Electrocoagulation of azo dye containing synthetic wastewater using monopolar iron electrodes and the characterization of the sludge

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Abstract

In this study, the decolourisation of Congo red dye is studied using the natural coagulant Maize Seed Powder (MSP); a suitable alternative for chemical coagulants in electro coagulation (EC) using iron electrodes. The effects of various parameters such as initial dye concentration, pH, applied voltage and time on the decolourisation of dye were studied. The cost of water treatment is increasing due to suspended and colloidal particle load. The coagulation process can be used as a primary step for water and wastewater treatment processes. Among plant materials that have been tested, the seeds of maize have been shown to be one of the most effective primary coagulants in water and wastewater treatment. The removal efficiency of the dye with and without the presence of MSP as a coagulant aid was determined. In the EC process maximum Congo red removal was achieved by using the natural coagulant MSP. Congo red (CR) decolourisation efficiency is 95.23% at a coagulant dosage of 50 mg/lit, pH of 5, operating time of 15 minutes, and a power of 40 volts with iron electrodes. In the absence of coagulant MSP, Congo red decolourisation efficiency was found to be 80.31% at pH of 5, operating time of 15 minutes, and a power of 40 volts with iron electrodes.

Key words: Congo red dye, electro coagulation, maize seed powder, natural coagulant

INTRODUCTION

The Niti Aayog report reads that by 2030, India's water demand is projected to be twice the available supply. This will cause severe water scarcity. The decrease in the availability of water induces the research work for the treatment of effluents (AlHamedi *et al.* 2009). Wastewater released from textile industries can cause environmental and health hazards because of the toxic content of dyes. Most of the dyes used in the textile industry and their degradation products are carcinogenic (Dalvand *et al.* 2011). The disposal of untreated effluent into water resources alters physical and chemical properties such as pH, biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) values. Currently, there is a great focus on reusing the effluent water in the dyeing process. Hence there is an urgent need to develop an economical treatment system for the treatment of wastewater, which can meet the strict quality standards (Tijani *et al.* 2014). Azo dyes are predominantly used in textile dying because of their chemical stability and versatility (Sathish *et al.* 2018). Dyes are widely used in textile, rubber and paper industries to color their products. The dyes are invariably left as the major waste in these industries. The removal of dyes from the effluent before they are discharged into the water sources plays a vital role in health and for sustainable environmental management (Sharma & Janveja 2008). Due to their complex chemical structures, the organic dyes are hazardous and may affect aquatic life and even the food chain. For example, congo red dye (1-Naphthalenesulfonic acid, 3, 3′-(4, 4′ biphenylene bis (azo) bis 4-amino) di

sodium salt) is a benzedene based dye, it has to metabolize into benzedene, a known human carcinogen. Exposure to the dye has been known to cause an allergic reaction and possibly anaphylactic shock. Several conventional methods have been carried out for the treatment of textile wastewater such as adsorption, coagulation, and flocculation and chemical oxidation (Oller *et al.* 2011). The operating cost of these methods is too high (Jiang *et al.* 2010). Biological method is cheaper but the efficiency is lower because of the high concentration of toxic pollutants (Lopez-Lopez *et al.* 2016). Electrocoagulation (EC) is an emerging, eco-friendly technique for the treatment of water and wastewater without requiring the addition of chemicals to avoid secondary sludge generation (Agustina *et al.* 2005). During the past decade the process of EC has been extensively studied for the treatment of different types of industrial wastewaters, since it is less expensive, simpler to operate and generates less sludge compared to other electrochemical methods and chemical coagulation/flocculation (Papadopoulos *et al.* 2019). The hypothesis behind EC, flocculation or coagulation is same. All methods focus on the expulsion of particles from wastewater through destabilizing or neutralizing the repulsive forces that keep the particles suspended in water. The suspended particles will form larger particles that can settle down for simpler removal from water. EC uses an electrical source between metal electrodes immersed in the effluent (Kos & Perkowski 2003). Metal electrodes such as iron or aluminum are dissolved by electrical current and these metal ions, at a suitable pH, can form wide ranges of coagulated species (Wang & Xu 2012). The metal hydroxides aggregate the suspended particles and adsorb dissolved contaminants (Chen 2004). The main advantage of EC over chemical coagulation is that addition of chemical such as metal salts or polyelectrolytes. In EC the coagulants are generated by the electrolytic oxidation of an appropriate anode material which results in decreased sludge generation (Moussa *et al.* 2017). The usage of polyelectrolyte for water and wastewater treatment was limited because of its cost and uncertainties regarding chemical impurities associated with polymer synthesis. Most of the naturally occurring polyelectrolytes are of plant origin and are generally nontoxic in nature. Maize (Zeemays) is commonly known as corn in some countries. Maize seeds are easily available in the Indian region (Patel & Vashi 2012). In this study the decolourisation of Congo red from aqueous solution by using agro based natural coagulant Maize Seed Powder (MSP) in EC process was studied. The effects of operational parameters such as initial pH, potential difference, electrolysis period, and initial dye concentration were examined. Moreover, the optimization studies were carried out by using response surface methodology.

