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Electrocoagulation for the efficient removal of Eriochrome Black T from wastewater using copper electrodes

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The present study is based on the application of the electrocoagulation process in removal of Eriochrome Black T dye pollutant. It is found that many factors like voltage, temperature, number of pairs of electrodes, contact time, inter electrode distance are affecting the electrocoagulation. As voltage is increased from 5 V DC to 30 V DC the removal efficiency increases linearly and attained 98.3% at 13 V DC and beyond that the removal of dye is constant. The temperature plays important role in electrocoagulation and maximum removal was observed at 28 °C, at high temperature electrocoagulation decreases. It is also found that inter-electrode distance of 0.5 cm is more favourable for removal. As the number of pair of electrodes increases the removal capacity also increases. If there is a rise in concentration of the solution from 10 ppm to 1000 ppm the efficiency decreases from 99.2% to 63.6%. The chemical oxygen demand of the treated solution drops from 1600 to 320 ppm under 13 V DC, 180 s of contact time for 25 ppm of dye solution. The energy consumption, anode dissolution also plays a crucial role in removal of dye.

Keywords: Electrocoagulation, Eriochrome Black T, Copper electrodes, Dye removal, COD

Today the whole world suffers from water toxicity and decreased quality along with pollution. Industrial effluents and dyes effluents are also one of the sources of water pollution that damage the ecosystem and also lead to a decrease in the quality of drinking water. These dyes are prepared to provide colour to the materials but later they turned out to be carcinogenic, mutagenic, and become hazardous material to the world. Textile industries, painting, paper industries are the major sources of these dyes[1]. These effluents are released into the nearby water sources like rivers, lakes, and ponds, the chemical components that are present in the dyes are mixed up with water and are dangerous to human health[2]. These effluents have a huge amount of suspended particles or solids that are invulnerable to temperature, less transparency, they are very stable to light, temperature and blocks the photosynthetic activity of aquatic plants and indirectly decreases the dissolved oxygen level, also undergoes some biological and chemical changes and hence increases the chemical oxygen demand (COD) of the water[3]. The nitrogen and phosphorous contents in the dyes increase the production of biomass and lead to eutrophication, aesthetic pollution. These effluents are also causing harm to natural ecosystems like groundwater pollution, soil pollution, or chemical contaminated soil, and it causes health issues and irritation to other organs[4].

There are other methods classified under physical, chemical and biological methods for the treatment of these effluents, but they are suffered from drawbacks like the production of secondary pollutants in chemical coagulation, high maintenance cost, and basic requirements. Adsorption is one of the methods using widely in the process of dye removal by using adsorbents that are usually nano materials or organic biomass. An advanced oxidation technology like Fenton process is carried out by adding hydrogen peroxide and iron salts, and a combination of these two chemicals produces hydroxyl radicals which have high potential in dye removal. Photodegradation, ultrasonic decomposition, chemical degradation, bio-degradation, and precipitation are the other methods used widely[5]. Ozonation, membrane separation, and other biological methods result in high production of sludge, sewage and also inhibit bacterial growth[6]. Due to all these drawbacks researchers find electrocoagulation, the best method at low cost, easy operation, fewer additives, low maintenance, remove smallest colloidal particle, higher performance, shorter retention, efficient method, and coupling with other methods are used widely[7-8].

Electrocoagulation is an advanced technology compared to other technologies and it involves in situ generation of coagulants by electrolytic oxidation or dissolution of metallic anodes under the applied current[9], the oxidation of anode leads to the liberation of metal ions, which form a bond with the hydroxyl radical formed by breaking the water molecule into hydrogen gas and hydroxyl radicals at the cathode to form metal hydroxide. The production of metal hydroxide leads to the flotation of solid suspended particles[10-11]. These freshly formed hydroxides have a large surface area and help in rapid adsorption of the dye, and do not dissolve in water, the coagulant that aggregate and results in decolourization of the dye solution, during the process froth will be generated and later that will settle down at the bottom, and hence adsorb more dye molecules and increases the decolourization[7-11]. These freshly formed hydroxides function as destabilization ingredients that brings up neutralization of dye's charge in addition these colloidal particles are also be removed by electro flotation when they adsorbed the hydrogen gas liberated from cathode[12-14]. The most effective adsorbent is activated carbon in wastewater treatment, but it is expensive and it is very difficult to regenerate the carbon[13]. The reactions that take place during electrolysis when Cu used as electrodes is given as follows.

Anode: $Cu \rightarrow Cu^{2+} + 2e^{-}$ …(1)

Cathode: $2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2\,OH^{-}{}_{(aqua)}$ …(2)

Formation of Metal Hydroxide

$Cu^{2+} + 2OH^{-} \rightarrow Cu(OH)_{2(s)}$. …(3)

Electrocoagulation coupled with other methods will be more efficient than a single method to remove the suspended particles, and achieve more efficiency. The other methods include the electro-Fenton process, photo electro-Fenton process, peroxicoagulation, electrochemical advanced oxidation process, electro-oxidation, etc.[10,13,18]. The efficiency of the electrocoagulation process is based on some of the parameters like pH and temperature of the solution. As the pH and temperature increase, the efficiency goes on decreasing. The type of electrodes, electrode distance along with the number of pair of electrodes also plays an important role.

There are many literature surveys available on electrocoagulation. Al-Khafaji et al.[18] perform continuous electro-Fenton and photo electro-Fenton process using stable anode (DSA Ti-RuO_2/IrO_2 mesh) and activated carbon fiber felt cathode. They observed 73.33% COD removal with energy consumption of 0.901 kW h/kg and under a UVA lamp the removal efficiency increased to 81.1% and it even increases upto 86% under two UVA lamps. Sadik et al.[11] studies say that using aluminium electrodes at 750 mA removes 98.1% of reactive dye from a textile mill waste water at an electrolysis time of 120 min and power consumption is about 6 kW h/m^3. Gunduz et al.[14] investigated the efficiency of the electrocoagulation process using three different electrodes namely iron, aluminium, and zinc, and their investigation shows that 99% of removal efficiency of Reactive Red 195 dye using iron electrodes under 10 mA/cm^2 at the electrolysis time of 45 min. Al-Raad et al.[17] showed that the saline water can be treated using the electrocoagulation process and they achieved 91% removal of TDS and claimed that it is a reliable technique for removal of salts from aqueous environments. Kessentini et al.[19] discussed the importance of stirring effect and concludes that with increasing the stirring speed the removal efficiency enhances and they achieved 99% of removal of metallic copper ions at 80.90 rpm and a time of 74.28 min.

