22.84	38.72	77.06	92.47	55.02
5	**22**	25	100	US	0.11	1.02	5.04	32.20	1.03
24	**23**	45	100	EC/US	22.48	41.48	76.35	97.95	56.02
10	**24**	45	50	sono-EC	23.32	36.35	77.92	99.07	52.07

The significant effect of process variables on electrocoagulation efficiency has been verified by analysis of variance (ANOVA). The P value is used to estimate whether the F test values are large enough to

indicate statistical significance. The F test values of the present model is significant at the 5% level (i.e. P <0.05). It shows the model match with experimental values and can explain the significance of individual parameter. Furthermore, the closer the R^2 value is to 1, the better the model fits. As it can be seen in Table 3, selected factorial models show a good fit to the experimental values with p values less than 0,05. The P-values of the individual terms in the model are, also, shown in Table 3. It is evident that the only significant term is Factor C – treatment. The only exception is the chromium removal model, in which all of the main effects (A, B, C), as well as interactions AC and BC, appear to be significant. This suggests that unlike the removal of Mn, Ni, Cd and Co, the efficiency of the Cr removal depends, not only on the type of treatment, but also on the frequency and ultrasound intensity used. The normal plot of the residuals is shown in Figure 2, while Figure 3 shows graphical comparison between actual and predicted values.

Table 3. Results of ANOVA analysis

		model		p-value					
	F-value	**p-value**	**R2**	**A**	**B**	**C**	**AB**	**AC**	**BC**
Mn	13.3400	0.0021	0.9742	0.6666	0.3379	0.0001	0.1991	0.7520	0.1544
Ni	10.3688	0.0042	0.9671	0.7050	0.6435	0.0001	0.4310	0.7284	0.4380
Cd	14.6700	0.0016	0.9765	0.9904	0.3114	0.0000	0.7824	0.4698	0.1974
Cr	13.7700	0.0019	0.9750	0.0094	0.0100	0.0001	0.5539	0.0300	0.0361
Co	23.8150	0.0004	0.9854	0.9505	0.9383	0.0000	0.4193	0.4045	0.6447

