

Comparative study on the electrocatalytic activity of dissimilar electrode combinations for the treatment of textile effluent by electrocoagulation process and their subsequent reuse

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ABSTRACT

The synthetic dyes which are largely used in the textile industries pollute the total ecosystem. They can be treated using different technologies but in order to avoid secondary pollution and to carry out an eco-friendly technique, an electrocoagulation process has been adopted. In this work, two sets of electrodes which act as the electrocatalysts for the process of electrocoagulation, with one set containing aluminium as an anode and the other with copper as anode has been used to contrast and compare the removal efficacies. The colour removal efficiency was observed as 98.42% for Al-Cu, and 95.12% for Cu-Al electrodes. The COD and BOD removal efficiency was found to be 89.74%, 86.1% for Al-Cu and 87.15%, 85.23% for Cu-Al electrodes. The cost for the treatment process was 3.31 US\$/m³ and 0.22 US\$/m³ for Al-Cu and Cu-Al electrodes respectively. The sludge was subjected to EDX, SEM, and XPS analysis which showed the formation of hydroxides and dissolution of an anode implying copper as the best anode material. The energy and electrode consumption, operating cost was minimum for copper than aluminium. Due to high COD and BOD removal, the treated water can be reused for agriculture and for fish growth.

Keywords: BOD, Catalytic activity, COD reduction, Dissimilar electrodes, Textile effluent.

1. Introduction

Textile industries are increasing in many places, mainly in the southern part of Tamil Nadu, India and an immense need for the purification and treatment of the wastewater that has been sent out from these manufactory units has also expanded. Though many of industries use water as the main source of their production, the textile industry in particular avails enormous measures of fresh water in the fabricating processes [1]. The utilization of water in the processing unit of the textile industry sums up to three-fold usage compared with other units. It has been reported that an approximate of about 100-150 litters of water is needed to generate 1kg of cotton garments [2]. An average of 50-100 litres of water is used to process 1kg of textile

product [3]. Around 1.3 million tonnes of dyes and pigments are thought to be sold globally each year, with a value of US\$ 16 billion. European nations including Italy, France, Spain, and Germany as well as Asian nations like India, Japan, China, Korea, and Pakistan are also the top nations that produces dyes. Although Europe contributed 40% of the global yield of dyestuff, as days went by, the textile industries gradually amended towards Asia due to reducing production costs in this area [4]. The importance of the treatment of dye polluted water is due to the presence of organic materials. These organic substances are one of the major pollutants in the effluent as the dyes used for the textile dyeing process is mostly organic in nature causing hazardous impacts to the human ecosystem. These organic synthetic dyes have to be degraded before

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releasing the contaminated water into the environment so that its negative impact on the ecosystem gets reduced [5-7].

Therefore, these effluents that are expelled out from the textile units also probably comprise of phthalates, organochlorines, and Polybrominated Diphenyl Ether (PBDE) which are the sources in producing various hazardous issues to life in the atmosphere [8]. The effluent from the distinctive dyeing units will possess an uncertain pH, intense colour, and enormous quantity of dissolved and suspended particles, high Chemical Oxygen Demand (COD), and heat [9]. Apart from the above-mentioned characteristics, the wastewater may also contain detergents, levelling agents, chlorinated compounds, dispersing agents, and formaldehyde [10]. If metal-based dyes are used, the wastewater may contain some heavy metals such as zinc, copper, aluminium, and chromium [11-12].

A vast group of colourants in terms of both quantity and production volume, the azo dyes account for 70% of all organic dyes manufactured globally and hence it is used for dyeing fabrics in various dyeing units [13]. According to numerous reports, it is clear that the toxicity of the dyes present in textile wastewater can cause sarcoma and allergies [14-15]. Azo dyes were discovered to be poisonous to a variety of aquatic life such as algae, plants, and fishes. Though the acute toxicity of the dyes is very low; the wastewaters are being sent out continuously from the manufacturing units which eventually gives chronic toxicity to the whole environment [16].

These azo dyes present in the wastewater interfere with a number of biological processes, many of which are crucial to the environment. For instance, by limiting light penetration, they can prevent algae photosynthesis. Likewise, dyes have been found to prevent microbial colonies from reducing their COD and breathing. This could prevent several microbiological processes affecting life in aquatic systems [17]. Azo dyes can also negatively impact a plant's ability to grow by preventing the germination of seeds, seedling survival, shoot and root elongation, etc. [18]. It has also been discovered that benzidine present in the dyes, block DNA synthesis in the nucleus and disrupts calcium homeostasis, completely destroying the cells in the maize root tip [19].

In the surroundings of Tirupur and Erode districts in Tamil Nadu, many small-scale as well as large-scale textile manufacturing units are located. The river Noyyal which runs through these districts is also being affected by these discharged effluents. As these textile dyes do not adhere to the fabric tightly, they are mixed

in the wastewater which is released into aquatic habitats like lakes, streams, rivers, and ponds. These dyes have hazardous effects on living organisms and pose major ecotoxicological risks [20]. Due to the complex structure of the dyes in the effluent, increased COD, and Biological Oxygen Demand (BOD), mutagenesis takes place in various organisms. This is the cause of cancer in mammals and particularly human beings. The xanthene class of dye called Erythrosine is highly toxic and causes DNA damage. Disperse Orange 1, Malachite Green, and Disperse Blue 291 affect the mutagenicity thereby hiking the micronuclei in human hepatoma [21-24].

Therefore, to avoid the hazards caused by the textile effluents that is being radiated out from the industries, where fixation of the dyes to the garments is never achieved thoroughly, many treatment procedures can be adopted. It is approximately known that 2-50% of the colourants used during the process of dyeing are obscured in the effluent [25]. Some of the electrochemical treatment processes like electrocoagulation, electro-oxidation, and electroflotation have been found to be much effective [26-27]. These methods are green alternatives with small negative environmental footprints, little sludge production, and no chemical additions [28-29]. When a current is delivered during the electrocoagulation process, the sacrificial anodes get dissolved, creating an active coagulant which is responsible to withdraw the pollutants from the wastewater [30]. Therefore, in comparison to conventional coagulation and flocculation techniques, the electrocoagulation process has a number of benefits which include increased efficacy, a shorter retention period, avoidance of secondary contamination brought on by the addition of chemicals, and ease of use [31-32]. The selection of electrode materials and its geometry have an impact on the removal efficacies [33-35]. Various metals were used as electrode materials for the electrocoagulation process in the literature. The combinations such as Al-Al, Fe-Fe, SS-SS [36], Fe-Al, Al-Fe [37], Fe-steel wool, Fe-SS [38], Fe-carbon [39], Al-graphite, Fe-graphite [40], MS-MS [41], MS-SS [42], graphite-graphite [43], carbon steel-carbon steel [44], Cu-Cu [45], Cu-SS, SS-Cu [46] and Ti-Ti [47]. Initially, aluminium and iron were widely used as electrode materials for the process of electrocoagulation. Even though aluminium undergoes high dissolution than iron, it was capable of high COD removal than iron electrodes. Iron also undergoes high corrosion thereby making it highly consumable [48]. Whereas stainless electrodes prevented corrosion than iron. But the SS electrodes

implied high removal of heavy metals than the colour when compared in the literature [49].

In general, the oxidation and reduction processes in any system is brought about by harmful oxidizing or reducing agents. When chemicals are used, it produces wastes that cause toxicity to the environment. In order to overcome the secondary pollution by the use of chemical catalysts, the electrochemical system which provides the catalytic activity for the process of dye degradation has been adopted [50-53]. The catalytic activity of platinum (Pt) is higher due to its homogeneity and surface area. In many studies, Pt and its alloys have been used as catalysts. The main disadvantage of Pt catalysts is that the surface of the electrode undergoes poisoning effect and high cost [54-55]. So, as aluminium could remove colour and COD at a high rate as reported in literature, and copper as it treats the effluent and makes it fit for consumption for humans without creating secondary pollution [46], the combination of Al-Cu and Cu-Al electrode treatment was explored with the motive to reduce the cost thereby making it an effective process. Also, aluminium undergoes pitting type of corrosion whereas copper undergoes only uniform corrosion that to in a negligible manner [56].