## MATERIALS AND METHODS

Coagulant aid preparation

MSP natural coagulant was used as an aid in EC. Compared to chemical coagulants, a natural coagulant has many advantages such as biodegradability, low toxicity, low residual sludge production and low cost (de Carvalho *et al.* 2015). The mature maize seeds were washed with water and were dried at 600 °C. The dried seeds were crushed to 0.18 mm (Mesh No-BSS 85) and stored in an air tight container that can be used for further studies (Herney-Ramirez *et al.* 2010). The zeta potential of the MSP was determined by using a Zetasizer instrument at room temperature. To determine the role of surface charge, the zeta potential of the MSP has to be calculated (Boulaadjoul *et al.* 2018).

Chemicals and reagents

The azo dye (Congo red) and the chemicals were of reagent grade. The chemicals and reagent used was of AR grade and of high purity (Bautista *et al.* 2008). All the solutions were prepared by dissolving the requisite quantity of dye in distilled water.

Electrocoagulation process

The schematic figure of electrochemical reactor is shown in Figure 1. In spite of the simplicity of the EC setup, it requires huge electrode surface area to overcome the metal dissociation rate; this is overcome by using monopolar electrode setups in series or parallel connections. The experiments were carried out in a divided double-electrode electrochemical cell which consists of a 1,000 ml glass beaker equipped with vertical electrodes and an electrode gap of 5 cm (Bernal-Martinez *et al.* 2010). The thermostated electrocoagulator was at constant stirring speed where the cathode and anode were pieces of iron of 40 mm × 50 mm × 3 mm, which were plunged into the cell (Ganzenko *et al.* 2014). The electrodes were connected in monopolar parallel mode to a DC regulated power supply. Sigma 60 V, 10A, DC RPS was used for providing reasonable voltage was connected to the electrodes. The dye solution was stirred at 100–500 rpm by a magnetic stirrer (Sh Brand). MSP was added for the aid of EC (Aoudj *et al.* 2010).
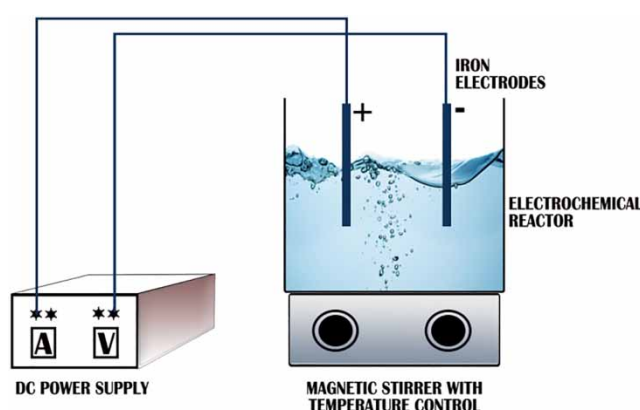
Figure 1 | Schematic representation of electrocoagulation.

All experiments were done at constant temperature of 30 °C. The solution pH was adjusted and controlled by adding 1M NaOH or 1M HCl during experiments. Before and after EC, the electrodes were first washed with dilute HCl (5% by volume) and then rinsed with distilled water to remove the solid residue on the surfaces, dried and reweighed. For electro-coagulation experiments, about 500 mL of synthetic dye solution was introduced to the EC reactor. After that, the reactor content was stirred during experiments and at predetermined time interval, the sample was taken to determine the absorbance value using UV-Vis spectrophotometer (systronics Model-119) at 530 nm. The percentage decolourisation can be determined by using initial and final concentration of dye solution.

$$\text{Percentage decolourisation} = \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100$$

Several experimental parameters such as potential difference, EC time, pH and initial dye concentration were studied (Mollah *et al.* 2004).