Eriochrome Black T dye (EBT) is a mono azo dye with a formula $C_{20}H_{12}N_3O_7SNa$ and molar mass of 461.381g/mol used as a complexometric indicator in complexometric titration which used in the determination of water hardness, in EDTA titration, paper, and textile industries. It is also used to detect the presence of rare earth metals. The dye is blue in its deprotonated form. It causes respiratory tract irritation when inhaled, eye irritation, skin irritation when absorbed through a skin and even it is harmful when swallowed. The structure of the dye is as shown in Fig. 1a. Removal EBT dye by electrocoagulation technique is discussed in our study. To the best of our knowledge, copper wire in form of solenoid was used

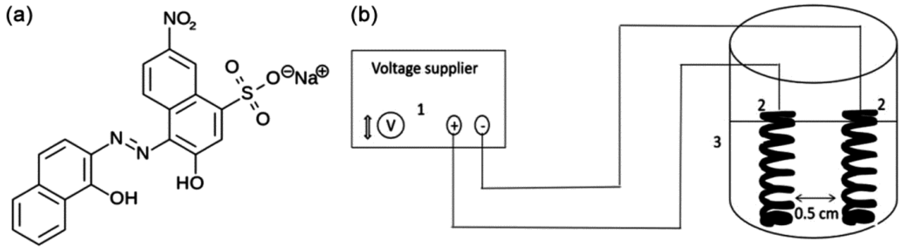

Fig. 1 — (a) Structure of Eriochrome Black T and (b) Batch reactors setup (1: DC power supply; 2: Electrode pairs; 3: Beaker)

as electrodes for the first time in the electrocoagulation for dye removal. Shaker et al.[23] conducted studies on removal of heavy metal ions using copper electrodes. Mustafa et al.[24] showed that maximum removal efficiency of xanthate was achieved using copper as compared to aluminium and iron. Kalivel et al.[25] compare the efficiency of both copper and aluminium electrodes for the removal of Red BFL dye and shows that the optimized pH value of Cu-Cu electrode is 9.0 whereas for Al-Al it is pH 7.5. In addition to above, aluminium hydroxide decomposes to aluminium oxide at 575°C whereas copper hydroxide decomposes to copper oxide at 80°C useful in sludge management.

Experimental Section

Materials

EBT dye powder (90% purity, from Shree Umiya Dye Chem Industries) has been purchased from the scientific store is used as a model dye. A 30 V DC regulated supplier TC-97 is used investigate all the parameters. Copper electrode of surface area 5.915 cm^2 and volume of 0.36 cm^3 was prepared in the form of a solenoid using copper wire. After the treatment, the dye solution was centrifuged at 4500 rpm for 10 min using a Centrifuge machine (Remi-24). The supernatant solution was taken in a test tube and measured optical density using UV-visible spectrophotometer (SL-150). The COD of the treated solution was determined with the help of a COD digester (SECOA) followed by titration. The temperature of the dye solution is maintained with the help of a water bath (manufacturer: Ozone Scientific) and the pH of the dye solution for study on effect of pH on removal efficiency was fixed using the pH meter (Etico L1 613). The obtained sludge is characterized by XRD model Philips X-ray diffractometer (PW/1050/70/76) with CuK$_\alpha$ radiation (λ = 1.54 Å) at room temperature.

Preparation of dye solution and procedure for its removal

25 mg of EBT is weighed and dissolved in a litre of distilled water in a plastic beaker and stirred on a magnetic stirrer for 30 min. For each study, 150 mL (25 ppm) of the prepared dye solution was utilized. The copper wire (length: 15 cm and diameter: 0.125 cm) wound on a glass rod (diameter: 0.5 cm) was taken as both anode and cathode, while the total volume of the wire is 0.36 cm^3. In this study, the electrolysis was carried out at a normal room temperature between 23-26°C. 150 mL of EBT solution was taken in 250 mL plastic beaker, electrodes were placed in the solution and then the electrolysis was carried out. The treated solution for a fixed voltage and a time at an electrode separation distance of 0.5 cm was centrifuged at a fixed 4500 rpm for a fixed time of 10 min using Remi-24 centrifuge machine. The filtrate was transferred to a dry test tube and the absorbance of that sample was recorded using UV-visible spectrophotometer and removal efficiency was calculated. Fig. 1b shows the elctrocoagulation experimental setting used in the present investigation.

Analytical measurements

The absorbance of that solution was measured and the % of removal efficiency was calculated as follows.

$$\text{Removal efficiency (\%)} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \qquad ...(4)$$

Where, C_0 is the initial concentration of the solution and C_e is the equilibrium concentration of the solution.

Faraday Law gives the precise amount of anode utilized or dissolved during the process and it is calculated by using the following formula

$$\phi = \left(\frac{M.I.T}{n.F} \right) \times 100 \qquad ...(5)$$

Where, **I** represent current density (mA/cm^2), **F** is the Faraday constant (96487 Cmol^{-1}), **n** is the number of electrons, **M** is the molecular weight of the metal used (g), **t** is the saturation time (s), and by knowing these things **ϕ** can be calculated [5].

It was estimated that 3.50 mg/cm^2 of the anode is dissolved during 180 s of contact time at 13 V. In total 20.74 mg was dissolved in 150 mL of dye solution.

The energy consumed by electrodes during electrolysis is given by

$$E = \mathrm{U} \times \mathrm{I} \times \mathrm{t} \qquad \ldots(6)$$

Where, **U** is the voltage applied (V), **I** be the current expressed in mA, and **t** is electrolysis time. In the present work, 227.5 mWh amount of energy is utilized during the process.