In this present research work, an electrocoagulation process is applied to treat the textile wastewater received from a textile hub near Erode. The wastewater was treated using the two sets of electrodes to contrast the efficacy and operational costs. The main focus of this work is to attain maximum efficacy in colour, COD and BOD removal by using dissimilar metal electrodes and to study about the catalytic activity of the metal electrodes used. The second focus is to reduce the

overall operational cost and to reuse the treated effluent for agricultural purposes and for the growth of fish.

2. Experimental

2.1. Characteristics of real-time textile effluent

The characteristics of the textile effluent are shown in **Table 1**.

2.2. Electrocoagulation set-up

The electrocoagulation process was done in batch scale and the setup is shown in **Fig. 1**. The reactor consists of a 200 ml glass beaker placed on the magnetic stirrer. Two electrodes were dipped in the solution which was connected to an external Direct Current (DC) power supply. In order to expedite the migration of ions and floc formation, an electrolyte (NaCl) was added to the effluent before the electrocoagulation process. Two sets of experiments were carried out wherein Al was used as an anode and Cu as cathode in one set and vice versa for another set to compare the efficacy of the process. The copper and aluminium plate used for the electrocoagulation process measures to about 9 cm × 3.5 cm × 0.5 mm. The submerged surface area of the electrode was 17.85 cm². The two electrodes were placed at a gap of 4 cm. The stirring speed was maintained at 500 rpm so that rapid floc formation takes place. The operational parameters like pH (4, 5, 6, 7, 8, 9, 10, 11, 12), electrolysis time (5, 10, 15, 20, 25, 30, 35, and 40 min) and concentration of electrolyte (0.5, 1, 1.5, 2, 2.5 g/L) was optimized. The pH of the effluent was altered by adding concentrated hydrochloric acid (HCl) to make the solution acidic and concentrated sodium

Table 1. Characteristics of the textile effluent

Parameter	Unit	Value
Colour		Orange
pH		13.58
Total Dissolved Solids (TDS)	mg/L	11928
Total Suspended Solids (TSS)	mg/L	545
Electrical conductivity (EC)	mS/cm	2.67
Chemical Oxygen Demand (COD)	mg/L	1989
Biological Oxygen Demand (BOD)	mg/L	486
Turbidity	NTU	19.45
Total alkalinity	mg/L	2505
Total hardness	mg/L	1567.32
Chloride (as Cl)	mg/L	1114.9
Nitrate (as NO ₃)	mg/L	2.41
Sulphate	mg/L	11.58
Phenolic compounds	mg/L	23.1
Total Organic Carbon (TOC)	mg/L	24.89
Wavelength	nm	480.6

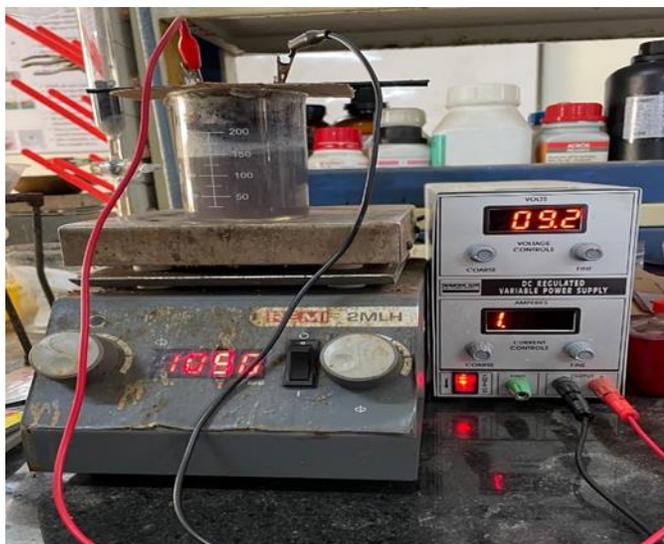


Fig. 1. Electrocoagulation set up

hydroxide (NaOH) to make the solution alkaline. The altering of pH was done by adding HCl or NaOH in dropwise to attain the desired pH. The samples after the electrocoagulation process were taken and filtered to collect the sludge for further analysis. The eluted liquid is then analysed for other parameters and other toxicity assessments.

2.3. Analysis

The effluent sample and the treated samples were subjected to COD, BOD, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Total Organic Carbon (TOC), and turbidity measurements and it was done according to the standard methods [57]. The colour removal efficiency after the electrocoagulation process was calculated using the formula,

$$CRE \% = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are the absorbances before and after the treatment process. The Colour Removal Efficiency (CRE%) was calculated after the electrocoagulation process. The turbidity, TOC, COD, and BOD elimination is determined using the formula,

$$Removal\ efficiency\ (\%) = \frac{X_0 - X_1}{X_0} \times 100 \quad (2)$$

Where X is the variable parameter (COD, BOD, TOC, and turbidity), X_0 is the initial value of each variable and X_1 is the final value of each variable after the electrocoagulation process [58].

The absorbance was found to calculate the colour removal efficiency and the Ultra Violet (UV) spectrum was recorded by JASCO V-770. To examine the presence of a number of components before and after the treatment, High-Performance Liquid Chromatography (HPLC) was recorded using Waters 1525 Binary HPLC pump 00G-4608-EO Kinetex 5UC8 100A. The solvent used for dissolving the filtrate is methanol and the UV detector was tuned at 290 nm. The sludge was characterized through Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Diffraction (EDX) to study its morphology and composition of metals present through F E I Quanta FEG 200. The X-Ray Photoelectron Spectroscopy (XPS) studies was done to confirm the hydroxide formation and the valence state of the metal. The spectrum was recorded by using Al monochromatic light as a source and an energy of 1486.6 eV in the Scienta Omicron Nanotechnology by Oxford Instrument.

3. Results and Discussion

3.1. UV-Visible spectrum

The removal efficiency was determined through the absorption spectra and it is represented in **Fig. 2**. The UV graph was plotted for different electrolysis time, to study the degradation efficiency. The maximum absorbance (λ_{max}) was observed at 480.6 nm. In both **Fig. 2** (a) and (b) which is representing the spectrum of treated effluent after treatment using Al-Cu and Cu-Al electrodes respectively, it is conspicuous that the absorption peaks in both the cases have declined at the end of 30 min of electrocoagulation. The concentration of the solution has also come to normal and it is clear from the UV plot at 30 min. Additionally, in the visible and UV region, there were no new absorption peaks indicating an efficient removal.

3.1. Metal electrode as electrocatalyst for the EC process

Electrocoagulation is a method of electrochemically treating wastewater using an electrochemical cell in which direct current is supplied to the sacrificial electrodes. Typically, electrochemical reactions taking place on anode and cathode cause the coagulation process. But the solution reaction plays a significant part in this technique causing hydroxide formation [59].