RESULT AND DISCUSSION

Zeta potential of the coagulant aid

The zeta potential of the calcined MSP at 600 °C was measured by dissolving in an aqueous solution for a time period of 20, 40, and 60 min. The zeta potential of the MSP was found to be -2.26, -5.2, and -6.8 mV respectively. This result shows that the surface of the MSP particles had moderate negative

charges. It was studied that the depending on the nature of coagulant aid the negatively charged organic particles can be removed from the effluent by sweep coagulation (Boulaadjoul *et al.* 2018).

**Effect of initial dye concentration**

The effect of initial dye concentration on the decolourisation efficiency has been studied in the range of 25 to 200 mg/L. As shown in Figure 2, the decolourisation efficiency decreases with the increase in initial dye concentration. Increasing the dye concentration decreases the decolourisation efficiency from 71.20% to 32.01% for MSP used as an aid in the EC process. In the absence of coagulant aid the efficiency decreases from 65% to 32.01. The decrease in dye removal efficiency with increases in initial dye concentration is due to the fact that the amounts of dissolved Fe^{3+} ions are constant at the same constant current density and time (according to Faraday's law) (Zarrabi *et al.* 2015). So, it is obvious that the lower initial dye concentration is better for higher removal efficiencies and lower consumption under present experimental conditions.
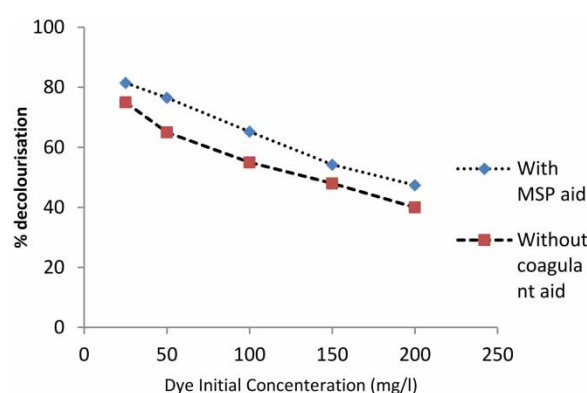
Figure 2 | Effect of initial dye concentration on CR removal in the EC process.

Effect of pH

The effect of pH on the decolourisation of Congo red dye by the EC process was studied with different initial pH (2 to 10). Figure 3 shows that the maximum decolourisation efficiency was at acidic pHs. At pH 6 and after 20 min contact time, 80% of dye was removed by both electrodes.

$$2Fe^{2+} + 0.5O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH^-$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
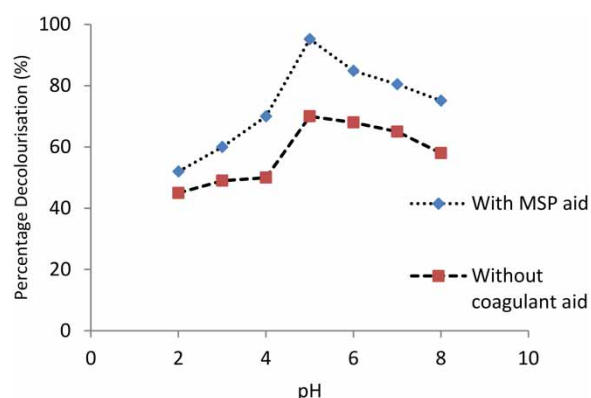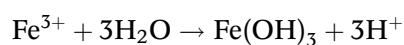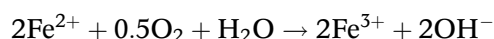
Figure 3 | Effect of pH on CR removal by EC process.

At higher pHs the percentage of decolourisation increases may be due to the nature of the reaction between Fe^{3+} ions and hydroxide ions. At alkaline pHs, electrodes will be oxidized to Fe^{+3}. On the other hand, at an alkaline pH more hydroxyl ions will exist, thereby the hydroxides gelatinous compound is more likely to be formed, leading to increase in removal efficiency (Khandegar & Saroha 2013).

