

Removal of cadmium heavy metal ions from wastewater by electrosorption using modified activated carbon felt electrodes

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ABSTRACT

Cadmium contamination in industrial wastewater is an environmental issue posing a great threat to human and animal life. However, the available methods for the removal of cadmium toxicity at lower concentrations are limited. Such processes are often accompanied by sludge formation and lead to heavy metal wastage. This paper focuses on the application of electrosorption process using modified Activated Carbon Felt (MACF) electrodes for the removal and recovery of lower concentration of cadmium from simulated wastewater sample without sludge formation. Activated Carbon Felt (ACF) electrodes were treated with 20% HNO₃ for removing surface impurities and improving the surface area. The effect of the electrode modification was analyzed by performing various characterization including SEM, FTIR, XRD and cyclic voltammetry. The adsorption isotherm and kinetic models have also been studied. The effect of operating parameters including pH, voltage, initial concentration and time were analyzed and optimized using Box-Behnken design and were obtained as 6.42, 1.44 V, 0.50 mg/L and 131.51 min respectively. During the regeneration of electrodes, a concentrated cadmium solution of 18.55 mg/L, which showed the possibility of cadmium recovery. The maximum cadmium removal was 60.60% at the optimized conditions revealing the significance of electrosorption for heavy metal treatment.

Key words | activated carbon felt, cadmium removal, electrode regeneration, electrosorption, parameter optimisation, response surface methodology

HIGHLIGHTS

- Modification of activated carbon felt (ACF) using 20% nitric acid.
- Electrosorption using modified ACF electrodes for cadmium removal.
- ACF and MACF were characterised by SEM, XRD, FTIR and Cyclic Voltammetry.
- Effects of different parameters on cadmium removal were studied and optimised using response surface method.
- Cadmium recovery in concentrated form.

INTRODUCTION

The rapid industrial development and population growth have led to worldwide concerns over the freshwater shortage. One of the major factors contributing to this is the contamination of the water resources with heavy metals from different industrial sources such as battery

manufacturing, pesticides, paper industries, mining, tanneries, chemical manufacturing, metallurgy, metal finishing and electroplating (Chen *et al.* 2014). Particularly in developing nations, wastewaters are being discharged in huge quantities into the environment,

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either directly or indirectly as a result of the growth of such industries.

Most of the heavy metals are toxic non-biodegradable, bioaccumulative and carcinogenic, which when released to water bodies put forth major health and environmental concerns. In the treatment of wastewater from industries, toxic heavy metals including chromium, lead, zinc, cadmium, mercury, nickel, and copper, require particular importance. These are being widely used in several industrial segments and can cause dangerous impacts on humans as well as the natural environment (Santos *et al.* 2016).

Cadmium has several applications in various industrial sectors including stabilizers for plastics, alloys, coatings inhibiting corrosion, pigments, rechargeable batteries, and solar energy capturing devices. However, the toxicity of cadmium present in wastewater as a result of these uses leads to severe consequences (Abbar *et al.* 2019). The leaching of landfills and the waste streams cause the majority of the industrial cadmium release to the environment. Cadmium has been categorized as a probable human carcinogen by the United States Environmental Protection Agency (US EPA). 0.005 mg/L was prescribed as the maximum contaminant level of cadmium in drinking water by the US EPA whereas the World Health Organisation (WHO) limits this value to 0.003 mg/L (Water Quality Association 2013). Deleterious effects like liver injury, shock, diarrhoea, sensory disturbances, damage of bone marrow, salivation, vomiting, kidney dysfunction, yellow colouration of teeth, nausea, loss of calcium from bones, reduced red blood cell count, muscle cramps, etc. might result from the chronic cadmium exposure and high levels of exposure can ultimately lead to death (Chen *et al.* 2014). The 'Itai-itai' disease that occurred in Japan as a result of cadmium contamination in 1970 revealed the severe effects of cadmium (Nordberg 2009). Severe legal limitations are being enforced for cadmium effluent discharge into the sewer, and mandatory treatment has to be done to minimize the cadmium contamination.

Several heavy metal removal methods are available, such as physical, chemical, and biological methods, including solvent extraction, adsorption, bio-adsorption, ion exchange, membrane filtration, chemical precipitation, etc. as well as new electrochemical processes like bio-electrochemical systems electrocoagulation and electrodeposition. Nevertheless, these methods might not necessarily be efficient in all the scenarios involving the treatment of industrial wastewaters and have various disadvantages (Aziz *et al.* 2008). The treatment of wastewater containing a lower concentration (below 5 mg/L) of heavy metals yields poor performance by the conventional method of chemical precipitation (Dianati-Tilaki &

Shariat 2004). This method is costly, and the sludge produced during the process again leads to environmental issues because of their disposal (Liu *et al.* 2013). Most of the available heavy metal removal methods simply transfer the heavy metals in the wastewater into the sludge produced. Costly landfills are needed for the disposal of this sludge which also leads to the loss of valuable metals. The high energy consumed by the methods, including certain traditional electrochemical processes and membrane filtration might not be affordable for remote areas and regions due to lack of cheap electricity. When the Cd(II) concentration is very less, these methods exhibit operational difficulties and lower removal efficiencies (Chen *et al.* 2014). The tolerance limits prescribed by the Central Pollution Control Board (CPCB), India for the disposal of industrial effluents into public sewers is 1 mg/L, and that into inland surface water is 2 mg/L. Therefore, detailed studies about removal methods having high efficiencies with lower strength samples have to be conducted (Central Pollution Control Board 2000).

One of the most effective alternatives to the traditional methods is the electrochemical method in which reduction reactions take place in the electrochemical reactors where the heavy metal ions are removed from the wastewater. The studies over the past few years have introduced electrosorption as a technology involving no sludge production that can be used for the treatment of different concentrations of heavy metal contaminated wastewater much cost-effectively than the majority of the existing alternative methods. (Chang *et al.* 2011). Electrosorption is an electrochemical approach, in which the removal of metals takes place under the influence of an electric field and is the fundamental process behind capacitive deionization (CDI). Proper heavy metal removal and water purification can be made possible using the low-cost electrosorption process, which is easy to operate. CDI is an electrosorption process where the ions from one solution are adsorbed on the electrical double layers of the porous electrodes upon providing it with a low voltage electric field (Chen *et al.* 2014). Purified as well as deionized water is obtained as the positively charged anode attracts anions while the negatively charged cathode adsorbs cations including heavy metal ions. Compared to the traditional methods, less energy is consumed by the CDI technology and is very cost-effective. Since the addition of chemicals is not involved in this method, the water after treatment will be reusable. CDI performs the electrode regeneration by utilizing the electrical methods, including short-circuiting and reversal of voltage, unlike the ion exchange process where different kinds of concentrated acids were used to regenerate the resin. Secondary heavy metal treatment and

the reuse of electrode materials can be made possible by the effective regeneration of CDI electrodes using short-circuiting (Li *et al.* 2018).