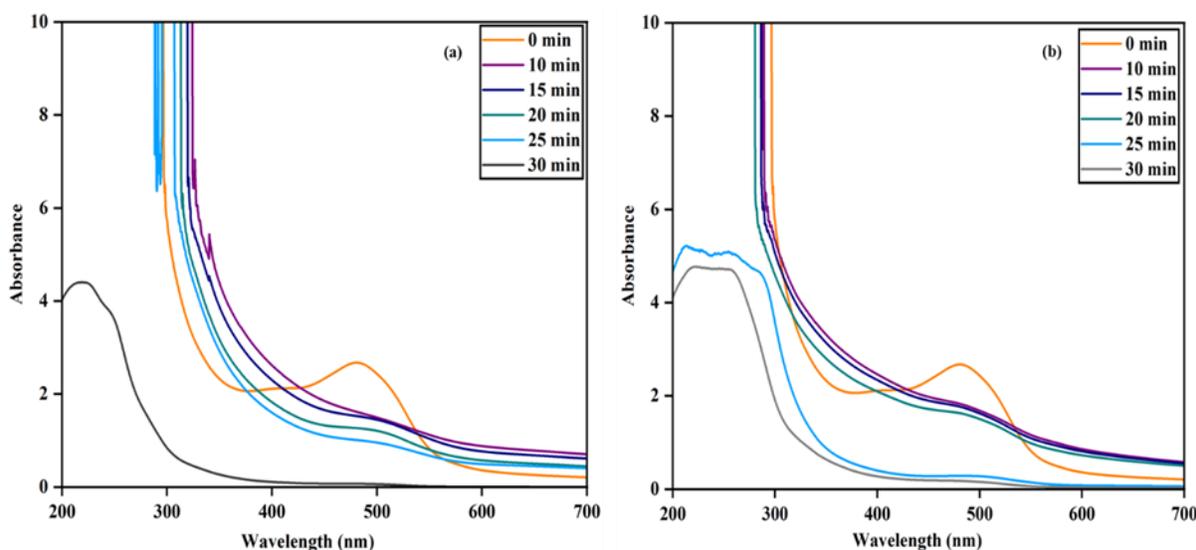
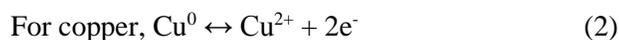
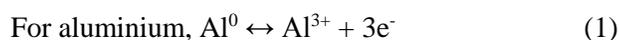
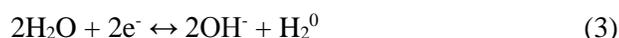


Fig. 2. Absorption spectrum at varied electrolysis time with (a) Al-Cu and (b) Cu-Al electrodes

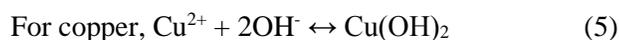
The anodic reaction can be given as:



The cathodic process can be given as:



The overall solution reaction can be represented as:



From reactions (1) and (2), it can be identified that, metal cations are produced due to anodic oxidation. Reaction (3) indicates the cathodic reduction, in which the water molecules are electrolyzed which gives off hydrogen bubbles and hydroxide ions. The solution reaction (4) and (5) implies the formation of hydroxide complexes which eventually absorbs the contaminants and aggregates as coagulants [60-61]. As a result, the electrochemical reactor primarily functions as an electrochemical dosing reactor where the metal ions produced from the metal electrode is controlled acting as a metal catalyst facilitating colloidal aggregation leading to an increased size and floc production. When it comes to the generation of bubbles by cathode, a low applied current results in fewer bubbles, which helps the flocs to settle out more quickly. The formation of bubbles rises as the applied current is increased. Thus, flotation becomes the main removal route due to the elevated aggregation and bubble generation. Therefore, the metal electrodes used in this technique play a major

role in the pollutant removal proving that the process is significantly catalysed by these electrodes [62-64]. When the metal electrodes act as an electrocatalyst for the electrocoagulation process, the applied current controls the anodic and cathodic reactions taking place in this reactor thus altering the chemical rate. The measure of metallic electrodes dissolved and the corresponding applied current can be related to Faraday law [65]. Also, most of the contaminants present in the effluent are in the form of colloids. These colloidal particles possess a negative charge around them. When the current is applied to the reactor, the metal cations produced from the metal electrodes combine with the negatively charged colloids and neutralize it. Hence, the repulsion of colloids is ceased and the formation of flocs outset thereby leading to sedimentation and separation from the wastewater [59]. From the above evidence of the electrocoagulation mechanism, it can be clearly stated that the metal electrodes act as electrocatalysts for the efficient removal of the contaminants. The electrochemical production of $\text{Al}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$ absorbs the dye contaminants due to the constant stirring and flocculation occurs rapidly till the optimum time after which there is no production of electrocoagulants thereby causing no secondary pollution. When these hydroxides are directly added to the effluent, the optimum amount to be added for the precipitation of dye particles is trivial and could generate large amount of sludge which will be another concern.

3.2. Impact of operational parameters on CRE%

3.3.1. Impact on CRE% due to the effect of pH

The effectiveness of electrocoagulation technique is significantly influenced by pH as an operating parameter [66-70]. For examining this, the initial pH of the wastewater was varied from 4 to 12. The **Fig. 3** (a) shows the CRE% plotted against various pH range for both sets of electrodes. Initially at pH 4, the CRE% exhibited by the textile effluent after the treatment process with Al-Cu, and Cu-Al electrodes was 97.98 and 87.86 respectively and the other parameters were kept constant (10 V, 30 min, IED-4 cm). While increasing the pH from 5 to 9, a gradual fall in CRE% was noted and when the pH was further increased there was a significant fall in the removal efficacy while Al was used as anode. As the hike in pH, edges to the Al(OH)_4^- production, the adsorption of the pollutants from the effluent is impossible as the formed Al(OH)_4^- is soluble [70-71]. While using Cu as anode, an inflation in CRE% from pH 4 to 7 was witnessed, and weakened from pH 8 to 12. According to the observations made while using Cu as anode, when the pH increased to 9, 10, 11, and 12, the sludge was not detached from the solution which eventually implied the minimal removal of dye particles from the effluent. Therefore, these two sets of electrodes manifested poor attainment of pollutant removal at a higher pH range. The maximal colour removal occurred at pH 4 while using Al-Cu electrodes because the aluminium hydroxide dominates for the pH range 4 to 9.5 [72]. When Cu-Al electrodes was used, high CRE% was seen at pH 7, due to the fact that when copper dissolves, it produces divalent Cu^{2+} ions, which then forms copper hydroxide, thermodynamically it is formed at 7.7 [73]. Therefore, an optimum pH range was taken as 4 and 7 for Al-Cu and Cu-Al electrodes respectively.

3.3.2. Impact on CRE% due to the effect of time

The electrolysis time is a vital parameter which influences the CRE%. The electrolysis time was varied from 5 to 40 min, in order to optimize the minimal time required for high pollutant removal. During this experiment, the voltage was kept constant as 10V, with pH of 4 for Al-Cu and pH 7 for Cu-Al electrodes and without adding electrolyte with IED of 4 cm. The increment in removal efficacy was noticed with increase in time indicating it as directly proportional. Greater the concentration of metal ions and hydroxyl ions produced from anode and cathode due to oxidation and reduction respectively, higher is the removal efficacy [74]. The CRE% was 23.56 and 39.49 at 5 min for Al-Cu and Cu-Al electrodes. It then gradually upturned to 97.98% and

95.12% at the end of 30 min reaction time as shown in **Fig. 3** (b). This is because, the discharged ions from the electrodes combine together to form more of metal hydroxide flocs which eventually adsorbs the dye particles present in the textile wastewater only when the electrolysis time is protracted [75]. Further increase in time to 25 and 40 min, a meagre elevation in CRE% of 98.34 and 89.95 for Al-Cu and Cu-Al respectively at the end of 40 min. Yet because of the high energy and electrode consumption which causes huge operating costs, going beyond the ideal electrolysis period which only modestly boosted the removal efficiency was not taken [76]. This may also be associated with charge loading and can alter the electrocoagulation process on the eviction of colour [77]. It could also knock off cathodic reduction and may liberate incipient electro coagulant flocs [78]. Therefore, the optimum time was taken as 30 min for both the set of electrodes.