Effect of operating time

As can be seen from Figure 3, removal efficiency was increased with increases in reaction time. After 15 min of reaction time, 98% of dye decolourisation was achieved in EC with an aid. In addition, with increase in reaction time from 5 to 25 min, dye removal efficiency increased from 35% to 92% and from 20% to 80% for iron electrode with and without MSP aid, respectively (Figure 4). According to Faraday's law, increases in electrolysis time leads to increase in Fe^{+3} species in the EC reactor and their hydroxide flocs so the EC process yield is enhanced. Further increases in time led to reductions in decolourisation efficiency, which may be due to cathode passivation, which affects the process performance (Un *et al.* 2016). Eventually, a maximum removal efficiency of 95.12% was obtained within 15 min of operating time with the presence of MSP coagulant aid.
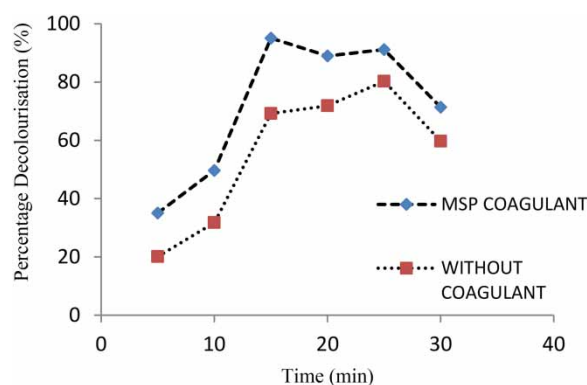

Figure 4 | Influence of operating time on CR removal by EC.

Effect of potential difference between electrodes

It is an important parameter which determines the rate of coagulant dosage in the EC process. The effect of potential difference was studied at 60 mg/L of dye concentration and pH 5 for 30 min. A significant increase in the dye removal efficiencies was observed up to 50 V. The amount of dissolved hydroxides increased over time, and also resulted in an increase in floc formation. Further increase in voltage meant the removal efficiency was reduced to 54%. It can also be observed that the use of MSP increased the removal efficiency to 92.04% up to 50 V and then the removal efficiency reduced to 72.14% when the voltage increase beyond 50 V. This is due to the effect of cathode passivation. In general, the amount of dissolved iron will increase in proportion to applied voltages, which can result in higher removal efficiency, but also with a proportional increase in electric energy consumption (Zarrabi *et al.* 2015). Therefore, the selection of an optimum voltage, which gives high removal efficiency with relatively low electric energy consumption, is necessary. In our study, in order to obtain direct dischargeable effluents, the experiments were performed at 40 to 50 V with the aid of MSP coagulant, which gave a 92% removal of the dye (Figure 5).

Interaction effects and regression analysis

The interactive effect of two independent variables on percentage decolourisation can be shown on a 3D surface plot. The effect of two independent variables with another variable at fixed level on the dye
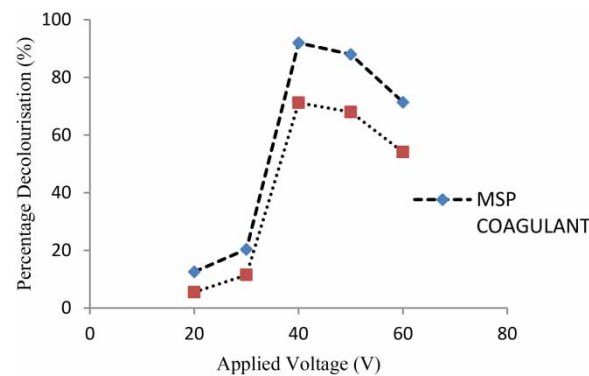
Figure 5 | Influence of voltage between electrodes on CR removal by EC.