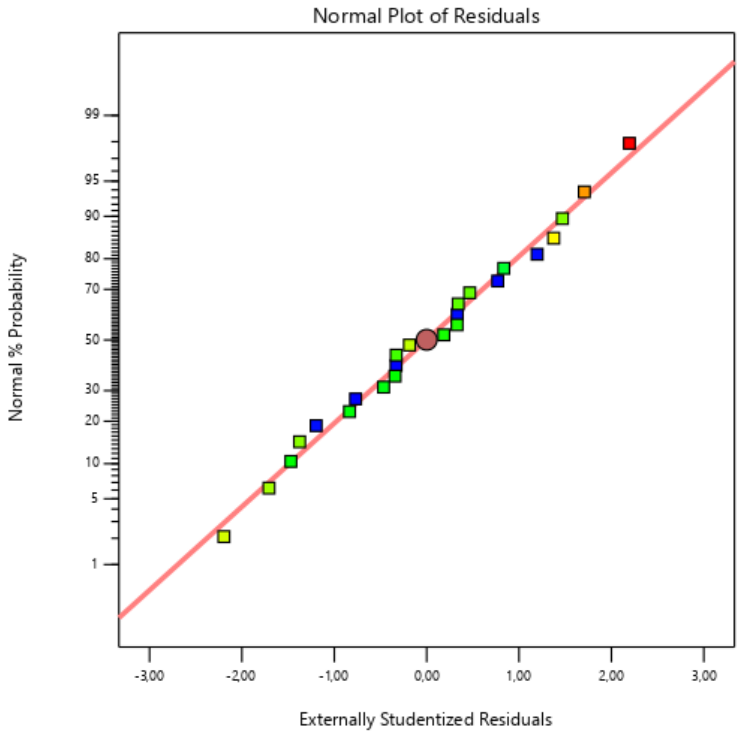

Figure 3. Normal plot of the residuals for manganese removal

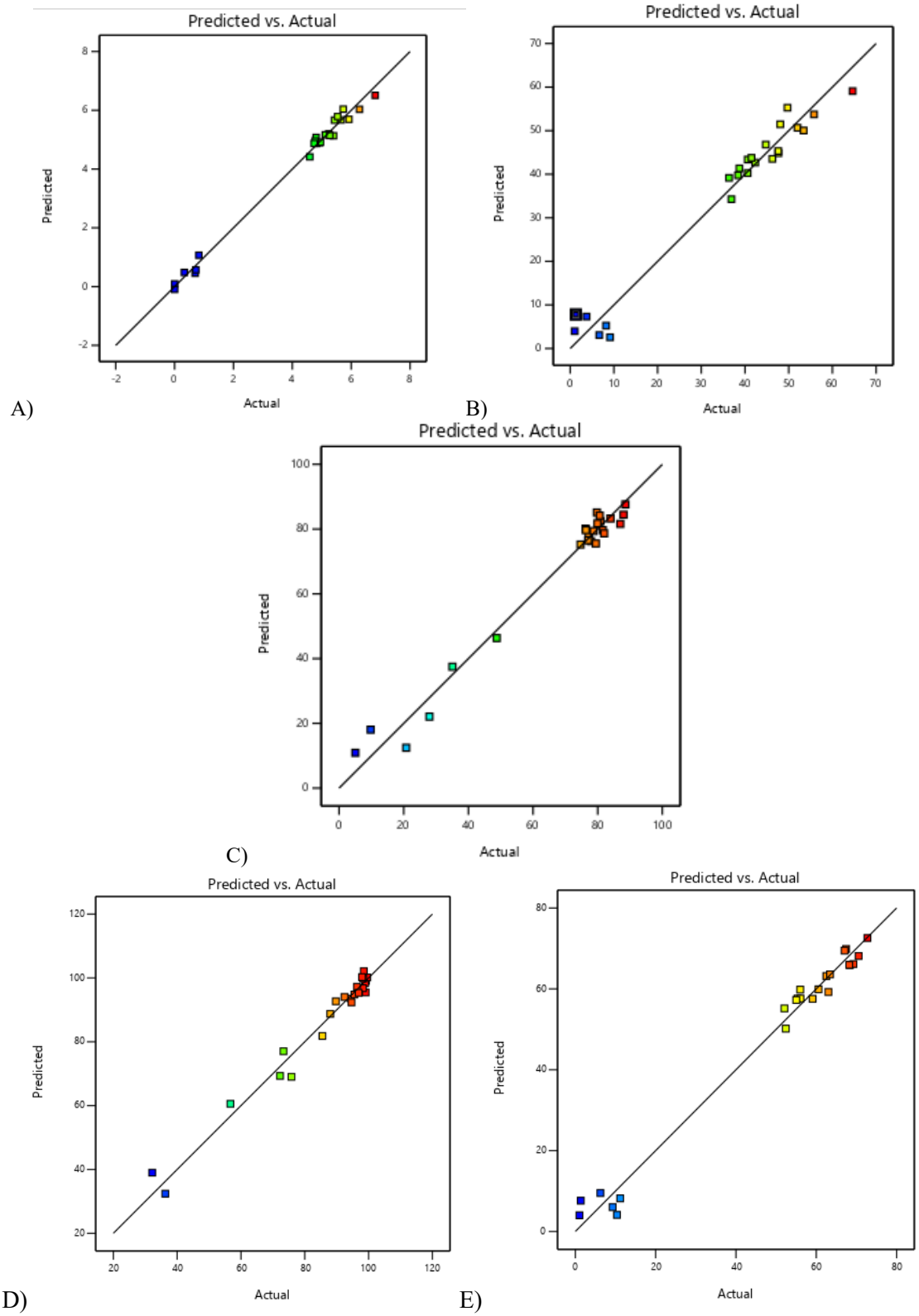

Figure 4. Predicted versus actual values for the removal of A) manganese B) nickel C) cadmium D) chromium E) cobalt

US treatment as a standalone process was found to be unsuitable for the removal of heavy metals, as it gave the lowest efficiencies for all of the investigated metals. For manganese and nickel removal, the highest efficiency was obtained during the sono-electrocoagulation treatment at 45 kHz and 10% US intensity. Sono-EC was, also, the most efficient treatment for cadmium, but at 25 kHz. Chromium was

the easiest heavy metal to remove, with the highest efficiency of 99.59% in the case of US treatment at 45 kHz and 10% intensity followed by EC. The best choice for cobalt removal was the same process but at 100% US intensity. Considering the differences in the removal of each heavy metal, Design Expert software was used to determine the optimal conditions (Figure 5). The best compromise is US treatment at 45 kHz and 100% intensity followed by EC resulting in 36.24%, 53.73%, 81.76%, 97.23% and 72.59% efficiency for the removal of Mn, Ni, Cd, Cr and Co, respectively. It is interesting to note that EC treatment followed by US, resulted in the highest aluminium concentrations in the effluent, possibly due to ultrasound disrupting the flocs formed in the EC process.