According to the underlying adsorption/desorption mechanism, the structure of the electrode materials and their physical properties determines the capacity of electrosorption. The physical structure and properties of porous carbon are advantageous to be used as proper electrodes. Conductive materials including vitreous carbon, carbon aerogel, ordered mesoporous carbon, carbon nanotubes, activated carbon fibres, activated carbon, stainless steel and graphite have found applications over the past few years as suitable electro sorbents having higher efficiency and feasibility for the electrosorption process. The heavy metal removal processes can be performed effectively with the widely used Activated carbon (AC) adsorbents (Chen *et al.* 2014). The high surface area of this material resulting from its large micropore and mesopore volumes contributes to its usefulness. One of the porous forms of activated carbon is Activated carbon felt (ACF), which has a great electrosorptive performance due to its higher specific surface area (Fu & Wang 2011).

Ash materials are involved in the industrial manufacturing of ACF, which goes into the pores and plug them, thereby reducing the overall pore size and subsequently leading to lower electrosorption efficiency and conductivity. Pre-treatment of ACF is necessary to get rid of these impurities and to improve the electrosorptive performance. 20% nitric acid (HNO_3) can be used for the modification of the ACF, which can make considerable improvements in the pore size, specific surface area and the number of functional groups holding oxygen. This method produced the best modification effect on ACF, providing higher electrical conductivity than most of the other reagents (Zhao *et al.* 2018).

Response surface methodology can be used effectively as a tool for the optimization process of finding out the conditions at which the cadmium removal efficiency is maximum. This work is aimed at optimizing the process of removal of cadmium and the parameters such as voltage, time, initial concentration and pH for high cadmium removal efficiency by electrosorption from a simulated wastewater sample utilizing modified Activated Carbon Felt (MACF) electrodes.

MATERIALS AND METHODS

Materials used

Carbon felt (1 cm × 2 cm), activated carbon cloth (1 cm × 2 cm) and Activated carbon felt (20 cm × 20 cm) were the

electrode materials utilized in work and were bought from Sainergy Fuel Cell India Private Limited, Chennai. The major chemical reagents involved in the research include 20% (W/V) HNO_3 , NaCl, HCl and NaOH. The voltage was maintained using a Sigma 30 V 2A DC regulated power supply. Atomic absorption spectrometer (AAS; Thermo Fisher Scientific- AA 303) was used to determine the cadmium concentrations. Ultrapure water of (ELGA PURELAB Option-Q; Specific resistance 18.2M Ω cm) was used throughout the work for different processes.

Selection of electrode

Experiments were carried out to identify the electrode with the best performance among the selected materials. Later, dimensions of the chosen electrode were fixed by conducting trials with electrodes of different sizes (0.5 cm × 1 cm, 1 cm × 1 cm, 1 cm × 2 cm, 2 cm × 2 cm).

Modification of activated carbon felt

The ACF sheet was cut into small rectangular pieces of dimensions 1 cm × 2 cm. 1,000 mL of ultrapure water was used for soaking the materials for 2 h and then rinsed repeatedly for 40 min with ultrapure water. The materials after washing were put in a conical flask containing 20% (W/V) HNO_3 and oscillated for 2 h using a thermostat oscillator. After oscillation, the materials were taken out and washed using ultrapure water until the washing liquid showed an electrical conductivity of less than 10 $\mu\text{S}/\text{cm}$. Finally, the materials were dried for 10 h at 130 °C and stored in a desiccator to protect the materials from moisture (Zhao *et al.* 2018).

ACF and MACF characterisation

Scanning Electron Microscopy (SEM; Carl Zeiss- Evo 18) was utilized so that the morphology of ACF and MACF surface can be analyzed. Fourier Transform Infrared (FTIR) analysis was performed for ACF using FTIR spectrometer (IR Affinity-1, Shimadzu) to find out the different functional groups existing on the materials. It was also carried out on the electrodes post modification (MACF) to inspect variations in the presence of functional groups. The characterization was done using X-ray diffraction (XRD; XRD-Bruker- D8 Advance) to investigate whether the electrode modification has triggered any change in the crystalline structure of the material.

Procedure for stock preparation

1,000 mg/l of cadmium stock solution was prepared by dissolving 2.32 g of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ in ultrapure water, and the final volume made up to 100 ml. The stock solution was then diluted to different required concentrations to perform the experimental tests. The initial and final concentration of cadmium ions was determined using the AAS.

Electrosorption procedure

MACF electrodes were used for electrosorption of cadmium ions in a symmetric cell. The cell was made by assembling the electrode materials with a rubber slice as a separator. Proper ionic diffusion was ensured by providing continuous stirring to the cell placed in a 250 mL beaker. A DC power supply was used to provide the voltage in the range 0.6 V–2 V to charge the electrodes for performing the procedure. The solution with CdSO_4 as a heavy metal pollutant was prepared to the required concentration. The volume of the solution was maintained at 200 mL at room temperature, and an initial sample was stored. Electrosorption process was carried out, Cd(II) concentrations of the untreated and treated samples were analyzed using AAS (Chen *et al.* 2014). The removal efficiency of Cd(II) was determined using Equation (1).

$$\text{Cadmium Removal Efficiency} = 100 * \frac{C_o - C_e}{C_o} \quad (1)$$

where C_o is the initial concentration of cadmium ions (mg/L) while C_e is the final equilibrium concentration (mg/L).

To optimize parameters such as pH, initial concentration, working voltage and electrosorption time corresponds to maximum cadmium removal using MACF, various experimental runs were carried out by different parameter combinations given by the Box-Behnken design. After each run, desorption was carried out for regeneration of the electrodes. The cadmium sample was removed, and the cell was filled with 200 mL ultrapure water. The electrodes were short-circuited using a short copper wire, so that desorption of the cadmium ions takes place from the cathode to the water sample (Li *et al.* 2018). This water sample was used throughout the experimental runs for regeneration to obtain a concentrated solution of cadmium metal ions. The electrodes after regeneration were dried at 70 °C in a hot air oven, and reusability tests were performed.

Design of experiments

Response surface methodology (RSM) is one among the most widely used tools for optimization of parameters in various experimental processes. It can be successfully used for the modelling and analysis of several problems where various parameters influence a particular response and are comprised of a collection of mathematical and statistical methods (Bezerra *et al.* 2008). Estimation of the relative impact caused by various parameters and the optimization of this response to obtain the best-operating conditions can be considered as the primary objectives of RSM.