decolourisation was shown. Figure 6(a) shows the effect of two variables pH (A) and time (B) on decolourisation. As time and pH increases, percentage decolourisation increased up to the optimum level. As time increased from 5 to 25 min and pH increased from 4 to 6 an increase in percentage decolourisation was observed. After that a decrease in the percentage decolourisation was observed with increase in time and pH .The maximum percentage degradation of 95.23% was found to be pH 5, time 15 to 20 min. The further increase in pH decreases the percentage decolourisation. Figure 6(b) shows the interactive effect on the pH (A) and voltage (C). As pH increased from 4 to 6 and voltage increased from 20 to 40 an increase in percentage decolourisation was observed. After that a decrease in decolourisation was observed with increase in pH and voltage. The maximum percentage decolourisation was found to be at the pH of 5 and the voltage of 40 V. The effect of two variables time (B) and voltage (A) on decolourisation is shown in Figure 6(c). As time and pH increases, decolourisation
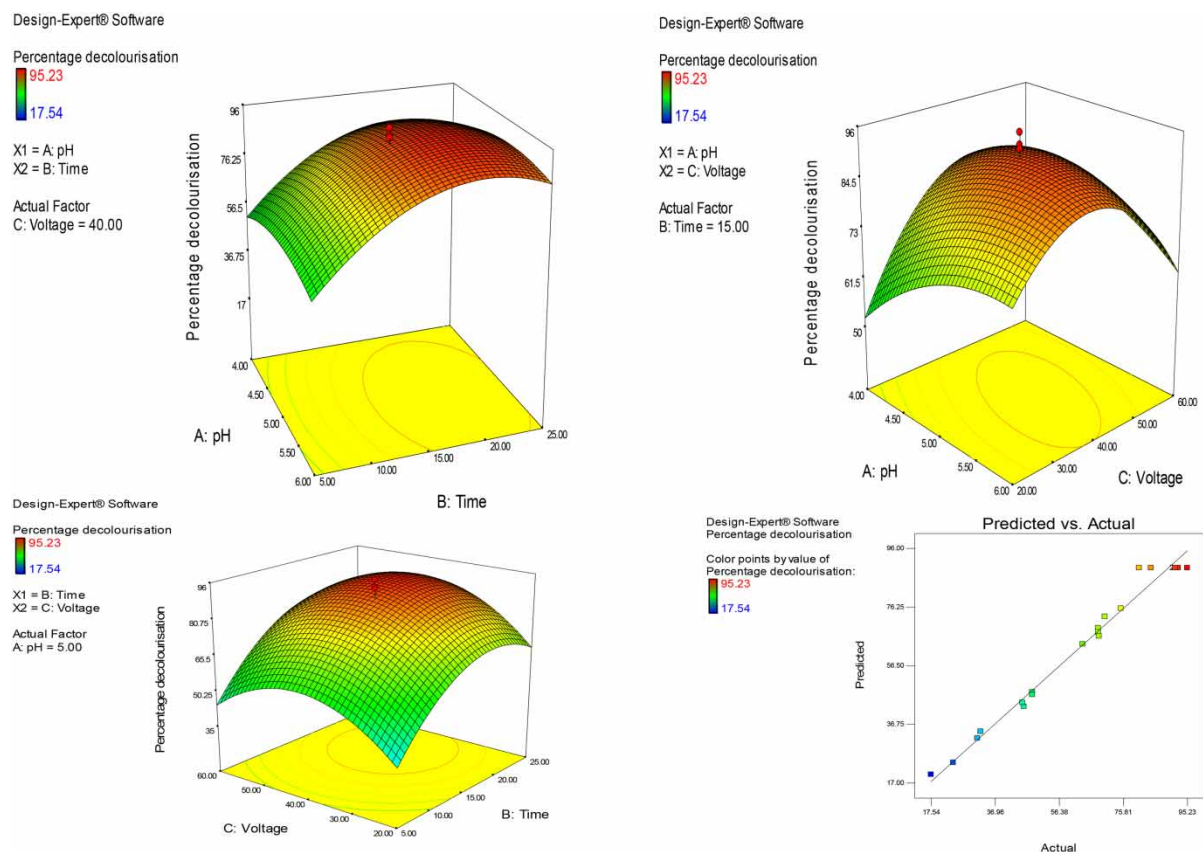
Figure 6 | Interaction effects of process parameters on CR removal by EC.

increased up to the optimum level. As time increased from 5 to 20 min and voltage increased from 20 to 40 V an increase in percentage decolourisation was observed. After that, a decrease in the decolourisation was observed with increase in time and voltage. Validation of the statistical model was carried out; the linear correlation plot between the adjusted R^2 and predicted R^2 indicate that the experimental values are in good agreement with predicted values as shown. Therefore, the models were found to be adequate in representing the response data of percentage degradation of the dye, which can be further used for analysis and prediction purposes.