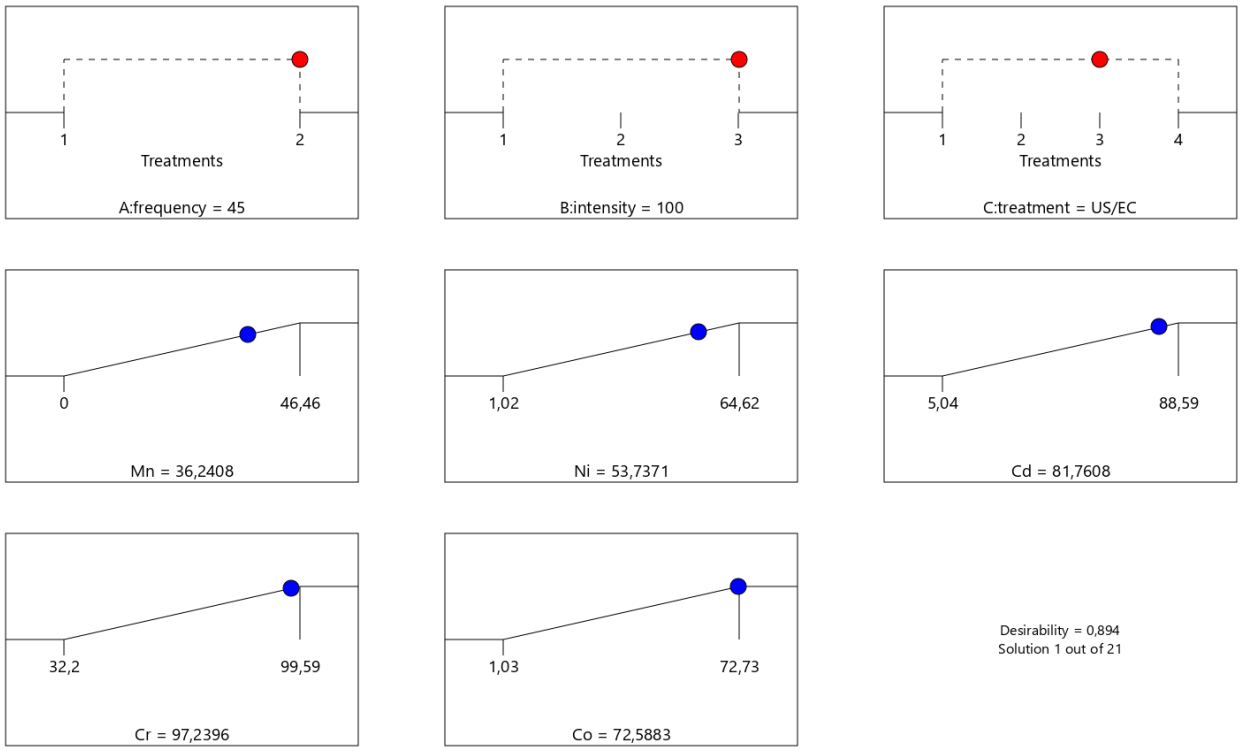

Figure 5. Ramp graphs showing the best solution obtained through process optimization

5 Conclusion

Unlike the ultrasonic treatment, the electrocoagulation process as a standalone treatment is efficient at removing heavy metals from water. However, combining EC with ultrasound results in higher efficiency. The US treatment at 45 kHz and 100% intensity followed by EC resulted in 36.24%, 53.73%, 81.76%, 97.23% and 72.59% efficiencies for the removal of Mn, Ni, Cd, Cr and Co, respectively. Similarly high efficiencies were obtained in the simultaneous US-EC process, proving that sonoelectrocoagulation is a promising alternative to conventional treatment methods for heavy metal contaminated water.

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