Amount of pollutant adsorbed is given by

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad \ldots(7)$$

Where, V represents volume dye solution in litre, C_e and C_0 stands for equilibrium and initial concentration of dye solution (mg/L), respectively, M stands for the quantity of anode dissolved (g). Here it is estimated to be 3.5 mg/g.

Specific energy consumption (SEC) can be calculated using.

$$\mathrm{SEC} = \frac{(\mathrm{U} \times \mathrm{I} \times \mathrm{t})}{V(C_0 - C_e)}. \qquad \ldots(8)$$

Where V is the volume of a dye solution in litres, C_0 and C_e are the initial and final concentration of 25 ppm dye in contaminated water, respectively (mg/L). It was found that 3.268 kWh/kg is consumed. The characteristics like current, amount of anode utilized, energy consumed, SEC and amount of dye adsorbed are summarized in Table 1.

Table 1 — Characteristics of the EC at optimum condition

Characteristic	Value
Current	0.350 A
Amount of anode utilized (ϕ)	3.507 mg/cm^2
Energy is consumed (E)	0.2275 Wh
Specific Energy Consumption (SEC)	3.268 kWh/Kg

Isotherm modelling

The adsorption behaviour and removal efficiency of dye using copper electrodes is illustrated by isotherm modelling. The suitability of adsorption isotherms is useful for predicting the pattern of adsorption on the adsorbent, which is useful for industrial applications and designing and this suitability and type of adsorption is based on the value of R^2. The model where the isotherm value is close to 1 is considered as the best model of adsorption. The Langmuir and Freundlich isotherms using equilibrium concentration were studied and evaluated in the present work.

Langmuir isotherm

Langmuir isotherm is based on the assumption that molecules of dye adsorbed uniformly on the adsorbent surface having active sites or simply surface adsorption phenomenon with monolayer adsorption[13]. The surface area of the adsorbent has active sites and dye molecules get adsorbed without transmitting into the adsorbent and uni-molecular adsorption takes place.

The expression of Langmuir isotherm is given below

$$q_e = \frac{K_L \cdot q_{max} \cdot C_e}{1 + K_L \cdot C_e} \qquad \ldots(9)$$

Where, C_e is the equilibrium concentration of dye solution, q_{max} represents the adsorption capacity of the adsorbent (mg/g), K_L represents the constant of binding affinity. Using all these, the graph C_e vs q_e is plotted and as shown in Fig. 2a.

The intensity of adsorption or separation factor in Langmuir isotherm is represented by

$$R_L = \frac{1}{1 + K_L \cdot C_0} \qquad \ldots(10)$$

C_0 represents original or initial dye concentration and $0<R_L<1$ is favourable of for adsorption, and

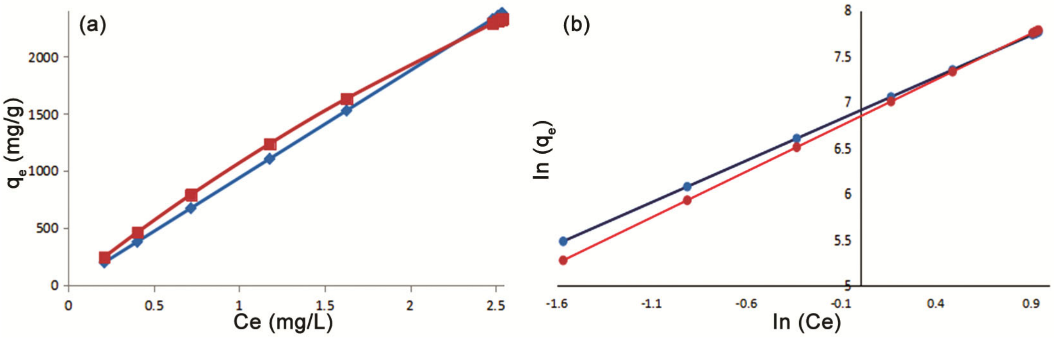

Fig. 2 — Plots for (a) Langmuir and (b) Freundlich isotherm

K_L value less than 1 is also favourable for adsorption. In our case, the value of Langmuir isotherm are $K_L = 0.12$, $R_L = 0.974$ and $R^2 = 0.996$.

Freundlich isotherm

The assumption of heterogeneous adsorption is given by Freundlich isotherm. It is given by

$$q_e = K_f \cdot C_e^{1/n} \quad \text{...(11)}$$

K_f represents the adsorption capacity, n represents the intensity of adsorption and also describes favourability of heterogeneous adsorption, 1/n is heterogeneity factor, and less than 1 indicates the favourable adsorption, and greater than 1 describes non-favourable adsorption on a heterogeneous surface. The graph $\log(q_e)$ versus $\log(C_e)$ illustrates the Freundlich isotherm as shown in Fig. 2b. The Freundlich isotherm value are$1/n = 0.909$ and $R^2 = 0.999$. From the above two isotherms the equilibrium data were fit better for Freundlich with $R^2 = 0.999$ compared to Langmuir isotherm of $R^2 = 0.996$. The value of R^2 greater than Langmuir isotherm and hence it can be claimed that adsorption follows Freundlich isotherm model. These values of models show that adsorption of EBT on metal hydroxide follows heterogeneous adsorption.

Kinetic study of electrocoagulation process

Pseudo - first order kinetic study

In the process of dye removal, the rate of removal of dye is proportional to concentration of the dye and amount of metal hydroxide. First order equation is given by

$$\frac{dQ_t}{dt} = -k_1(Q_e) \quad \text{...(12)}$$

where, Q_e (mg/g) is equilibrium dye concentration and Q_t (mg/g) is concentration at time 't'. On integration and further simplification, the above equation reduces to

$$\ln(Q_e - Q_t) = k_1 t \quad \text{...(13)}$$

where k_1 (min^{-1}) is rate constant can be estimated from slope of the plot of $\ln(Q_e\text{-}Q_t)$ vs t as shown in Fig. 3a. Singh et al.[5] claims that pseudo first order rate constant k_1 as 0.08 min^{-1} for indigo carmine dye and also 0.173 min^{-1} for Reactive Red 198 dye.