The Box–Behnken design (BBD) of the response surface method is adopted as the method of optimization for this research to confirm the effect of the electrosorption parameters on cadmium removal from a simulated wastewater sample. The input parameters of this 3-level 4-factor design were pH (A), voltage (B), initial concentration (C) and time (D) whereas the response of interest was the cadmium removal efficiency. The levels of input parameters were coded as 1 (high), 0 (middle) and –1 (low). The process variables with the selected levels are shown in Table 1. BBD provides the necessary statistical properties and develops designs with only a small part of the experiments necessary for a 3-level design having four parameters, thereby reducing the number of experimental runs. The experimental runs are selected based on the fitting of the quadratic model. Estimation of the number of sets of experimental runs (N) needed for BBD can be done using the Equation (2) given below.

$$N = 2k(k - 1) + C_p \quad (2)$$

where C_p is the replicated number of central point, and k is the number of parameters (Chen *et al.* 2013).

Box- Behnken gave twenty-seven experiments each with a different combination of parameters. The optimized model for the different parameters involved can be obtained by

Table 1 | Process variables and selected levels

Variables coded units	Selected Levels		
	Low (–1)	Middle (0)	High (+1)
A – pH	4	6	8
B – Voltage (V)	0.6	1.3	2
C – Initial Concentration (mg/L)	0.5	2.75	5
D – Time (min)	20	100	180

performing the experimental procedure for a different set of initial concentration, pH, voltage and time as proposed by the BBD. The analysis of variance was performed using the data obtained, and goodness of fit was found by calculating the regression coefficient (R^2).

Electrochemical performance

A three-electrode electrochemical workstation (CH Instruments, CHI 7201E) was utilized to analyze the electrochemical characteristics of the electrodes used (Chen *et al.* 2014). The cyclic voltammetry (CV) experiment was performed to analyze the capacitance value using 0.1 mol/L $\text{Cd}(\text{SO}_4)$. The cell has three compartments consisting of MACF or ACF electrodes as the working electrode, platinum wire electrode as the counter electrode and Calomel electrode as the reference electrode. The experiment was carried out with a sweep rate of 0.1 V/s and at a scanning voltage of -1 to 1 V.

Point of zero charge (pH_{pzc})

Assessment of the pH_{pzc} of modified ACF was done by performing six sets of batch experiments at various pH values. 240 mL of 0.01 M NaCl solution was prepared, and 40 mL of this was used in each of the batch tests. The pH values of all the six solutions were adjusted between 2 and 12 using 0.1 M HCl or NaOH solutions in the desired quantity, and the initial pH was noted. A modified ACF electrode weighting 0.051 g was put into each of solutions, and continuously stirred at a rate of 200 rpm for 24 h. The final pH was found, and the difference in the pH values before and after the tests were calculated (ΔpH). A plot between the calculated values of ΔpH and the initial pH value of the solutions was utilized for determining the pH_{pzc} value (Babić *et al.* 1999).

RESULTS AND DISCUSSIONS

Selection of electrode

From the trial experiments, the percentage cadmium removal of the electrode materials was observed to be in the order Activated carbon cloth < Carbon felt < ACF indicating the superior electrosorptive capacity of ACF. Meanwhile, in the case of ACF electrode dimensions, the order of percentage removal was found as $0.5\text{ cm} \times 1\text{ cm}$ < $1\text{ cm} \times 1\text{ cm}$ < $1\text{ cm} \times 2\text{ cm}$ < $2\text{ cm} \times 2\text{ cm}$. Even though

the maximum efficiency was obtained for the electrode with $2\text{ cm} \times 2\text{ cm}$ dimensions, it had only a slight increase than that with the $1\text{ cm} \times 2\text{ cm}$ electrode. Hence, ACF electrodes with dimensions $1\text{ cm} \times 2\text{ cm}$ were found to be ideal for the electrosorption of cadmium.

ACF and MACF characterisation

SEM

The ACF before modification had a vast number of irregular fibres arranged disorderly with typical felt characteristics, including similar size and normal shape as displayed in Figure 1(a) and 1(b). Certain grooves of various depths were seen on fibres with irregularly spaced voids and discontinuities in between. The felt surface had a rough texture and was relatively flat. Some impurities in the form of deposition were visible on the outer surface of the felt fibres. Figure 1(c) and 1(d) shows that the ACF surface appeared to be smooth after modification and more prominent longitudinal grooves were present (Zhao *et al.* 2018). The impurities present on the surface of raw ACF were efficiently removed. Since the specific surface area of the ACF increased after the modification in the felt structure, the number of sites for effective adsorption also increased. Small and uneven deposits indicating the presence of cadmium were found on the modified felt surface after electrosorption, as shown in Figure 1(e) and 1(f).

XRD

Figure S1(a) and S1(b) depicts the XRD spectra of the ACF and MACF electrodes, respectively. Broad peaks of diffraction were obtained at 25.2 and 43.5 from the XRD spectra of ACF which corresponds respectively to the crystal planes 002 and 100 which are the characteristic profiles of disordered carbon annealed at a lower temperature (Chen *et al.* 2014). After modification, the diffraction peak profiles remained the same, indicating that the modification did not affect the crystal structure of the material. However, while the face 100 did not change, the intensity of face 002 was slightly increased, which might be due to the interaction with acid during modification.

FTIR

The FTIR spectra of both the ACF and MACF were obtained as given in Figure 2(a) and 2(b). Three major absorption