3.3.3. Impact on CRE% due to the effect of electrolyte concentration

Generally, the conductivity of the solution that is subjected to the electrocoagulation process depends on the type of the electrolyte added and its concentration. Therefore, NaCl was added to the two sets of experiments and the treatment process was carried out under optimized conditions of pH 4, 10 V, 30 min, IED-4 cm and pH 7, 10 V, 30 min, IED-4 cm for Al-Cu and Cu-Al electrodes respectively. The concentration of the electrolyte was varied from 0.5 to 2.5 g/L. When 0.1 g of NaCl was added to 200 ml of the textile effluent, the CRE% was 98.42 and 95.12. Further increasing the concentration of the electrolyte to 0.2, 0.3, 0.4, and 0.5 g, the CRE% steadily declined as in **Fig. 3** (c). This weakening of CRE% is due to the decrease in voltage and energy consumption leading to less liberation of flocs which is responsible for the dye removal. When high concentration of the electrolyte is added to the solution, enormous consumption of the electrode and its surface could be destroyed thus resulting in greater operating cost [79]. As the electrical conductivity of the effluent is sufficient for the pollutant removal, and only a negligible change in CRE% is seen by the addition of NaCl while Al was used as anode whereas a significant change in removal was observed while Cu was used as anode. Therefore, without catalyst was taken as the optimized condition for high colour removal efficiency for Al-Cu electrodes and 0.5 g/L of NaCl as the optimized value for Cu-Al electrodes.

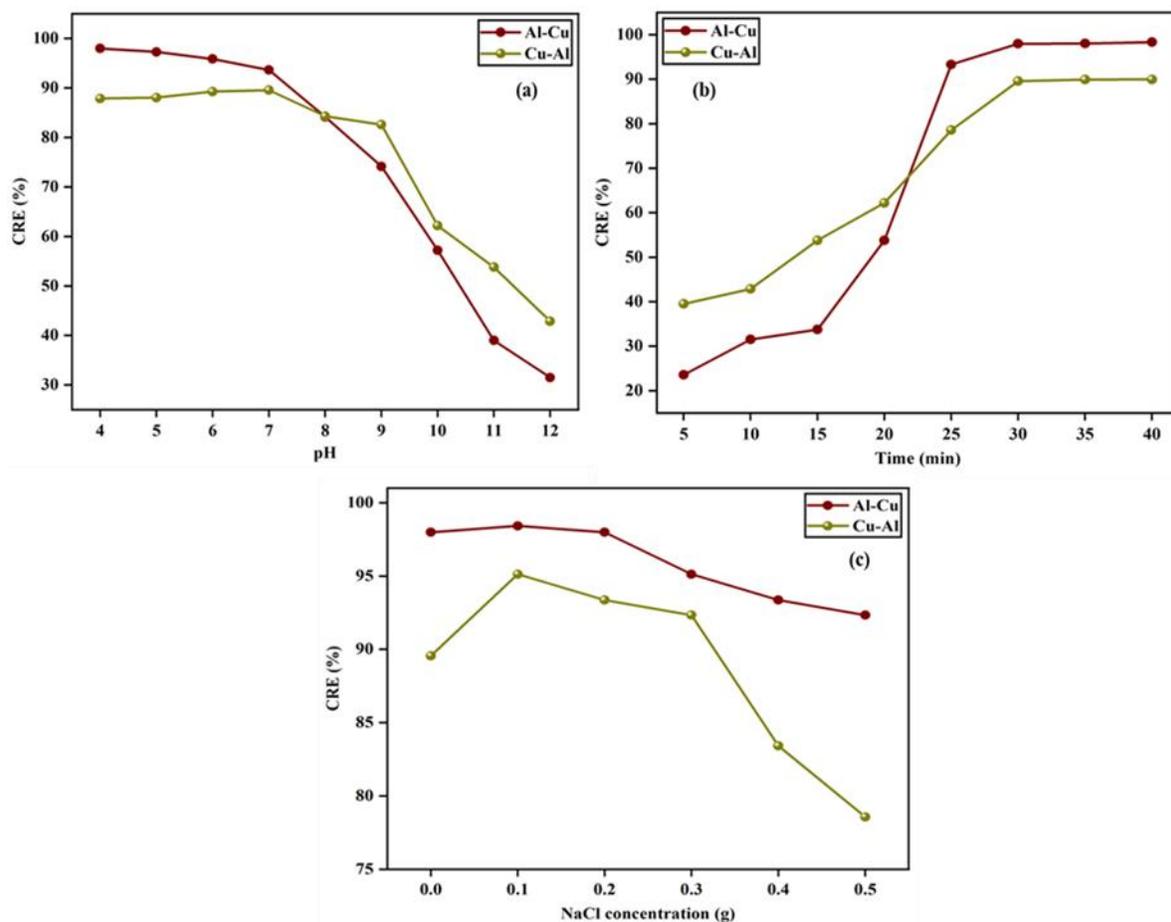


Fig. 3. CRE% vs (a) pH (b) Time (c) NaCl concentration

3.3. Economical parameters for the EC process

3.4.1. Consumption of energy

Consumption of energy is a compelling aspect in all the electrochemical techniques and it is directly connected with the total operating cost of the process [80-81]. The energy consumption increases with hike in electrical current supplied during the treatment process [66]. The consumption of energy was calculated for the treatment of 200 ml of wastewater per cubic meter using the following equation, where V is the applied voltage (V), I is the current (A), t is the time (hours) [82].

$$C_{en} = \frac{VIt}{m^3 \text{ wastewater} \times 1000} \quad (3)$$

The calculated value for Al-Cu and Cu-Al electrodes at the optimized conditions was found to be 45 and 2.925 kWh/m³ respectively. These values fall within the range cited in the literature ranging from 0.002 and 58 kWh/m³ [83]. According to the literature, at 0.021 A/cm², the energy consumption was 0.86 and 0.8 kWh/m³ when similar electrodes of copper and aluminium was used as anode and cathode [84]. Fig. 4 (a) shows the effect of initial pH on energy consumption. While employing Al

as anode, the energy consumed during the electrocoagulation process was continual from pH 4 to 8. When the pH is inflates to 9, 10, 11, and 12, the energy consumed also elevates indicating the optimized pH for high colour removal with less energy consumption as pH 4. On the other hand, when Cu acts as anode, the utilization of energy at pH 4 was 8.575 kWh/m³ which then depletes to 2.925 kWh/m³ at pH 7 which is the minimal among pH range taken for studies. The energy utilization then surges at pH >8. Thus, pH 7 can be taken as the optimized pH for copper electrode acting as an anode. In the present work, at 0.047 A/cm², and with dissimilar sets of electrodes, 45 and 2.925 kWh/m³ of energy consumption was obtained. This indicates that the energy was consumed less while Cu-Al was used than Al-Cu electrodes. It can also be concluded that use of dissimilar electrodes in the process of electrocoagulation gives minimal consumption of energy.

3.4.2. Consumption of electrode

During the process of electrocoagulation, the anode undergoes oxidation to produce metal ions which gets dissolved in the solution that is kept for the treatment.

The relationship between current density and the volume of anode material dissolved in the solution can be outlined by Faraday's law [85]. Therefore, the amount of electrode material consumed can be calculated using the formula,

$$C_{el} = \frac{itM}{Fz} \quad (4)$$

where, I is the current (A), t is time (s), M is the molar mass of the electrode material used (g/mol), F is Faraday constant (96485 Cmol⁻¹) and z is the number of electrons [82].

The consumption of electrodes was found to be 0.302 g and 0.07 g for Al-Cu and Cu-Al electrodes respectively at the optimized condition. The Fig. 4 (b) gives the graph of initial pH vs electrode usage. Similar to the energy consumption, when Al acted as anode, the consumption of electrode was perpetual at pH <8. This is due to the stable current observed during the process of electrocoagulation. The minimum consumption of energy as well as electrode was obtained at pH 4. While Cu acted as anode, the electrode expenditure downturned while increase in pH was made. The pH >7 implied high electrode usage. There was no dissolution of cathode during the electrocoagulation process. This indicates that when copper is used as an anode, the electrode consumption is minimum and can be used for a greater number of cycles than aluminium.