Pseudo - second order kinetic study

The second order kinetics at equilibrium adsorption is given by

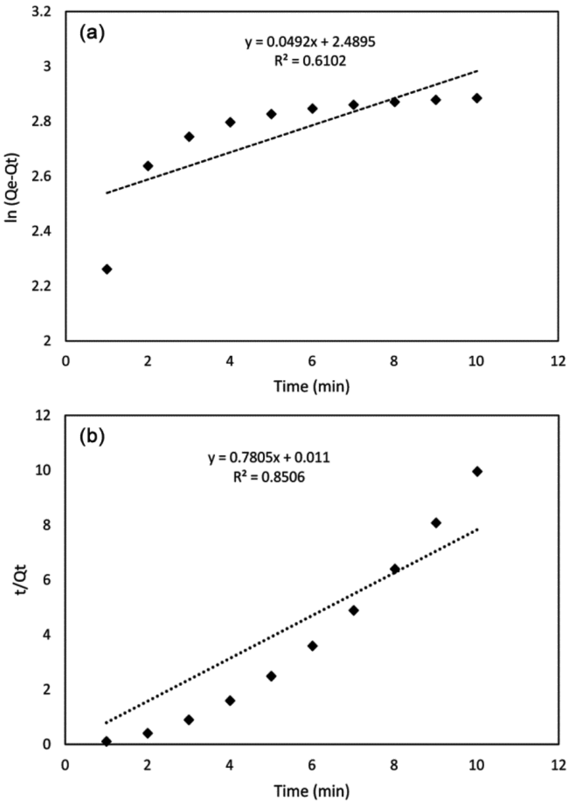

Fig. 3 — Plots for (a) pseudo first and (b) pseudo second order kinetics

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad \text{...(14)}$$

The values Q_e and k_2 which is a rate constant (g/mg/min) estimated from the slope of least square fit of t/qt vs t plot as shown in Fig. 3b. $R^2=0.9498$ suggest that dye removal process follows second order kinetics.

A study on removal of crystal violet using aluminium electrodes by Vidya et al.[1] claimed the process to be of first order with a good linearity experimental data. The value of k_1 ranges from 0.0398/min to 0.0379/min as concentration increases from 20 mg/L to 100 mg/L with $R^2>0.92$ while the value of k_2 from 0.00028 to 0.00001131 as the concentration increases. El-Hosiny et al.[10] reported that first order kinetics is showing a good linearity for the removal of different dye using electo-flotation process with $R^2>0.93$. Adeogum et al.[16] studied removal of Bromophenol blue dye from aqueous solution using Al-Fe electrodes and showed that first order kinetics fit well with the experimental data with a rate constant varies from 0.09/min to 0.12/min as the concentration varies from 10 mg/L to 50 mg/L while Q_e increases from 9.51 to 50.34 with $R^2=0.99$ while in second order, the rate constant k_2 (g/mg/min) varies from 3.76 x 10^{-3} to 1.41 x 10^{-3} as the concentration increases. Also, the value of Q_e (mg/g) increases from 18.86 to 81.44 with R^2=0.98. Studies on adsorption of Rhodamine B on to acid modified banana peels by Oyekanmi et al.[22] shows that adsorption follows second order kinetics with k_2 close to 1 indicating a chemisorptive bond. The values of both pseudo first and second order values are given in Table 2.

Results and Discussion

Effect of change in voltage

The voltage which is directly proportional to current plays a vital role in electrocoagulation and directly affects the process by altering or increasing the production of bubbles and coagulant dosage[14]. In the present study, electrodes were placed in 150 mL of 25 ppm dye solution and voltage varied from 5 V to 30 V DC using a DC regulated power supply while maintaining the constant electrolysis time of 300 s. The treated solution was filled into round bottom shaped centrifuge tubes and it was centrifuged at fixed rpm and time, after centrifuge, the supernatant solution was transferred to a dry test tube and the absorbance was measured. Fig. 4a shows that an increase in voltage increases the removal efficiency due to the huge production of metal hydroxide and flocculation by the process of oxidation of anodes[7,14].

Table 2 — Kinetic study parameters for adsorption of dye on metal hydroxide

Type of kinetics	Slope	Intercept	Q_e	Rate constant	R^2
Pseudo-first order	0.0492	2.4895	12.05525	0.00491	0.6102
Pseudo-second order	0.7805	0.011	1.28123	55.38002	0.9498