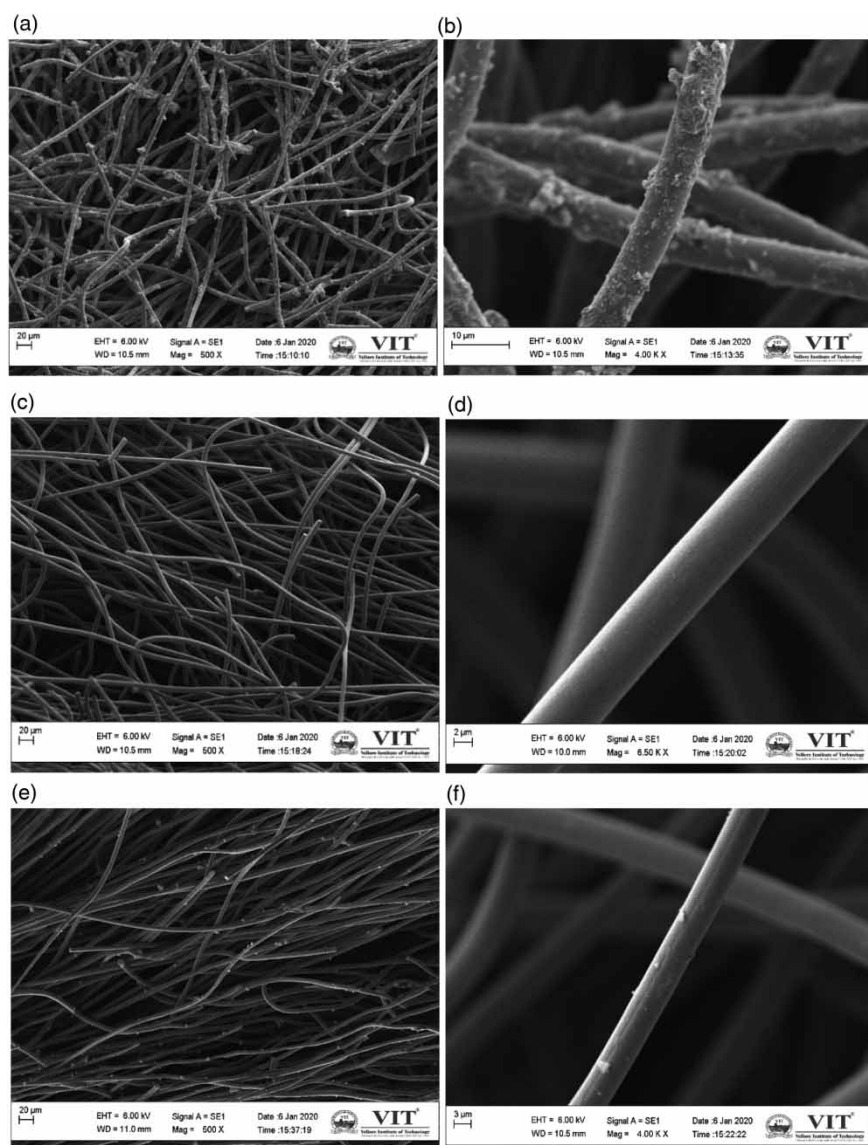


Figure 1 | SEM images of (a), (b) ACF; (c), (d) MACF; (e), (f) MACF after electrosorption.

peaks were obtained for ACF corresponding to C-H, C = O and O-H. Both alkene and alkane C-H peaks were present at 960 and $1,398\text{ cm}^{-1}$ respectively whereas the peaks of the oxygen-containing functional groups including C = O and O-H were present at $1,627$ and $3,385\text{ cm}^{-1}$ respectively. The vibrations at $2,300\text{ cm}^{-1}$ might be due to the presence of CO_2 . After felt modification, there were significant enhancements in the vibration peaks of functional groups holding oxygen ($1,627$ and $3,385\text{ cm}^{-1}$), of which OH peak had a drastic increase. This indicates the addition of oxygen-containing acidic functional groups including hydroxyl, carbonyl and carboxyl groups to the surface. Such groups

can effectively increase the electrosorption capacity of the adsorbent material for cadmium adsorption since they provide sufficient active sites for adsorption (Zhao *et al.* 2018).

Cyclic Voltammetry

The CV results revealed the presence of similar peaks in the case of both ACF and MACF, as depicted in Figure 3. The presence of specific distinct peaks at the CV curve indicates that during the process, the electrodes underwent oxidation and reduction reactions. The area under CV curves is directly

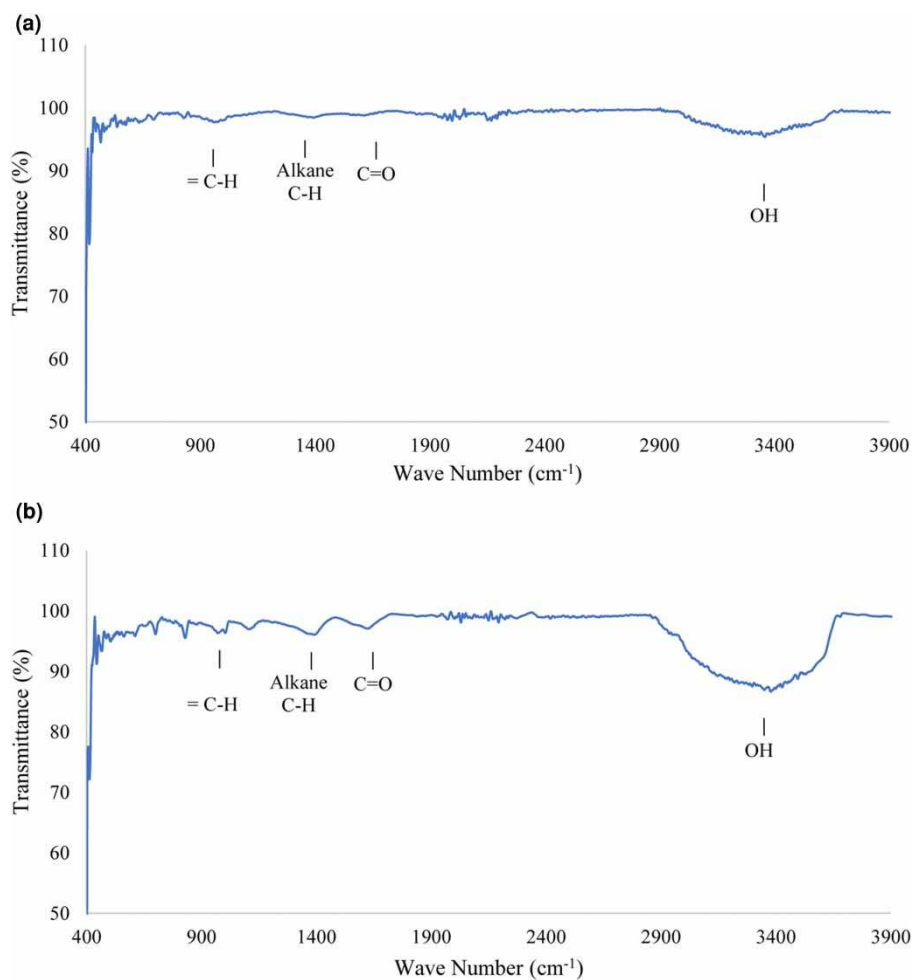


Figure 2 | FTIR spectra of (a) ACF and (b) MACF.

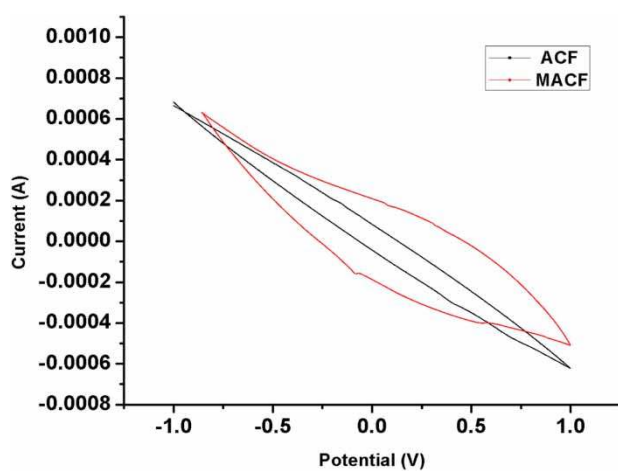


Figure 3 | Cyclic voltammetry plot for ACF and MACF.

proportional to the capacitance value (Chen *et al.* 2014). Thus, the MACF electrode having higher area has more capacitance and hence the higher electrosorption capacity

Point of zero charge

The pH_{pzc} of modified ACF was found as 6.13 as depicted in Figure 4. Depending on the surface charge of MACF, the pH_{pzc} is closely related to the electrosorption capacity.