The regression equation contains three linear terms (A, B, C), three square terms (A^2, B^2, C^2), and three cross-interaction terms (AB, AC, BC) plus 1 block term (Table 1). The empirical mathematical model was tested with ANOVA with a 5% level of significance. The statistical significance of the second-order model equation was determined by F-value (Table 2). In general, the calculated F-value should be greater than the tabulated F-value to reject the null hypothesis, where all the regression coefficients are zero.

$$\text{Percentage degradation} = 89.42 + 2.38 + 13.85B + 3.7C$$
$$+ 0.69AB - 7.72AC + 1.31BC - 6.23A^2 - 16.367B^2 - 17.28C^2$$

Table 1 | Coded value of physical parameters

Code	Parameter	Low Range	High Range
A	pH	4	6
B	Time (min)	15	25
C	Voltage (Volt)	20	60

Table 2 | Design table for Congo red decolourisation

				Percentage decolourisation (%)	
Run	A:pH	B:Time min	C:Voltage volt	Actual	Predicted
1	6	25	60	63.54	63.75
2	5	15	6.36	32.58	34.31
3	5	31.82	40	68.47	66.42
4	6	25	20	68.21	69.18
5	5	15	40	80.64	89.42
6	5	15	73.63	48.24	46.76
7	5	15	40	95.23	89.42
8	6.68	15	40	75.12	75.80
9	5	15	40	92.45	89.42
10	6	5	60	31.57	32.06
11	5	15	40	91.54	89.42
12	5	1.81	40	17.54	19.84
13	4	5	60	45.25	44.11
14	6	5	20	45.67	42.71
15	4	25	60	70.25	73.04
16	4	5	20	24.26	23.87
17	5	15	40	92.45	89.42
18	5	15	40	84.25	89.42
19	3.31	15	40	68.21	67.77
20	4	25	20	48.24	47.58

Multiple regression analysis was carried out considering the full quadratic model equation on the responses to evaluate the adequacy of fit and results are reported in Table 3. The coefficient of determination (R^2 values) for the model equation are $R^2 = 0.982481$, adjusted $R^2 = 0.9667$ and predicted $R^2 = 0.954246$ for the responses were reported. These values suggested that the predicted values are in a linear relation with experiment values (Table 4).

Table 3 | Analysis of variance (ANOVA) for dye removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	10,957.67	9	1,217.519	62.31345	<0.0001	significant
A-pH	77.87222	1	77.87222	3.985553	0.0738	
B-Time	2,619.589	1	2,619.589	134.0723	<0.0001	
C-Voltage	187.2326	1	187.2326	9.582694	0.0113	
AB	3.822613	1	3.822613	0.195644	0.6677	
AC	476.9416	1	476.9416	24.41019	0.0006	
BC	13.65031	1	13.65031	0.698632	0.4228	
A^2	559.9572	1	559.9572	28.65899	0.0003	
B^2	3,860.126	1	3,860.126	197.5639	<0.0001	
C^2	4,305.044	1	4,305.044	220.3351	<0.0001	
Residual	195.3862	10	19.53862			
Lack of Fit	34.9569	5	6.991381	0.217896	0.9400	not significant
Pure Error	160.4293	5	32.08587			
Cor Total	11,153.06	19				
Std. Dev.		4.420252	R^2		0.982481	
Mean		62.1855	Adj R^2		0.966715	
C.V. %		7.108171	Pred R^2		0.954246	
PRESS		510.2992	Adeq Precision		22.2624	

Table 4 | Optimized values of physical parameters

Parameter	Experimental	Simulation
pH	5 (Figure 3) acidic pH	5 (Figure 6)
Time (min)	15 (Figure 4)	15 (Figure 6)
Voltage (Volt)	40–50 V (Figure 5)	40 V (Figure 6)