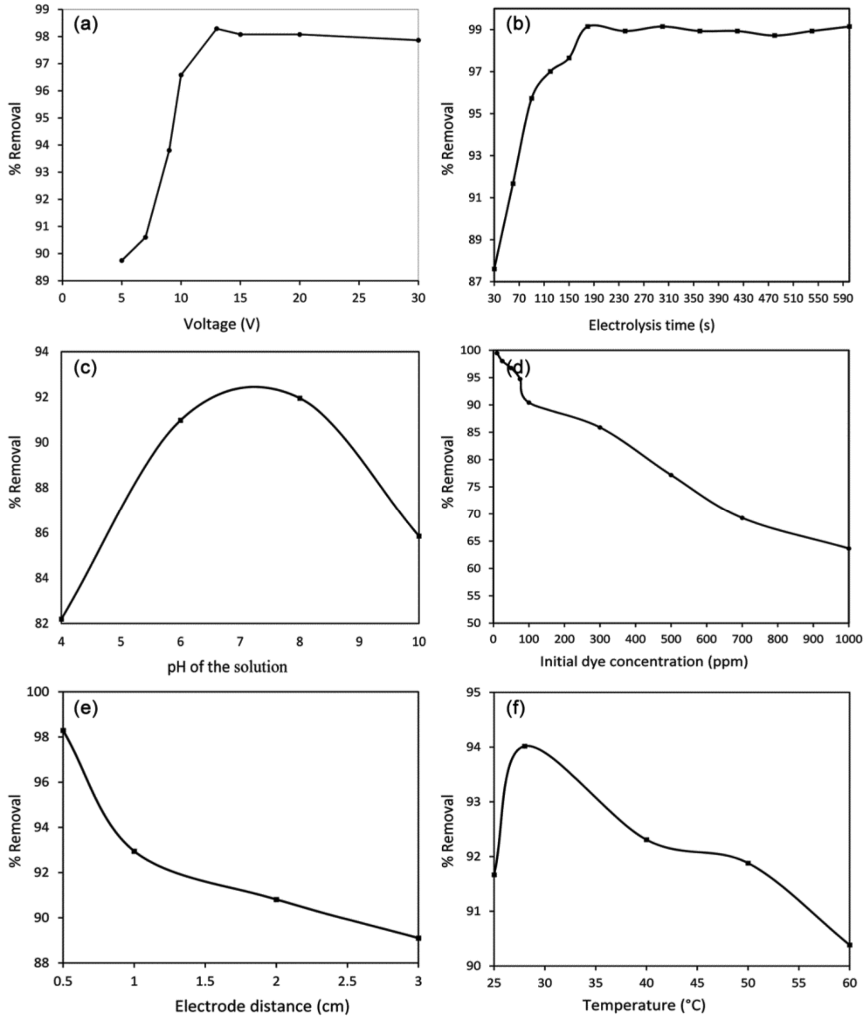

Fig. 4 — Effect of (a) voltage, (b) Electrolysis time, (c) pH, (d) initial dye concentration, (e) inter electrode distance and (f) temperature on dye removal efficiency

As the voltage across the electrodes increases, the current also increases, so that the concentration of the electrons increases near the cathode which breaks the water molecule as given in Eqn 2. The metallic cations, produced at the anode also increase and hence the total production of M-OH increase which have a higher surface area to adsorb the dye molecules. By increasing the current from 5 V to 13 V, the removal efficiency increases up to 98.5% due to the more production of metal ions and hydroxide radical density which directly increases the removal efficiency[15], but after 13 V, the removal efficiency is constant indicates that no further removal of dye takes place. This might be due to (a) some of the free pollutants which are away from the adsorbents may not adsorbed on the metal hydroxide and (b) the freely suspended or lightweight flocs which may not be coagulated may affect the absorbance.

The removal efficiency reached up to 98.29% at 13 V, but initially, at 5 V the removal efficiency is about 89.7%. The rapid decolourization is due to the production of a large amount of metal hydroxide in the solution with an increase in froth and flocculation as stated above. So, 13 V is taken as an optimum voltage and it has been fixed for all the other parameters. An increase in voltage amount results in increase in the anode consumption[15]. In the present study, the amount of anode consumed is calculated using Eqn 5 and it is found out that anode consumption increases from 3.34 mg/cm^2 to 13.194 mg/cm^2 and at 13V the consumption is 5.84 mg/cm^2. The total energy of 0.379 Wh of energy is consumed whereas SEC is 5.49 kWh/kg. In the literature survey, 99% of the Reactive Red 195 dye is removed from aqueous solution at initial pH 4, for 45 min at a current density of 40 mA/cm^2 using aluminium electrodes as stated by Gunduz et al.[14] and the highest removal efficiency of Reactive red is achieved at 120 min of reaction time at a 750 mA using aluminium electrodes is stated by Sadik[11]. Bazrafshan showed that 98% of the BR-18 dye is removed at 50 V at a contact time of 40 min.

Electrolysis time

Electrolysis time plays a very important role in the electrocoagulation process, so as electrolysis time increases, the concentration of metal ions by anode dissolution and metal hydroxides also increases and hence colour removal efficiency[5]. In the present study the electrolysis time is varied from 30 s to 600 s, the optimized voltage is kept constant and applied to dye solution for different electrolysis times. Fig. 4b shows that the removal efficiency increases from 87.06% to 99.14% with an increase in time from 30 – 180 s, the maximum amount of dye is removed at 180 s (up to 99.14%) and a further increase in time has no effect on removal efficiency. The time determines the rate of production of metal ions in the solution, so as the time increases the production of metal ions by the oxidation of anode increases[2]. Also, the formation OH increases near the cathode. The freshly produced adsorbent having a higher surface area is sufficient to adsorb the dye molecules. It is also observed that as time increases, the anode consumption increases from 0.58 mg/cm^2 for 30 s to 11.69 mg/cm^2 for 600 s, whereas, the energy consumption increases from 0.037 Wh to 0.758 Wh and SEC be 0.6 kWh/kg to 10.89 kWh/kg. At 180 s of time, 20.74 mg of the anode is consumed in 150 mL of dye solution, while the energy consumption be 227 mWh and SEC be 3.268 kWh/kg.

Gunduz et al.[14] have reported that the removal efficiency was reached to 95% at 5 min of operating time for all current values using iron electrodes and also mentioned that at 45 minutes of contact time 99% removal was achieved using aluminium electrodes, 97% using zinc electrodes and 100% using iron electrodes. Liu et al.[20] reported that the removal efficiency of methylene blue dye increased from 12.42 to 98.78% with the increase in electrolysis time from 3 to 30 min using Aluminium electrodes with a constant current density of 5 mA/cm^2. So, based the amount of anode dissolved, energy consumption and removal efficiency, 180 s of electrolysis time is economic and hence it is considered as an optimized value.

Effect of pH

The pH is one of the most influencing parameters in the process of electrochemical process and effect of pH is reported in. many literature. The pH of the solution determines the removal efficiency either by the formation of a wide range of hydroxides or destabilization of suspended particles[14]. EBT is sensitive at low pH so it loses its colour. In the present study, the pH is studied for 4, 6, 8, 10 pH under the obtained optimum condition, and the pH of the solution is set by adding H_2SO_4 and NaOH using Etico L1613 pH meter, the further procedure is carried out as stated in the previous case but the electrolysis time is reduced to 60 s because the removal efficiency is already reached maximum at

180 s and determining the effect of pH on removal efficiency at 180 s is insensitive. Fig. 4c shows that at lower pH the removal efficiency is less and reaches a maximum at nearest to neutral pH and as the pH increases above neutral pH the removal efficiency is decreasing. As mentioned earlier the production of copper hydroxide decides the removal efficiency[2]. At lower pH, the decreases in efficiency is due to the soluble of Cu^{2+} and the metal hydroxides, which does not precipitate at lower pH[15, 9] and at higher pH from 8 to 10 the removal efficiency decreases and this is due to the formation of $Cu(OH)_2$ which do not adsorb and coagulate any dye molecules[15].