3.4.3. Operating cost

One of the most denoting aspects that can influence in choosing a wastewater treatment technology is the operational cost. As reported in the literature, destabilization, and accumulation are the two processes occurring during electrocoagulation. Often, the first step is the shortest and the second step is the longest. Reaction time is a very essential characteristic since it affects the cost of electricity and metal mass usage which are the crucial operating parameters deciding the cost-effectiveness [86-87]. The operating cost can be calculated using the formula,

$$C_{op} = a C_{en} + b C_{el} \quad (5)$$

Where a is the energy cost per unit, C_{en} is energy consumption, b is the cost of the electrode plate and C_{el} is the electrode consumption [82]. From the above equation, the operating cost was calculated as 3.31 US\$/m³ and 0.22 US\$/m³ for Al-Cu and Cu-Al electrodes respectively. Therefore, copper can be used

as anode for the electrocoagulation technique for an effective removal of pollutants, and due to its low cost.

3.5. COD removal

According to the literature, the effluent generally possesses COD values greater than 2000 mg/L [88-91]. Some industrial effluents which are inclusive of phenolic and aromatic compounds showed COD values of about 3700 mg/L [88]. The lessening of colour does not always entail a reduction in COD. The elimination of colour can be due to the dye degradation process or evolution of organic/organometallic complexes or the aggregation of both. The most efficient way to lower the COD is anticipated to be when a dye completely degrades [41]. The COD of the treated water was determined by varying initial pH and time, and Fig. 5 (a) represents the graph of initial pH vs. COD removal and Fig. 5 (b) represents the graph of electrolysis time vs. COD removal. The percentage of COD removal for Al-Cu and Cu-Al electrodes at pH 4 was found to be 89.74% and 87.15% and it reduced to 31.67% and 12.52% at pH 12 respectively. An Increase in initial pH resulted decrease in COD removal efficacy implying acidic medium as a convenient condition which is also cited in the literature [67, 92-93]. Similarly, at 5 min of reaction time the removal percentage was observed as 0.45% and 0.2% for Al-Cu and Cu-Al electrodes respectively. Whereas, at 30 min of electrolysis time, COD removal for Al-Cu and Cu-Al was 89.74% and 87.15%. Therefore, the COD removal efficacy increases with operating time due to the fact that the coagulating species concentration and the hydroxide flocs raises [94]. At optimized conditions, for Al-Cu (pH 4, 30 min, without electrolyte) and for Cu-Al (pH 7, 30 min, 0.1g NaCl), the maximum COD removal was calculated as 89.74% and 87.15%.

3.6. Removal efficiencies of other parameters

The electrocoagulation process was carried out at different pH, time and electrolyte concentration to substantiate the maximum removal of pollutant at optimal conditions. The levels of COD, BOD, TSS, TDS, turbidity, and phenolic compounds were used to evaluate the electrochemical reactor's performance. Due to high COD and very low dissolved oxygen, the aquatic lives exhibited many convoluted physiological and biochemical changes in its body [95-97]. Similarly high amount of BOD and COD has led to soil infertility,

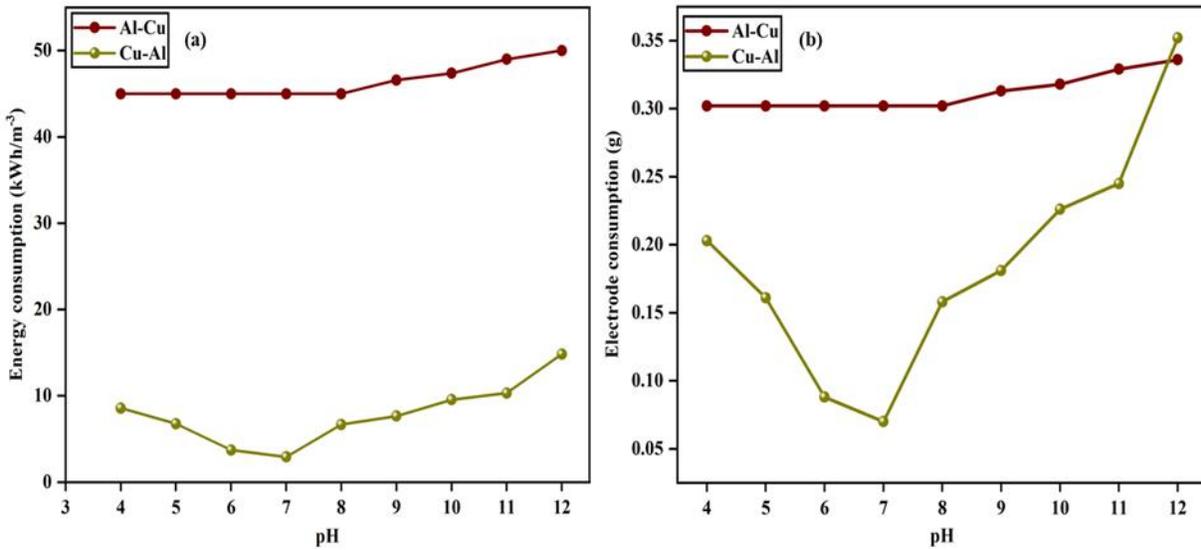


Fig. 4. Effect of initial pH on (a) energy consumption and (b) electrode consumption

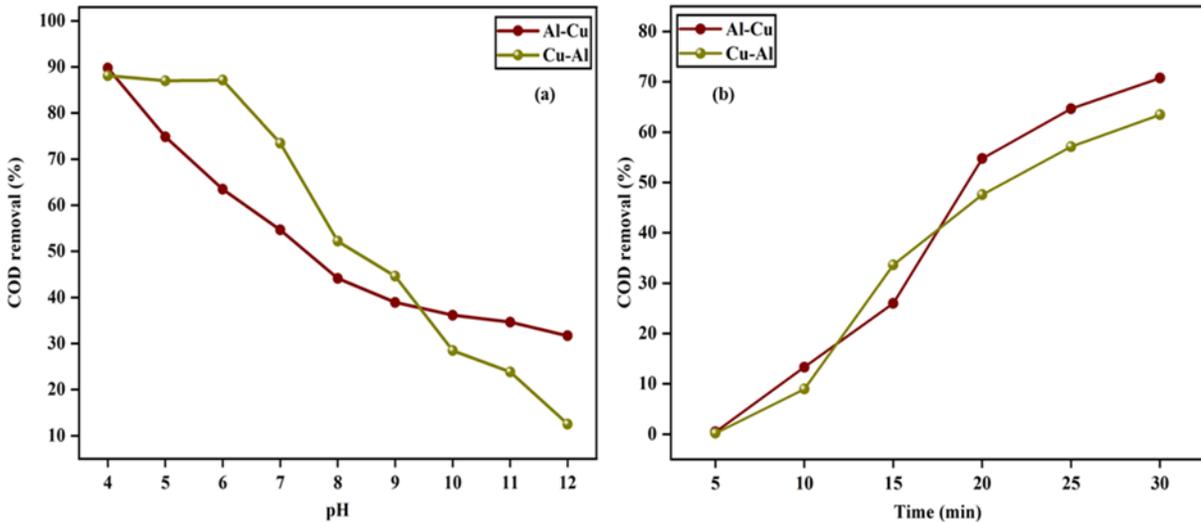


Fig. 5. Effect of COD removal on (a) varying pH and (b) varying time

affecting photosynthesis, food chain blockage and producing toxic effects to the people consuming the plants cultivated from the areas located near to the textile units [98-99]. The overall removal efficiency of the parameters is represented in **Fig. 6**. While correlating the removal efficacies of Al-Cu and Cu-Al electrodes, the performance of the electrochemical reactor with aluminium as anode exhibited a higher removal percentage. Consequently, the results obtained while using copper as anode, produced low cost and the removal efficiencies were significant with that of the first set of experiment. Md. Milon Hossain et al. carried out the treatment of textile wastewater by the electrocoagulation process using Fe electrodes and obtained a COD removal of 45.21% at 50 min [100]. Mervat A. Sadik investigated the treatment process of textile wastewater using Al as the sacrificial anode