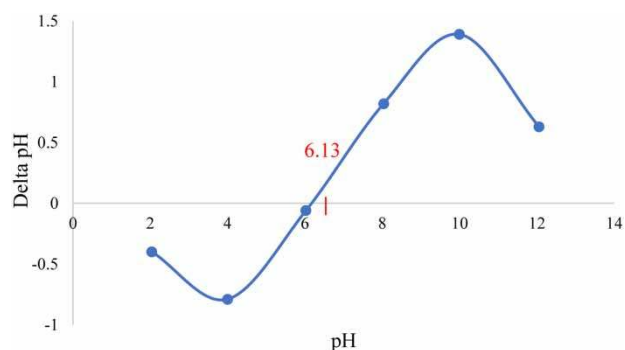


Figure 4 | Point of zero charge of MACF.

When the obtained optimum pH value is higher than the pH_{pzc} , cation adsorption takes place easily, whereas a lower pH value will favour adsorption of anions. In the present work, the optimum pH at which cadmium removal was found to be maximum had a value higher than the calculated pH_{pzc} indicating that the optimized values can be considered to be reliable. There might have been the presence of a stronger electrostatic pull between the surface of ACF fibres and the cadmium ions (Abraham *et al.* 2018).

Adsorption isotherms

Two models Langmuir and Freundlich, were utilized to carry out the adsorption isotherm studies. The values of the adsorption energy constant in the reaction (K_a) and maximum adsorption capacity (q_m) of the Langmuir model were determined from the plot between $1/q_e$ and $1/C_e$ (Figure 5(a)) as 0.56 L/mg and 5.17 mg/g respectively. In Langmuir model, an R^2 value of 0.99 was obtained for the adsorption of cadmium on to the MACF surface. Based on the separation factor (R_L) value of 0.26, it was found that the cadmium adsorption mechanism using MACF was favourable. A graph plotted between $\log q_e$ and $\log C_e$ gave

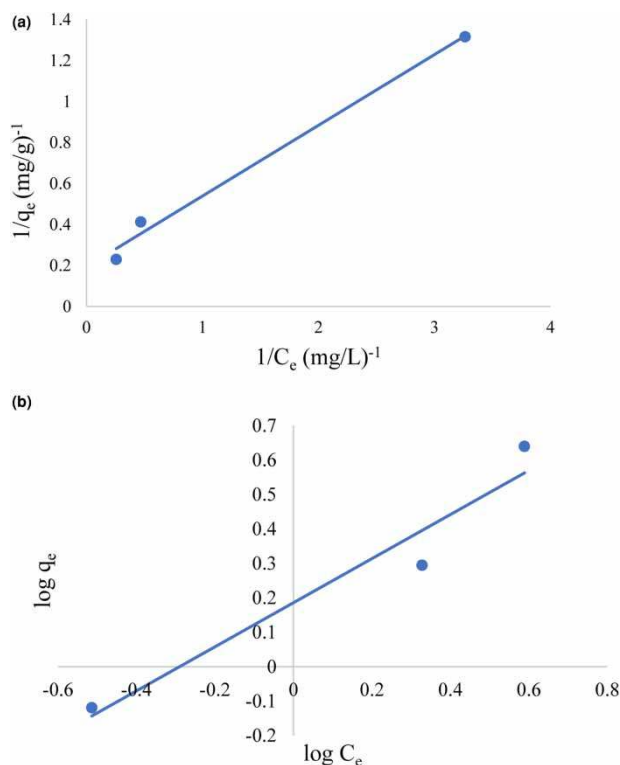


Figure 5 | Linear plot of (a) Langmuir isotherm and (b) Freundlich isotherm for cadmium adsorption.

a linear line ($R^2 = 0.94$) having an intercept of $\log K_f$ and a slope of $1/n$ in case of the Freundlich model as given in Figure 5(b). Heterogeneous adsorption is indicated by the higher values of Freundlich adsorption constant, K_f (1.62 mg/g) and Freundlich adsorption exponent, n (1.50) (Muthukumaran *et al.* 2016). The value of slope ($1/n$) in between 0 to 1 indicates surface heterogeneity. Since the slope is nearer to zero, high heterogeneity is present. The adsorption of cadmium ions onto the MACF surface can be clearly explained by the higher R^2 value attained for the Langmuir isotherm model. In Langmuir model, only monolayer adsorption occurs and once equilibrium is reached no further adsorption occurs, while heterogeneous kind of adsorption without limiting monolayer adsorption takes place in case of Freundlich model (Foo & Hameed 2010).

Adsorption kinetics

The adsorption rate for the removal of cadmium was determined by employing kinetic models, including Pseudo-first-order and pseudo-second-order models. When the pseudo-first-order model was used, the R^2 value obtained was 0.79 from the plot between $\log(q_e - q_t)$ and t (Figure 6(a)). Pseudo-second-order model gave more R^2 value (0.97) than the pseudo-first-order model and was obtained from the graph plotted among t/q_t and t with a slope $1/q_e$ and intercept $1/k^2 q_e^2$ (Figure 6(b)). The experimental adsorption capacity ($q_{e,exp}$) was obtained as 4.36 mg/g whereas the calculated adsorption capacity ($q_{e,cal}$) for the first-order and second-order models were 2.08 mg/g and 4.17 mg/g respectively. $q_{e,cal}$ was much closer to the $q_{e,exp}$ in the case of the pseudo-second-order model. Pseudo-second-order model was the best fit with the experimental results, which can be understood from the closer values of q_e and the higher value of R^2 (Saleh 2015). The rate constants (k_1 and k_2) for the first-order and second-order models were obtained as 0.011 min^{-1} and 0.017 g/mg min respectively, and the adsorption rate ($h = k_2 \times q_e^2$) had an initial positive effect. In the preliminary phase, adsorption might have occurred at a rapid rate, as indicated by the h value of 0.30 mg/g min . The values of k_1 , k_2 , and h were obtained at the optimum experimental conditions.