The maximum removal efficiency is obtained at neutral pH or original pH of the solution because of the higher production of metal hydroxide and which capable of adsorbing dye molecules[16]. So, it is better to carry out the electrocoagulation at the original pH of the dye solution. It is noted that anode consumption about 3.57 mg/cm^2 and energy consumption of about 0.04478 Wh is the same for all studies but the SEC at pH = 4 be 0.88466 kWh/kg and then decreases to 0.7908 kWh/kg at 8 pH and then increases to 0.847 kWh/kg at 10 pH. So, as the removal efficiency increases, the SEC decreases. In literature, Liu et al.[20] mentioned that 99.37% of the methylene blue dye removal efficiency was achieved at pH 7 using aluminium electrodes and there was a sharp decline at both lower and higher pH (pH=3, pH=11). 98% of the removal of BR-18 from aqueous solution at pH 7 using aluminum electrodes at 50 V for 60 min was claimed by Bazrafshan et al.[15].

Effect of change in initial dye concentration

Effluent from industries is of varying dye concentrations, leads us to perform experiment on variable dye concentrations. As the initial dye concentration increases the removal efficiency decreases due to the limited number availability of adsorption sites[5]. In the present study, the initial concentration is varied from 10 ppm to 1000 ppm under previously optimized conditions. Fig. 4d shows that, as the dye concentration increases the removal efficiency decreases because of an increase in the number of dye molecules in the solution and the produced metal hydroxide/coagulant is low and hence decrease in active sites, the limited number of sites is not sufficient to adsorb all the dye molecules[2].

In the present study, the removal efficiency decreases from 99.5% to 63.6% as the concentration of dye solution increases from 10 mg/L to 1000 mg/L, respectively, under the optimized conditions. Vinothkumar et al.[21] proclaimed that using copper-Mild steel electrodes for an Nigrosin dye, the removal efficiency drops from 99% to 83% with an increase in dye concentration from 20 ppm to 60 ppm with a constant current density of 0.015 A/cm^2 at 10 min of electrolysis time, but for Eosin dye the removal efficiency increases from 20% to 42% with an increase in dye concentration from 0.1 ppm to 0.5 ppm under a constant current density of 0.04 A/cm^2 with a contact time of 20 min. Amour et al.[7] have varied the concentration from 50-300 mg/L in continuous flow and show that 97% red nylosan dye removal using aluminium electrodes. Bazrafshan et al.[15] showed that the removal efficiency decreases from 97.16% to 73.28% for an BR-18 dye as the concentration increased from 25-200 mg/L using six aluminium electrodes connected in series. In this case, while maintaining all other parameters constant, only initial dye concentration is varied so the amount of anode consumption is 3.507 mg/cm^2 and energy consumption is 0.377 Wh but SEC decreases from 12.65 kWh/kg to 0.99 kWh/kg.

Effect of inter electrode distance

The distance between the cathode and anode plays a crucial role in the electrocoagulation process, as the distance increases the removal efficiency decreases due increase in the resistance[16]. As the distance increases the energy consumption also increases to reach the same efficiency with an increase in time and this is due to improper transferring of ions. At lower distances, the amount of energy utilized is less compared to higher distances[4]. In the present study, the inter-electrode distance is fixed at 0.5 cm for all the parameters. To find out the effect of inter-electrode distance which affects the dye removal, the distance between electrodes is varied and set using a glass rod and rubber pipe. The rubber pipe is cut down to the required length (1 cm, 2 cm and 3 cm), the glass rod is inserted into the rubber pipe, electrodes were hanged to the glass rod and a small piece of rubber is used to fix the electrodes, later the study is conducted.

Fig. 4e depicts that removal efficiency decreases from 98.3% to 89% as the electrode distance increases from 0.5 cm to 3 cm, the decrease in removal efficiency is due to a decrease in current density as the resistance between electrode distance increases, the decreasing current leads to lower production of hydroxyl ions[16,12] and less interaction between the metal ions from the anode and hydroxyl ions produced near the cathode due to increase in distance and results in limited production of metal hydroxide as a result removal efficiency decreases[5,14,16]. When the current decreases, the anode consumption also decreases as per Eqn 5, so the formation of ions in the solution also drops and hence the removal efficiency.

In the present, study the amount of anode consumed during the process is 3.507 mg/cm^2 and energy consumption is almost 0.377 Wh, but SEC increases from 5.47 kWh/kg to 5.88 kWh/kg. Abbas et al.[17] reported that maximum efficiency reached at 1 cm of electrode distance, for the treatment of saline water under current density of 2.0 mA/cm^2 and contact time of 80 min at 25 °C. Ahangarnokolaei et al.[4] reported that 99% of Acid Red 14 removal is achieved at 0.5 cm of electrode distance with electrolysis time of 24 min with an anode consumption of 6.4 kWh/kg.

Effect of temperature

Temperature is one of the main parameters in the electrocoagulation process, it plays a vital role in the process of dye removal. Here, the temperature of the solution varied from 20 to 60°C. 150 mL of 25 ppm of dye solution was taken in a 250 mL glass beaker and kept on a water bath and the temperature of the bath was increased, 13 V DC was applied for 60 s to know the effect of temperature. The temperature of the solution was measured using a thermometer, when the temperature of the solution attained, the voltage is applied for a minute, the solution was allowed to cool and it was centrifuged at fixed rpm and time.