FTIR analysis

The FTIR spectra of dye solution before and after treatment are shown (Figure 7). The spectra showed the peaks at 3,777.04, 3,483, 3,008.87, 2,357.63, 1,690.05, 1,482.88, 1,447.66, and 1,058.28 cm^{-1}, which correspond to aromatic esters, tertiary alcohol, $NH+$, $N=N$, $S - O$ and CHO stretching, respectively. The FTIR spectra analysis of the dye after EC observed five absorption bands between 4,000 and 500 cm^{-1} shown in Figure 7. Vibrant changes were observed at the 1,590–1,010 cm^{-1} position. The initial peaks of 3,391.24 cm^{-1}, 2,925 cm^{-1}, 2,358 cm^{-1}, 1,653.24 cm^{-1} and 1,432 correspond to amide groups and carboxylic acids formed during the process.

SEM characterization

The sludge resulting from EC using iron, at an initial dye concentration of 100 mg/L, was collected periodically to investigate the electrostatic characteristics of the sludge. The sludge was dewatered
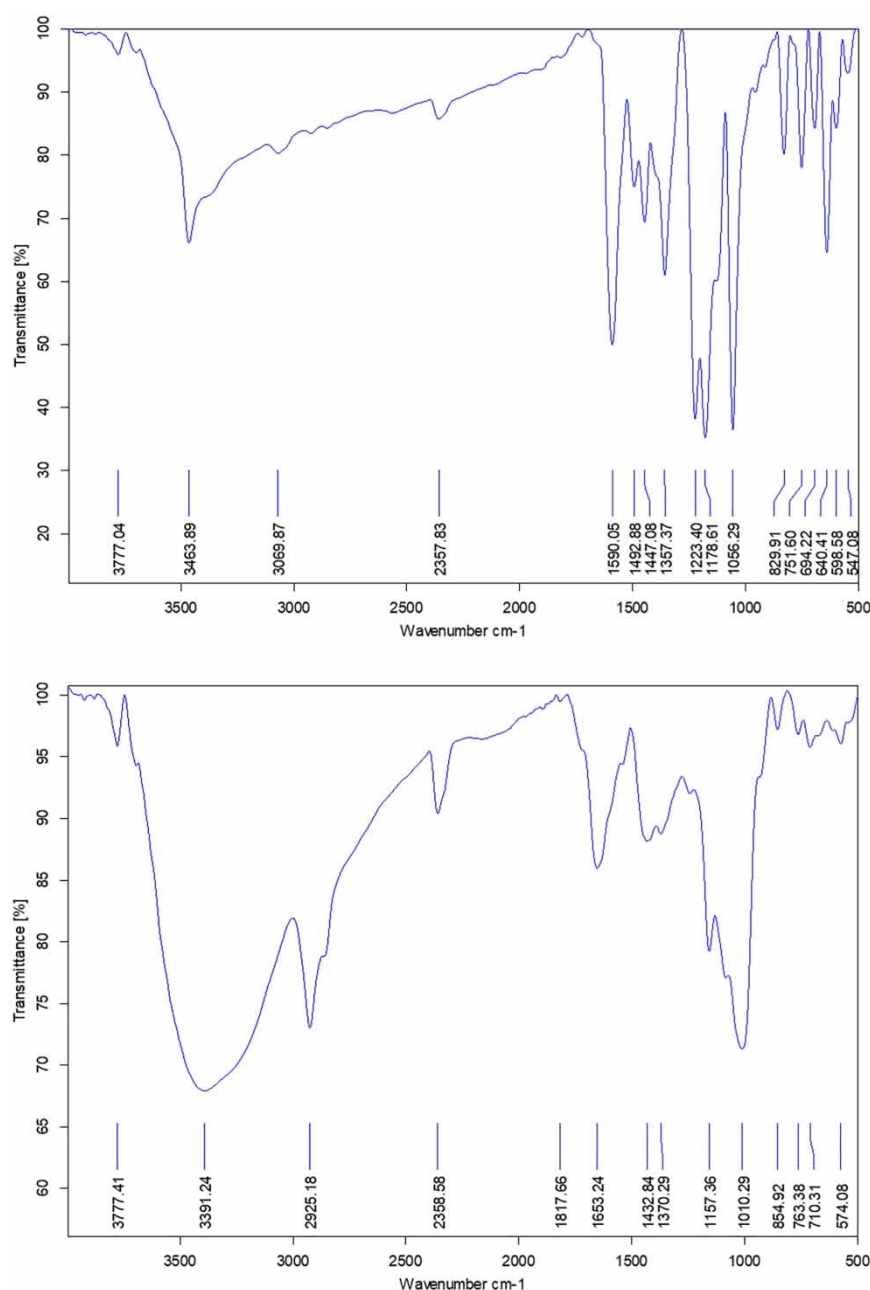
Figure 7 | FTIR spectrum of Congo red dye powder (before and after EC).