Statistical analysis

To study the combined effect of the independent parameters on the percentage removal of cadmium, statistically designed twenty-seven batch experiments as obtained from

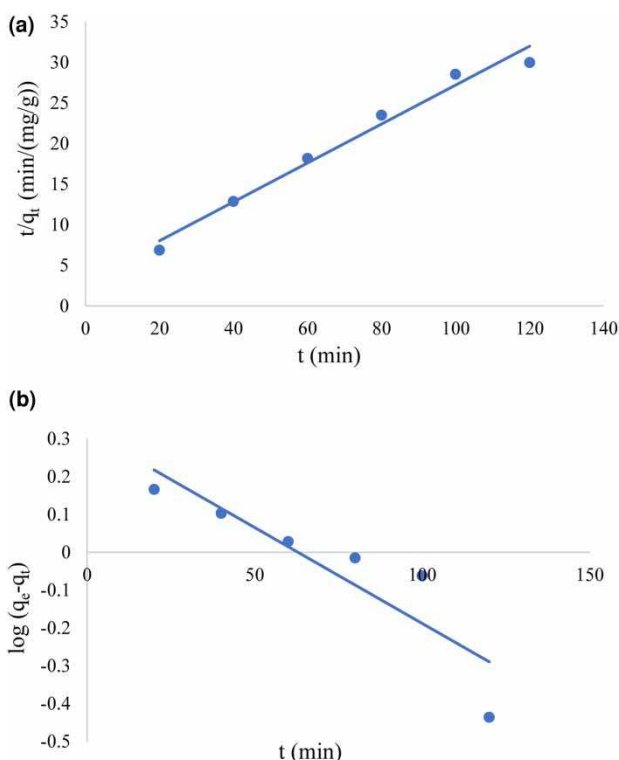


Figure 6 | Linear plot of (a) Pseudo-first order kinetics and (b) Pseudo-second order kinetics for cadmium adsorption.

the Minitab-17 software, were carried out for different combinations of the process variables. Table 2 shows the 27 sets of combinations and their results, including removal efficiency and energy consumption as the response functions. The obtained values of cadmium removal efficiency were in the range between 4.64 and 63.60%, while the energy consumption varied from 0.024 to 0.72 Wh.

An empirical relationship was formulated using Minitab-17 between the response and the independent variables by analyzing the results of the removal efficiency. The coded units A, B, C and D were used to represent the different independent parameters for expressing the removal efficiency (RE) in its concise quadratic form as given below:

$$\begin{aligned} \% \text{ Removal} = & -224.7 + 73.79A + 55.2B - 6.09C + 0.179D \\ & - 6.164A^2 - 24.13B^2 + 0.517C^2 \\ & - 0.001384D^2 + 1.68AB + 0.250AC \\ & + 0.0201AD - 1.46BC + 0.0371BD \\ & + 0.0043CD \end{aligned} \quad (3)$$

The effect that the individual parameters and the double interaction terms has on the removal of cadmium can be

clearly understood from this equation. Coefficients having negative values indicate that there is an inverse relationship between the removal efficiency and the individual or double interaction factors whereas the positive values of coefficient reveal that the removal is directly proportional to the affecting factors. From Equation (3), pH, voltage and time were found to have a positive impact on cadmium removal while the quadratic interactions had negative impacts. Only the initial concentration was found to have a negative influence among the parameters with its quadratic interaction, increasing the removal efficiency. All the double interactions, except the one involving voltage and concentration, improved the removal efficiency. One of the notable results is that the initial concentration has a negative effect on removal efficiency. This indicates that heavy metals at even low concentrations can be separated and removed effectively using electrosorption.

A statistical approach called ANOVA (analysis of variance) is necessary to analyze the reliability of the Box-Behnken design. The total variance of the entire data is split into small parts, and the hypotheses on various parameters were examined with different sources of variation (Huiping *et al.* 2007). The Fisher F-test and P-test of the ANOVA determine the adequacy of the data involved. The regression equation can be used to explain the majority of the variations in the response for higher values of F. The statistical significance of the process can be obtained from the F-value whereas the P-value determines whether F is large enough to be statistically significant. When the P-value is lesser than 0.05, the model is sufficient enough to explain 95% of the variability.

The ANOVA of the response surface model is displayed in Table 3 which includes the degree of freedom (DF), the adjusted mean of squares (Adj MS), the adjusted sum of squares (Adj SS), P-value and F-value. The regression model is found to be highly significant since the F-value and P-value were obtained as 12.56 and 0.000, respectively. The multiple correlation coefficient (R^2) value was used for checking the goodness of fit, which was obtained as 93.61%. The higher value of the multiple correlation coefficient indicates the statistical significance of the regression model, revealing that among the total variations, only 6.39% cannot be explained by the model.

pH, initial concentration and time are supposed to have a significant effect on the removal efficiency according to the results of ANOVA, whereas the applied voltage has a minor effect. The major contribution to the model with 28.24% was by the square term, followed with 14.98% by the linear term. Only a negligible contribution of 0.49%

Table 2 | Experimental results of Box–Behnken design

Run Order	pH	Voltage (V)	Initial concentration (mg/L)	Time (min)	Removal Efficiency (%)	Energy Consumption (Wh)
1	6	0.6	2.75	20	16.2051	0.024
2	4	1.3	5	100	7.1308	0.26
3	8	0.6	2.75	100	21.3258	0.12
4	8	1.3	0.5	100	38.8412	0.26
5	4	1.3	0.5	100	15.9067	0.26
6	6	0.6	5	100	28.9174	0.12
7	6	2	5	100	29.4844	0.4
8	8	1.3	2.75	20	15.5594	0.052
9	4	0.6	2.75	100	12.1158	0.12
10	8	1.3	2.75	180	28.4027	0.468
11	6	0.6	2.75	180	28.2937	0.216
12	6	1.3	2.75	100	44.6328	0.26
13	6	1.3	0.5	20	48.1223	0.052
14	8	2	2.75	100	23.7333	0.4
15	4	1.3	2.75	20	4.6410	0.052
16	6	2	2.75	180	38.8918	0.72
17	6	2	0.5	100	50.8823	0.4
18	4	2	2.75	100	5.1158	0.4
19	8	1.3	5	100	34.4494	0.26
20	6	1.3	5	180	45.0393	0.468
21	6	2	2.75	20	18.4885	0.08
22	4	1.3	2.75	180	4.8668	0.468
23	6	1.3	2.75	100	47.7059	0.26
24	6	0.6	0.5	100	41.1415	0.12
25	6	1.3	0.5	180	63.6029	0.468
26	6	1.3	2.75	100	48.6737	0.26
27	6	1.3	5	20	26.4844	0.052

was there due to the interaction between input parameters. The very high effect of pH means that the removal of a significant part of the cadmium concentration can be facilitated by adjusting the pH of the solution to the required conditions.