Fig. 4f clearly shows that as the temperature increases from 25°C to 60°C the removal efficiency increases due to the rapid movement of ions inside the solution and this aids the collision between the molecules and the sludge and thereby facilitating the removal[18], the increased temperature reduces the conductivity of the solution and reduces the energy consumption along with an increase in the pH value which leads to increase in the removal efficiency[11]. A further increase in temperature the removal efficiency decreases and this is because of the increase in solubility of precipitates or formation of unsuitable flocs[5]. At 28°C the removal efficiency is about 94% and at 60°C the removal efficiency is dropped to 90.4%. The decrease in efficiency is also may be due to the rapid and random motion of ions, which means the increase in temperature leads to an increase in kinetic energy of the ions, leads to higher speed and this will not favor the coagulation. It is observed that 28°C has higher efficiency and this may due to the movement of ions at that temperature favor the coagulation effectively, although the kinetic energy of the ions increases with an increase in temperature.

Many works of literature have raised that increase in temperature favours coagulation and they raised the temperature to 45°C but in this study, the temperature raised to 60°C. Even at 45°C, the removal efficiency is high as compared to 25°C but after that the efficiency decreases. Here, the anode consumption is about 1.169 mg/cm^2 whereas SEC drops from 1.13 kWh/kg to 1.10 kWh/kg as the temperature increases from 25°C to 28°C and the same SEC increases from 1.10 kWh/kg to 1.14 kWh/kg as temperature increases above 28°C. Abbas et al.[17] reported that the removal of TDS, Br, SO_4^{2-} and Cl^- has reached more than 90% with an increase in temperature from 25-40°C. Singh et al.[5] has reported that the removal efficiency increases up to 28°C and greater than 30°C the removal efficiency decreases .

Effect of number of pairs of electrodes

The number of pairs of the electrode plays an important role in the process of dye removal. As the number of electrodes increases, the production of metal ions may be more, and hence the removal efficiency increases. In the present study, the number of pairs of electrodes was increased from a single pair to 3 pairs. To study the effect of a number of pairs of electrodes, 13 V DC is applied for 60 s for different number of pair of electrodes. As the pair of electrodes increases, the removal efficiency also increases and this might be due to the (a) production of a large number of Hydroxyl ions and metal ions from the cathode and anode, respectively, (b) the production of ions and hydroxyl radical at different places will improve the removal efficiency due to increase in conductivity and low resistance. Here, as the number of pairs increased from 1 to 3, the removal efficiency increases from 92.95% to 98.3%. Also, the SEC decreases from 0.701 kWh/kg to 0.663 kWh/kg while anode consumption is about 1.169 mg/cm^2. In the literature survey, there are very few mentions about the effect of the number of pairs of electrodes.

COD determination

COD is determined by closed reflux method refers to SNI 6989.2: 2009. The blank titration was carried out by adding 5 mL of 0.1 N potassium dichromate solution taken in a tube along with 5 mL of

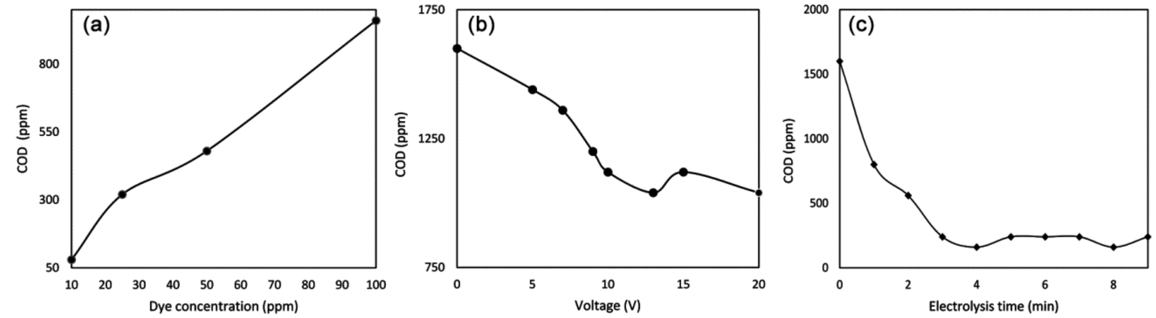

Fig. 5 — COD removal with (a) different dye concentration, (b) voltage and (c) electrolysis time

concentrated sulphuric acid and heated at 120 °C in COD digester for 120 min, and the obtained solution is taken in a conical flask, titrated with 0.1 N FAS using ferroin as indicator. Here, potassium dichromate solution is an oxidizing agent, which oxidizes the organic content in the in dye solution. For back titration, 5 mL of untreated dye solution is taken in a tube along with 5 mL of 0.1 N potassium dichromate and 5 mL of concentrated sulphuric acid, the mixture is digested in a COD digester for 120 min at 120°C. The solution is cooled and then it is titrated with 0.1 N FAS using ferroin as an indicator. The initial COD of the dye solution is found 1600 ppm. Similar procedure was followed for treated water (under 13V DC, 180 s of contact time for 25 ppm of dye solution). The COD value for treated dye solution is 320 ppm. Fig. 5a represents the COD removal at different dye concentration. As dye concentration increases COD is increasing because of the decreasing in removal efficiency so that more dye molecules are present in the treated solution and hence the higher will be the COD. The effect of voltage is also studied and results are shown in Fig. 5b in which the COD reduces with increase in applied voltage that might be due to the increased adsorption of the dye and it will attain constant after 13 V. Fig. 5c represents the COD removal with electrolysis time. As electrolysis time increases the COD removal decreases up-to 4 min and beyond that, the COD value attain constant and this might be due to increase in adsorption of these organic dye molecules on a freshly formed metal hydroxide.

Powder X-ray diffraction (PXRD)

To identify the chemical composition of the sludge, all samples were collected in a beaker and this sludge is separated from the contaminated water using a vacuum pump and filter paper. The obtained separated waste or coagulant is then dried in furnace at 40°C for an hour and the final powder is subjected to PXRD analysis. From Fig. 6, the characteristic peaks at 23.64°, 35.78°, 39.56° and very low intensity peaks at 37.98° and 33.96° are the peaks of copper hydroxide ($Cu(OH)_2$) with corresponding planes (021) (111) (130) (041) (002) [JCPDS no. 35-0505]. The peaks at 29.60° (110), 36.507° (111) and 42.4° (200) indicates the presence of Cu_2O [JCPDS no. 05-0667] because the copper hydroxide is metastable so that converts to copper oxide. The peak at 32.65° (110) is of CuO [JCPDS no. 48-1548]. The characteristic peak 43.3° can be matched to the (111) planes of the Cu [JCPDS no. 04-0836]. The peak at 24.23° (021) corresponds to CuO [JCPDS no. 801268] also peak at 31.41° corresponds to CuO [JCPDS no.41-0254].