material, where at an electrolysis time of 120 min, the COD removal efficiency was only 54-65% [56]. Samir Naje et al. at optimal conditions with 90 min of reaction time and the result was recorded as COD-92.6%; TSS-96.4%; TDS-87%; BOD-88%; colour-96.5%; turbidity-96%; phenolic compounds over 99% with operational cost of 1.76 US\$/m³ [92]. Merzouk et al. explored the textile wastewater treatment using electrocoagulation-electroflotation process in a batch reactor and achieved the removal efficacy of TSS-85.5%; COD-79.7%; BOD-88.9%; turbidity-76.2% and colour-93% [101]. The following outcomes were attained when copper and aluminium electrodes were utilized in an unconventional combination of Cu as anode and Al as cathode, the COD, BOD, TSS, TDS, turbidity, and phenolic compounds removal of 87.15%, 85.23%, 98.41%, 84%, 85.43%, and 99.65% respectively. When

compared to the literature mentioned above, the operational cost was found to be much lower with 0.22 US\$/m³. Consequently, it can be concluded that unconventional pairing of electrodes produces high removal efficiencies. As the COD and BOD reduction is obtained as 89.74, 87.15% and 86.1, 85.23% respectively after the treatment process, the treated effluent can be assessed for reuse purposes. It could possibly be used for agricultural purposes as well as for the fish growth.

3.6. SEM analysis

The surface morphologies and the structure of the sludge can be determined through the SEM analysis [102]. The floated sludge after the electrocoagulation process was taken and oven-dried at 80°C overnight. This dried sludge was subjected to SEM analysis and **Fig. 7** (a) and (c) represent the morphologies of the sludge obtained from Al-Cu and Cu-Al electrodes. The SEM micrograph of Al-Cu exhibits an amorphous nature and non-uniform distribution of the dye particles has been observed. A similar result was reported for the Al sludge in the literature during the treatment of terephthalic acid wastewater by Garg et al [103]. The micrograph of Cu-Al sludge shows a uniform layer with adsorbed dye particles from the effluent. When comparing to the bulky amorphous sludge, these has high surface area and better adsorption takes place with minimal corrosion [104]. According to Safwat et al. the morphology of Al and Cu electrodes exhibited the same

as like the sludge produced during the above process indicating copper as a better anode material due to its uniform corrosion [84]. **Fig. 7** (b) and (d) shows the evident formation of hydroxide flocs of the sludge obtained from the electrocoagulation process.

3.7. EDX studies

The EDX studies was done using the sludge obtained after the filtration process to check the dissolution rate of an anode and to confirm the formation of the hydroxides which is the key principle acting in the process of electrocoagulation in the removal of dye effluents. **Fig. 8** (a) and (b) shows the EDX spectrum of the sludge obtained from the treatment of the effluent using aluminium as an anode and using copper as anode respectively. From the EDX data, it can be proven that aluminium metal when used as an anode as well as cathode, the dissolution occurs thereby proving to increase the cost of the overall electrocoagulation process [105]. From the **Table 2** which represents the atomic weight percentage of the elements in the sludge, it is more obvious that, when copper is used as an anode, the cost of the process can be reduced than using aluminium as anode because of its very high dissolution rate. Based on EDX results, out of the two combinations of dissimilar electrodes used, it was observed that uniform anodization on Cu (Cu-Al), compared to Al-Cu pair, so Cu-Al plays better electrocatalyst in terms of the consumption of energy and electrode.

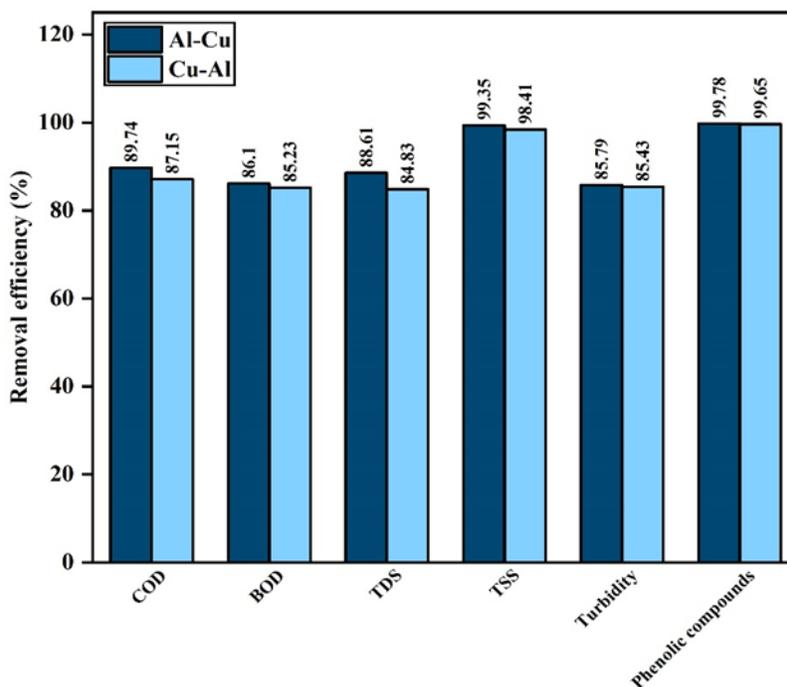


Fig. 6. Removal efficacy of various parameters of treated textile effluent using Al-Cu and Cu-Al electrodes at optimal conditions