The obtained Pareto chart, which is a vital tool for the determination of the magnitude of the effects and their significance is displayed in Figure S2 (Mohd *et al.* 2020). The absolute values of the various effects are generally shown in the Pareto chart, making it challenging to find out whether the effect decreases or increases the response function. The bars representing factors AA, A, BB, C, D and DD cross the reference line at 2.179, which denotes the statistical significance of these factors at a level of significance of 0.05. Thus pH, Initial concentration and time

are the most significant factors according to the Pareto chart.

Figure S3 depicts the obtained Normal plot, which indicates the direction in which the parameters affect or change the response along with their importance and the magnitude. The case when there were absolutely no effects of the parameters is represented in the Normal plot as a distribution fit line and is taken as reference. All the effects are shown in a standardized manner concerning to reference line. The statistical significance depends on the distance from the reference line, and the one most far away is having high significance. Statistically significant and insignificant effects can be distinguished from each other by their unique shape and colour. However, the intensity of these effects cannot be determined

Table 3 | Analysis of variance for removal of cadmium

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	6,584.72	470.34	12.56	0.000
Linear	4	2,244.76	561.19	14.98	0.000
pH	1	1,062.41	1,062.41	28.37	0.000
Voltage	1	28.83	28.83	0.77	0.397
Initial Concentration	1	629.03	629.03	16.80	0.001
Time	1	524.49	524.49	14.00	0.003
Square	4	4,230.62	1,057.66	28.24	0.000
pH*pH	1	3,242.13	3,242.13	86.57	0.000
Voltage*Voltage	1	745.54	745.54	19.91	0.001
Initial Concentration*Initial Concentration	1	36.52	36.52	0.98	0.343
Time*Time	1	418.30	418.30	11.17	0.006
2-Way interaction	6	109.34	18.22	0.49	0.806
pH*Voltage	1	22.12	22.12	0.59	0.457
pH*Initial concentration	1	5.05	5.05	0.13	0.720
pH*Time	1	41.50	41.50	1.11	0.313
Voltage*Initial Concentration	1	21.04	21.04	0.56	0.468
Voltage*Time	1	17.27	17.27	0.46	0.510
Initial Concentration*Time	1	2.36	2.36	0.06	0.806
Error	12	449.40	37.45		
Lack-of-Fit	10	448.80	44.88	0.42	0.223
Pure Error	2	0.60	0.30		
Total	26	7,034.13			

from the Normal plot. Factors A and D have a positive standardized effect while the factors AA, BB, C and DD have adverse effects.

To find out whether the data is distributed normally or not, the Normal probability plot given in Figure S4 can be used. Normally distributed data is represented by a diagonal, straight line and a skewed line to either side indicates that the data is not normally distributed. Since a straight, diagonal line was obtained in our plot, our data distribution can be considered as normal (Majeed *et al.* 2019).

Optimization of conditions

The software's numerical optimization was used to estimate a particular point at which the desirability function is maximized. The weight and importance of the goal to be attained can be specified. The weight was designated as 1, and the goal of the process was fixed as 'maximum' to maximize the removal efficiency. From the experimental results, the removal efficiency had a lower limit of 4.64%, whereas the

upper limit value was 63.60%. These boundaries and settings were utilized to perform the optimization procedure. The results are depicted in Table 4, where the first set of parameters obtained with the highest desirability value of 0.949 represents the optimized conditions. Confirmatory tests were performed at the optimized conditions to check and confirm the removal efficiency. From the optimized values, the voltage of 1.448 V could not be achieved on the DC power supply due to which a voltage of 1.5 V was selected based on the positive effect of voltage on the removal efficiency to give the best results. The concentration was taken as 0.5 mg/L and pH as 6.42 for a time duration of 131.51 minutes. The final removal efficiency attained from the confirmatory test was 58.12% and was within the range of the optimum removal provided by the software utilizing the desirability values (Table 4). This indicates that the optimization of the experimental design and the process parameters for the removal of cadmium can be done effectively by the Box–Behnken design with the respective desirability values.

Table 4 | Optimum parameters for maximum cadmium removal efficiency

Solution	pH	Voltage	Initial Concentration	Time	% Removal Fit	Composite Desirability
1	6.42424	1.44848	0.5	131.515	60.6018	0.949136
2	6.55187	2.00000	0.5	180.000	51.2258	0.790226
3	6.81128	0.93071	0.5	167.299	50.5017	0.777955

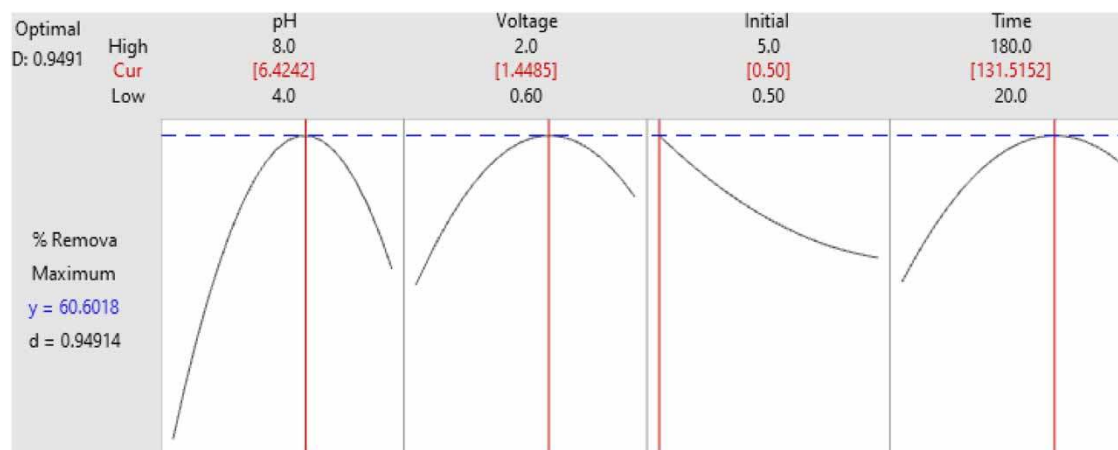
The surface plots revealing the correlation between the percentage removal and the most significant parameters are depicted in Figures S5(a) to S5(c). All these are having inverted sheet-like structure because of the rise and fall in the removal efficiency values. In the case of Percentage removal vs Initial concentration and pH, maximum removal of around 55% can be obtained at a slightly acidic pH and a low initial concentration while the voltage and time were constant at 1.3 V and 100 min respectively. A combination of a pH value around 6 and a time of just above 2 hours can provide a maximum removal efficiency of around 50% when the other two parameters were maintained at a constant value. With a constant pH and voltage, 55% cadmium removal can be obtained by experimenting with a low initial concentration of around 0.5 mg/L for 2 hours.