by filtration, washed with demineralised water and freeze-dried. SEM images and their corresponding elemental mapping results of EC sludge, generated at an initial dye concentration of 100 mg/L, are presented in Figure 8. Elemental mapping results show that more carbon and oxygen were found in the SEM images of sludge. Furthermore, the EDS analysis shows the weight fraction of the total weight of all the atoms in the sample (weight %). This indicates that dye was removed by coprecipitation by occlusion, where it was physically trapped inside the floc (Kima *et al.* 2013).

CONCLUSION

Our objective to enhance the percentage decolourisation of Congo red, using MSP as a natural coagulant aid in the EC process was studied. The obtained results show that the removal efficiency reached
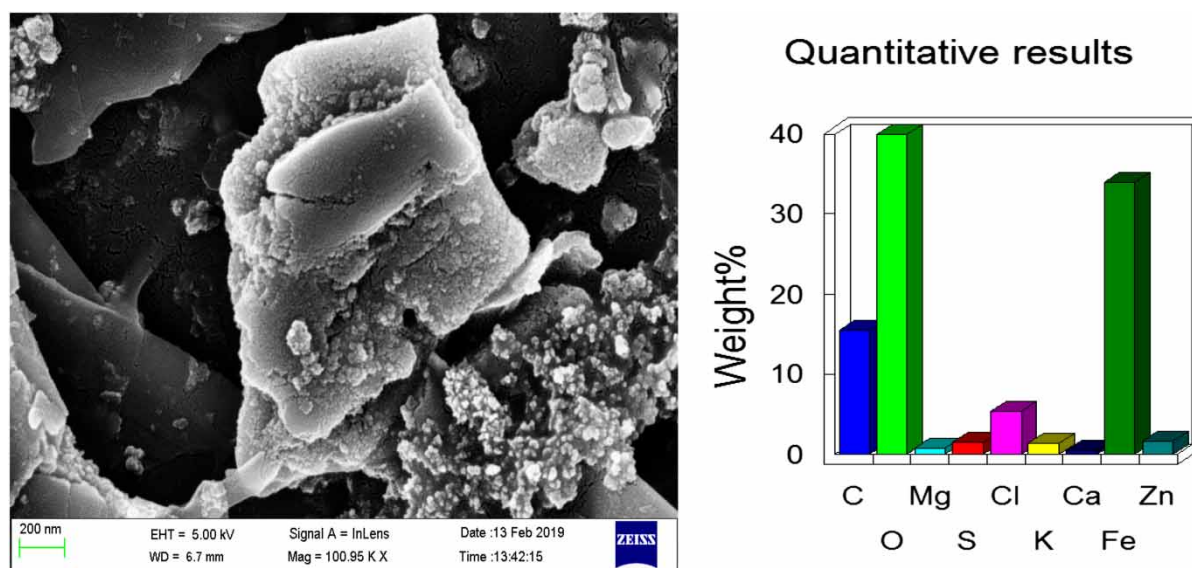
Figure 8 | SEM image of the sludge (Congo red dye + MSP coagulant) (after EC).

95.23% by using a MSP coagulant dosage of 300 mg/l. Furthermore, the process parameters were optimized by using RSM to achieve maximum decolourisation and it was found to be at the pH of 5, operating time of 15 to 20 minute, 40 Volt with iron electrodes. The process optimization of these parameters was also studied and highest decolourisation was achieved. FTIR analysis results showed that the protein content present in the MSP at the absorption band 1,653.24 cm^{-1} reacted with the dye, thereby achieving decolourisation. It can be inferred that the presence of MSP coagulant aids the decolourisation efficiency of Congo red decolourisation by the EC process.

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