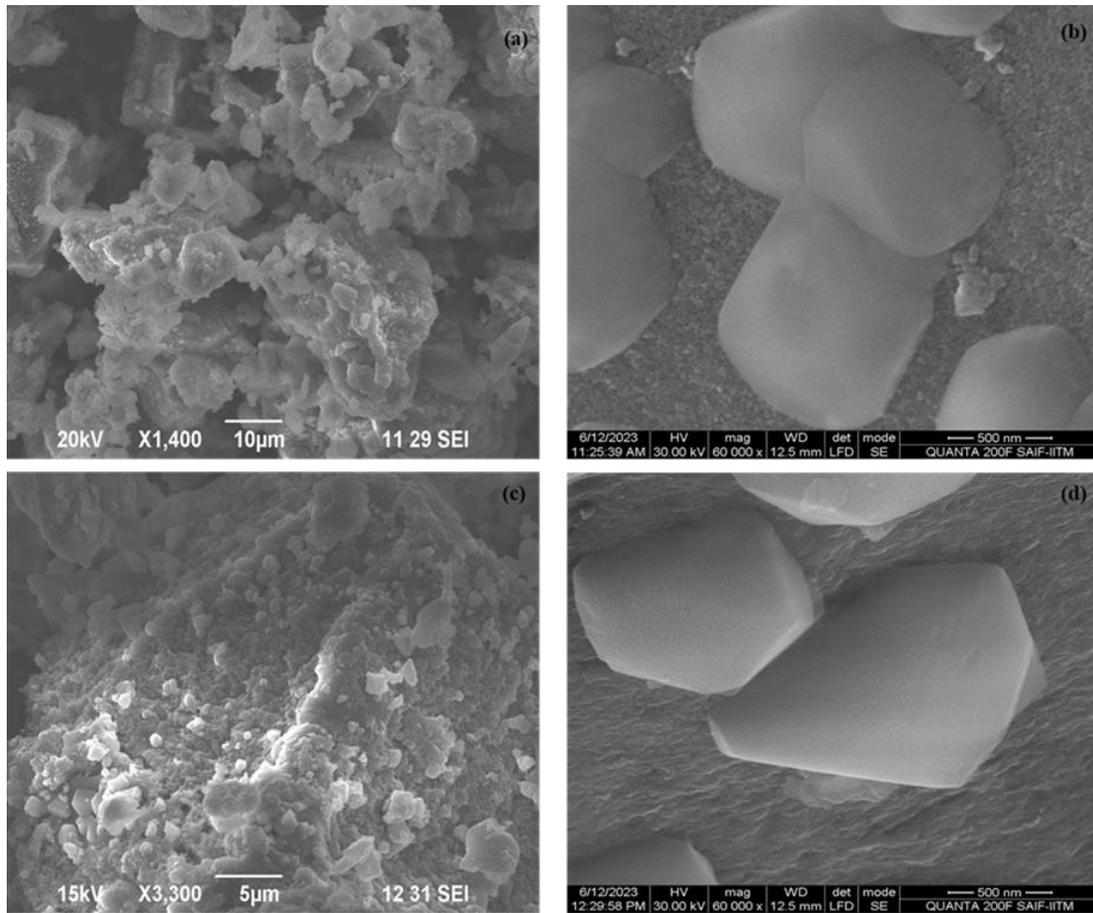


Fig. 7. SEM micrograph of (a)-(c) Al-Cu (b)-(d) Cu-Al sludge

Table 2. Atomic weight percentage of elements in EDX spectra

Element	Atomic % in Al-Cu sludge	Atomic % in Cu-Al sludge
O K	65.76	67.10
Al K	34.00	18.01
Cu K	0.24	14.89

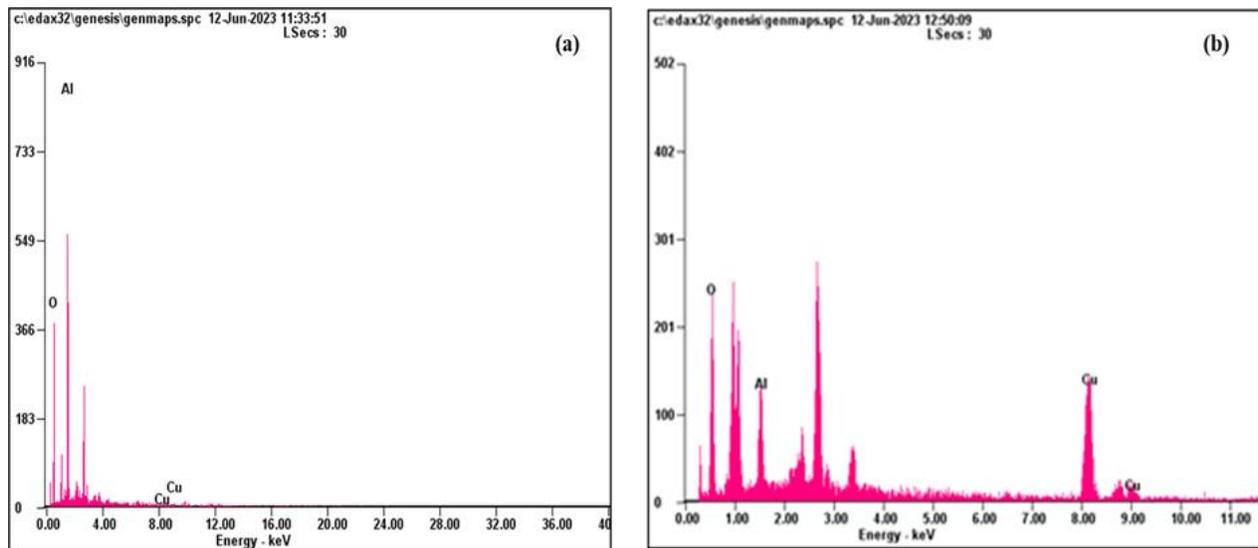


Fig. 8. EDX spectrum of the sludge from (a) Al-Cu (b) Cu-Al electrodes

3.8. HPLC analysis

The HPLC studies were done for the identification of a number of components present in the textile effluent as well as the treated effluent with Al-Cu and Cu-Al electrodes by the electrocoagulation process. C18 column was used for the analysis with methanol and water (50:50) as the mobile phase at a wavelength of 290 nm. The HPLC chromatogram of the raw effluent, and treated effluent with Al-Cu and Cu-Al is represented in **Fig. 9**. Initially from **Fig. 9** (a) which shows the graph for raw effluent, nine peaks were eluted implying the presence of nine compounds. The peak that was eluted at a retention time of 7.609 min with a percentage area of 52.8415 is notably due to the existence of organic compounds that is present in the dyes used during the process of dyeing in the textile industry. The other peaks eluted at various RT and its % area is shown in **Table 3**. The chromatogram of the treated effluent using Al-Cu electrodes as in **Fig. 9** (b) shows the desertion of one peak at RT 1.948 which is seen in the effluent chromatogram indicating the expulsion of high polar compound. In raw effluent, the eluted peaks were found at RT 2.20, 2.417 and 3.191 min whereas after an electrocoagulation process the peaks were eluted at RT 2.011, 2.143, 2.483, 3.034 and 3.208 min clearly stating the disintegration of the components present in the effluent. Consequently, at RT 7.493 a % area of 17.4771 was exhibited by the treated effluent using aluminium as anode which is reduced in comparison with the raw effluent having above 50% of area. Similarly, when the treatment was carried out using Cu-Al electrodes as in **Fig. 9** (c), the elimination of one peak at RT 2.417 min was observed. At RT 7.010, 7.586 and 9.866 min, the % area was found to be 5.3823, 4.5561, and 2.121 which is compared with that of the

raw effluent eluted at RT 7.124, 7.609, and 9.9 min % area of 0.4314, 52.8415 and 4.3751. From the above comparison, it is noteworthy to state that the % area was almost reduced to minimum which eventually substantiates the removal of the auxochromes and chromophoric groups which is responsible for the colour imparted from the dye. Correlating the two chromatograms of the treated effluent and though, the colour removal for Cu-Al (95.12 %) is little less than Al-Cu (98.42 %), the degradation of the organic compounds was competent while using copper as anode than using aluminium as anode material.

3.10. XPS studies

In the process of electrocoagulation, the metal electrodes used, significantly the anode material dissolves and liberate metal ions when an external current is applied. Simultaneously, the cathode also undergoes reduction and produces hydroxyl ions and thus combines with the metal ions forming metal hydroxide which is highly responsible for the adsorption of pollutants in the effluent [43]. In order to examine the formation of hydroxides, the sludge obtained after the filtration process was analysed using XPS analysis, and the **Figs. 10** (a) and **11** (a) represent the survey spectrum of sludge obtained for Al-Cu and Cu-Al electrode materials. The formation of a peak at 75 eV in **Fig. 10** (b) and 531.9 eV in **Fig. 10** (c) depicts the formation of Al(OH)₃ which corresponds to the bayerite structure which clearly signifies that aluminium exists as Al³⁺ [106]. According to the peak formed at the binding energy of 934.8 eV which is given in **Fig. 11** (b), the presence of copper at its +2-oxidation state (Cu²⁺) was confirmed [107]. The **Fig. 11** (c) attributes to the O 1s peak with binding energies at 531.8 and 533.5 eV. The

Table 3. HPLC data for the raw effluent and treated effluent with Al-Cu and Cu-Al electrodes