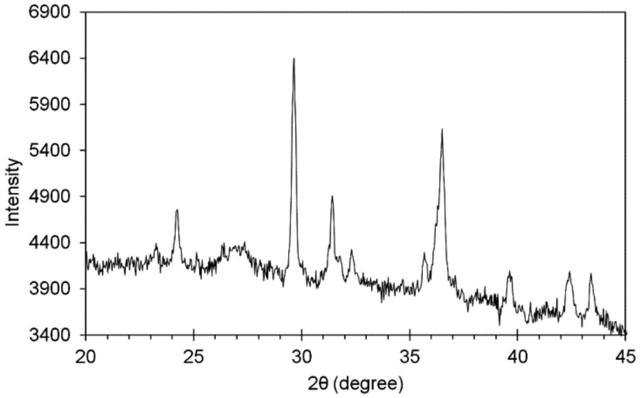

Fig. 6 — PXRD plot of the sludge

Conclusion

The result of this study reveals that electrocoagulation process is a best method for removal of Eriochrome Black T using copper electrodes of area 5.915 cm^2. The process depends on various parameters like voltage, current density, electrolysis time, initial dye concentration, solution pH, Temperature, distance between the electrodes. It has been observed that electrolysis time, voltage and current density plays an important role in the application electrocoagulation which determines the energy consumption. The removal efficiency reaches maximum value 99.14% at 13 V and 180 s with initial dye concentration of 25 ppm at pH 7.2. The adsorption follows Freundlich isotherm in this case with $R^2 = 0.999$ and pseudo second order kinetics which corresponds chemisorptive bond. The maximum removal efficiency is achieved around 28 °C above which removal efficiency decreases. On increasing the electrode distance, the removal efficiency decreases due to decrease in production of metal hydroxide along with decrease in energy consumption. As, the number of pair on electrodes increases, the removal efficiency increases and reaches a saturation more quickly. The COD analysis data indicates that COD of the treated solution decreases. At optimized values of all parameters, the anode dissolution is found to be 20.74 mg in 150 mL of the solution. XRD analysis of the obtained sludge shows peaks correspond to copper hydroxide, copper oxide and even the presence of copper of low intensity but various analytical method results show the absence of copper ions in the solution.

References

1 Vidya Vijay E V, Jerold M, Ramya M S, Lakshmanan S & Sivasubramanian, *Water Sci Technol*, 79 (2019) 597.
2 Bajpai M, Katoch S S, Kadier A, Singh Adarsh, *Environmental Science and Pollution Research*, 29 (2022) 15252
3 Arega Y & Chavan R B, *Adv Res Text Eng*, 3 (2018) 1024.
4 Ahangarnokolaei M A, Ganjidoust H & Ayati B, *J Water Reuse Desalin*, 8 (2018) 278.
5 Singh T S A & Ramesh S T, *Environ Eng Sci*, 30 (2013) 333.
6 Duan X, Wu P, Pi K, Zhqng H, Liu D & Gerson A R, *Int J Electrochem Sci*, 13 (2018) 557.
7 Amour A, Merzouk B, Leclerc J-P & Lapicque F, *Desalination and Water Treatment*, 57 (2015) 1.
8 Getaye M, Hagos S, Alemu Y, Tamene Z & Yadav O P, *J Anal Pharm Res*, 6 (2017) 119.
9 Zazou H, Afanga H, Akhouairi S, Ouchtak H, Addi A A, Akbour R A, Ali A, Douch J, Elmchaouri A, Duplay J, Jada A & Hamdani M, *J Water Pro Eng*, 28 (2019) 214.
10 El-Hosiny F I, Abdel-Khalek M A, Selim K A & Osama I, *Physicochemical Problems of Mineral Processing*, 54 (2018) 321.
11 Sadik M A, *Adv Chem Eng and Sci*, 9 (2019) 182.
12 Ghalwa N M A, Saqer A M & Farhat N B, *J Chem Eng Process Tech*, 7 (2016) 12.
13 Castaneda-Diaz J, Pavon-Silva T, Gutierrez-Segura E & Colin-Cruz A, *Hindawi J Chem*, 2017 (2017) 1.
14 Gunduz Z & Atabey M, *Int J Electrochem Sci*, 14 (2019) 5868.
15 Bazrafshsan E, Mahvi A M & Zazouli M A, *Iran J Health Sci*, 2 (2014) 16.
16 Adeogun A I & Balakrishnan R B, *J Phys Theor Chem IAU Iran*, 15 (2018) 87.
17 Al-Raad A A, Hanafiah M M, Naje A S, Ajeel M A, Basheer A O, Aljayashi T A & Toriman M E, *Processes MDPI*, 7 (2019) 242.
18 Al-Khafaji, R Q & Mohammaed A H A-K, *IOP Conf Ser: Mater Sci Eng*, 518 (2019) 062007.
19 Kessentini I, Mousser H, Zouari S & Bargui M, *Surf Eng Appl Electrochem*, 55 (2019) 210.
20 Liu N, Wu Y, *Ionics*, 25 (2019) 3953.
21 Vinothkumar K, Sugumaran T & Venkateshwari S, *J Appl Nat Sci*, 11 (2019) 97.
22 Oyekanmi A A, Ahmad A, Hossain A & Rafatullah M, *Kinetics and Isotherm Studies*, (Plos One, California, US) 2019.
23 Shaker O A, Matta M E & Safwat S M, *Desalination and Water Treatment*, 213 (2021) 371.
24 Çırak M, *Chemical Papers*, 76 (2022) 3661.
25 Kalivel P, Jisson J C, Kavitha S, Padmanabhan D, Bhagavathsingh J, Palanichamy J, Stephen A M M & David J J, *Int J Environ Anal Chem*, (2021) DOI: 10.1080/03067319.2021.1940988.