Effect of process variables on the removal efficiency of cadmium

Figure 7 shows the trend exhibited by the cadmium removal efficiency under the influence of the various affecting factors. It depicts the effects of the different parameters on cadmium electrosorption in water by the modified ACF. At pH 4, the cadmium removal efficiency was very low. On the surface

of the modified ACF, more positive charges are usually present in a low pH sample, thereby leading to an increased rate of electrostatic repulsion. There was a reduction in the electrostatic repulsion on the electrode surface as the pH values increased significantly, causing an increase in the cadmium removal efficiency. When the pH value was increased and maintained as 6, the maximum percentage removal of cadmium was obtained. With a further increase in pH, there was a gradual reduction in the cadmium removal percentage in the case of the MACF. This trend might be due to the OH^- complex formation under alkaline conditions which may reduce the cadmium available for electrosorption (Huang *et al.* 2016). It is understood that slightly acidic pH values are most suitable for efficient electrosorptive removal of heavy metals. Hence, for practical applications, wastewater having a neutral, slightly alkaline or heavily acidic pH has to be modified to bring the pH to a slightly acidic level to maximize the efficiency of the process.

The effects of voltage on the electrosorption of Cd by the MACF are also shown in Figure 7. An initial rise in the cadmium removal efficiency was obtained as the voltage was increased gradually. The electrosorption process on the MACF involving the removal of cadmium took place more effectively at higher voltages. As the voltage increased from 0.6 to 1.3 V, a significant rise in the percentage

**Figure 7** | Effect of different parameters on cadmium removal efficiency.

removal of cadmium was observed, reaching the maximum value and equilibrium was attained after almost 2 h of electrosorption. However, as the voltage was increased beyond 1.3 V, small amounts of bubbles started to appear in the water, and this can be attributed to the weak electrolysis reactions taking place in water triggered by the high voltage. Hence, after a particular voltage, modified ACF displayed a slight reduction in removal efficiency (Zhao *et al.* 2018).

The effect of initial cadmium concentration on the electrosorption of Cd(II) ions by modified ACF displayed an inverse proportionality, as shown in Figure 7. Cadmium concentrations of 0.5, 2.75 and 5 mg/L were utilized in the experimental procedure. As the concentration of cadmium increased, the percentage of removal was found to decrease with maximum removal at 0.5 mg/L. Even though there was an inverse trend, a significant cadmium removal was still taking place at higher concentration of 5 mg/L. The presence of active adsorption sites and the surface area are generally high at the low initial concentration of the solution due to which easy adsorption and removal take place. When the cadmium concentration is higher in the initial solution, less number of sites will be present for adsorption, which thereby leads to a decrease in removal efficiency (Wang *et al.* 2010).

The electrosorption time is one of the significant parameters affecting the removal of cadmium. Figure 7 portrays how the variation of the process time affects the removal efficiency. The percentage removal goes on increasing with time till the maximum value is obtained. This rapid initial rise in efficiency might be due to a large number of sites of adsorption and the increased surface area. After that, a slight reduction of efficiency takes place, which can be possible due to the accumulation of the cadmium ions at the verge of saturation. This rush of ions would have increased the desorption process causing the efficiency of removal to decline by a small value after the optimum duration.

Regeneration, reusability and cost analysis

Regeneration of the MACF electrodes was done by the process of desorption in which the surface-bound Cadmium ions are removed. Thus, a concentrated Cd²⁺ solution of 18.55 mg/L was obtained, indicating that the percentage recovery achieved is 94.01.

Reusability of electrodes is an important criterion which assesses the efficiency of electrosorption. The reusability test was conducted by repeating the electrosorption process using regenerated MACF. Even after five successive test cycles, it was found that the percentage of cadmium recovery dropped only by 2.09% (Figure 8) which revealed that

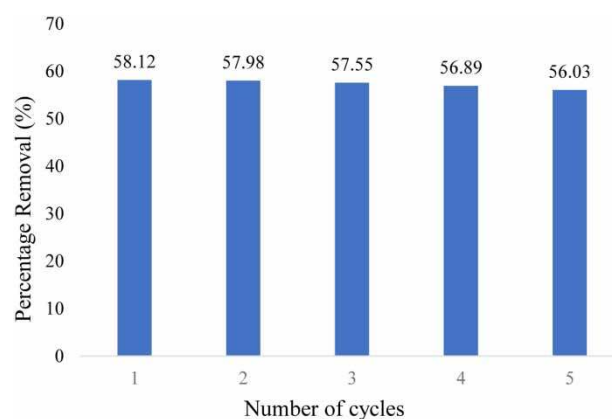


Figure 8 | Reusability of MACF electrode for cadmium adsorption.

the electrodes could be effectively recovered and reused without a significant reduction in the removal efficiency (Abraham *et al.* 2018).

The cost of materials, chemicals and power consumption were the key contributors to the expenses of the entire process. The total cost for treating 200 mL of wastewater was calculated to be approximately ₹50, implying that treatment can be performed at the cost of ₹250/L (supplementary material). The experimental process, including electrosorption, regeneration, and recovery, can be implemented at an industrial level by employing large reactors equipped with MACF electrodes of the corresponding size. Even though an initial capital will be required for the installation of reactors and facilities, the process might prove to be economical over the long run owing to the electrode reusability and process efficiency. The terminal process, such as evaporation might be utilized for the extraction and recovery of cadmium from the final concentrated solution (Li *et al.* 2018). Aside from the reduction of heavy metal, electrosorption also provides water desalination applications.

CONCLUSION

ACF with dimensions 1 cm × 2 cm was found to be the potential electrode for cadmium removal, which on modification gave enhanced electrosorptive performance. The characterization by SEM, FTIR, XRD and Cyclic voltammetry confirmed the modification of the ACF and its improved electrosorption properties. More number of carboxyl and carbonyl groups were present in the electrodes after modification. The Langmuir isotherm and Pseudo-second order kinetics models fitted well with the experimental data and maximum adsorption capacity was obtained as

5.1733 mg/g. The optimum conditions for maximum efficiency are pH (6.42), voltage (1.44 V), initial concentration (0.5 mg/L) and time (131.5 min) with a maximum removal efficiency of 60.60%. pH, initial concentration and time were found as the significant factors for cadmium electrosorption from the regression analysis results. The point of zero charge was obtained as 6.13. The electrosorption method is most suitable for removal of heavy metals in very low concentration in a slightly acidic water sample. The energy consumption is very less since the voltage involved is less than 2 V. Recovery of the cadmium heavy metal is possible as a solution of high metal concentration with 18.55 mg/L of cadmium was obtained after regeneration of the electrodes. It is feasible to reuse MACF for electrosorption even after five adsorption cycles since there was no considerable reduction in the removal efficiency. The results from different experimental analysis reveal the importance of MACF as an electrosorbent for efficient removal and recovery of cadmium from the effluents discharged into the natural environment by the industries.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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