Effluent		Effluent treated with Al-Cu electrodes		Effluent treated with Cu-Al electrodes	
RT	% Area	RT	% Area	RT	% Area
1.948	1.9401	2.011	20.2837	1.979	21.8378
2.200	14.7263	2.143	14.7365	2.161	46.2570
2.417	8.2390	2.483	5.3870	Removed	Removed
3.191	3.9232	3.034	2.0212	3.060	4.4924
6.273	0.5045	3.208	5.1972	3.726	0.8530
6.892	13.0188	6.696	22.8581	6.690	14.5004
7.124	0.4314	7.053	6.8834	7.010	5.3823
7.609	52.8415	7.493	17.4771	7.586	4.5561
9.900	4.3751	9.857	5.1558	9.866	2.1210

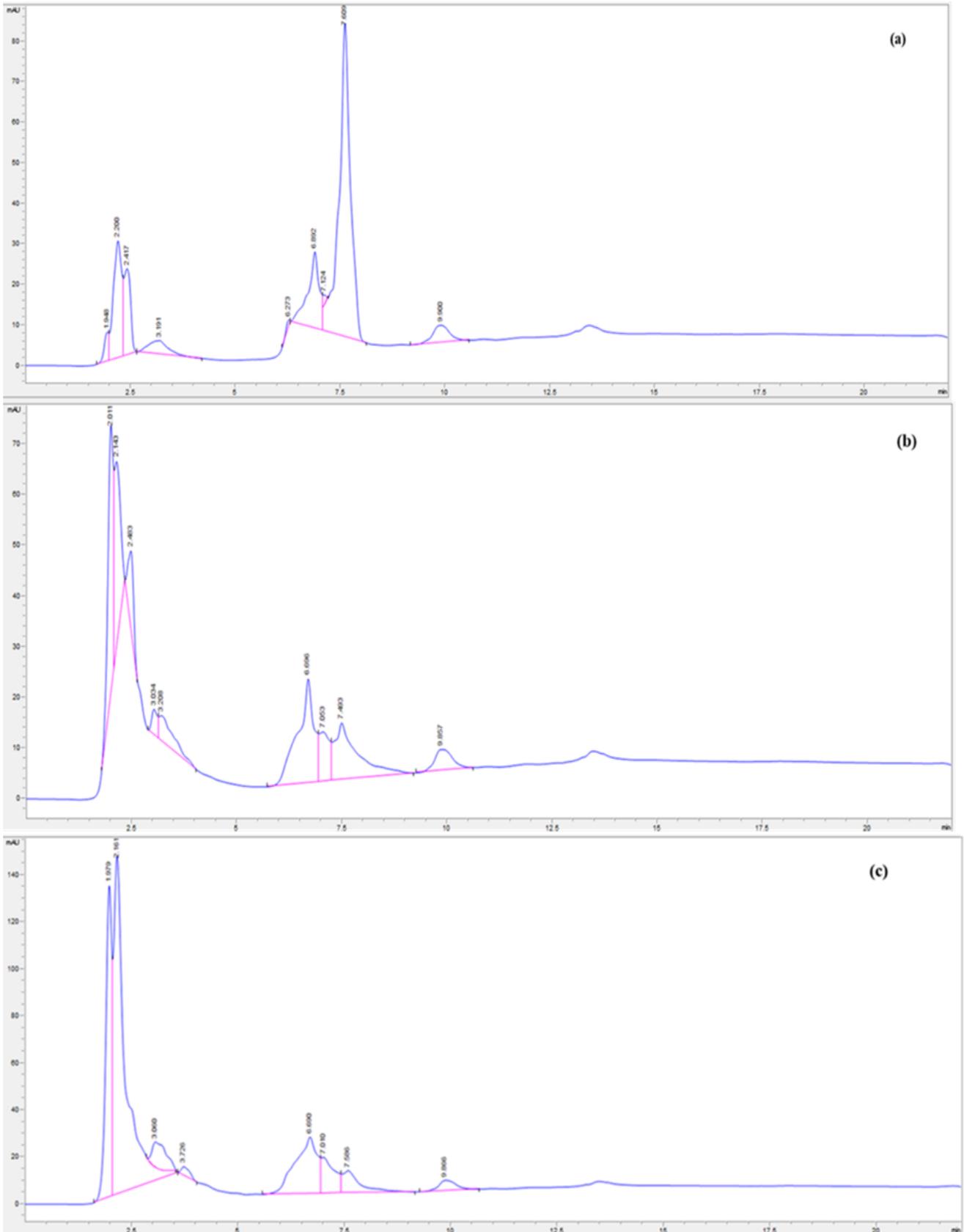


Fig. 9. HPLC chromatogram of (a) raw effluent, treated effluent with (b) Al-Cu and (c) Cu-Al electrodes

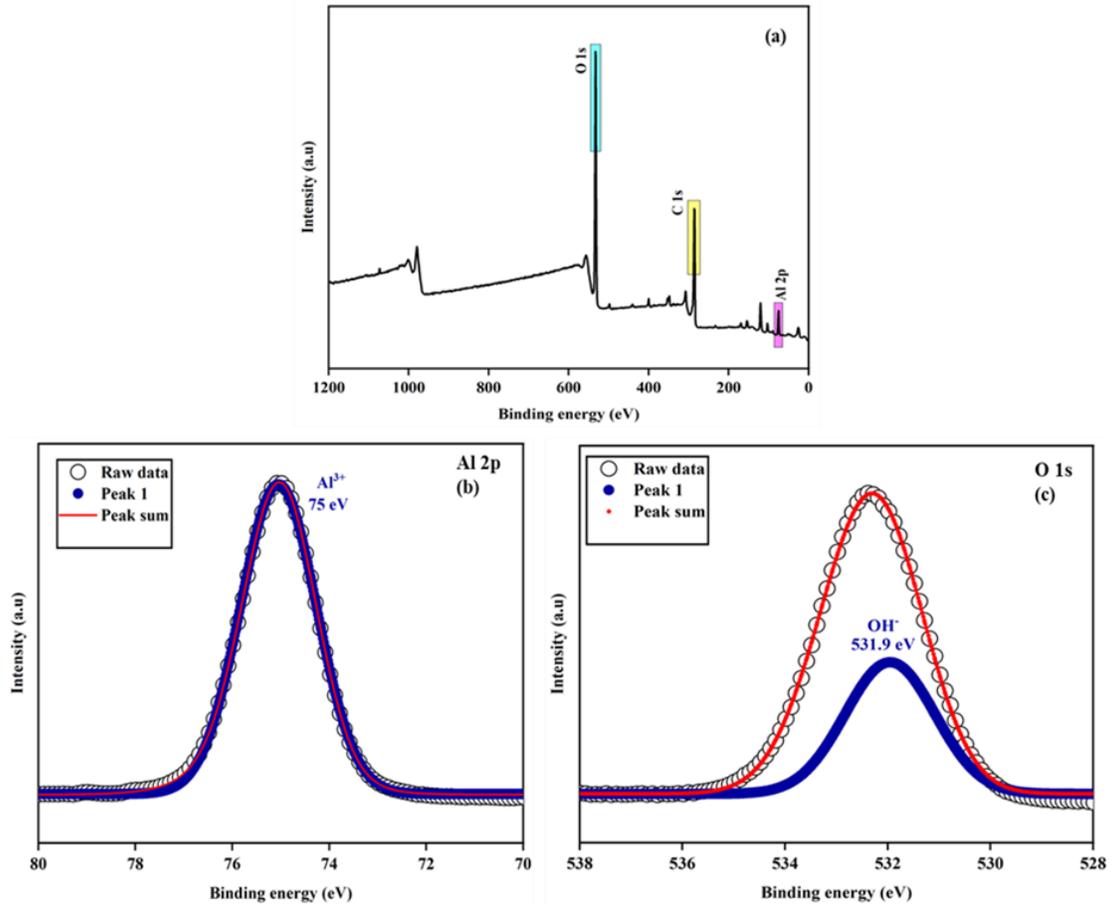


Fig. 10. XPS analysis spectrum of sludge obtained from Al-Cu electrodes (a) survey spectra (b) Al 2p (c) O 1s

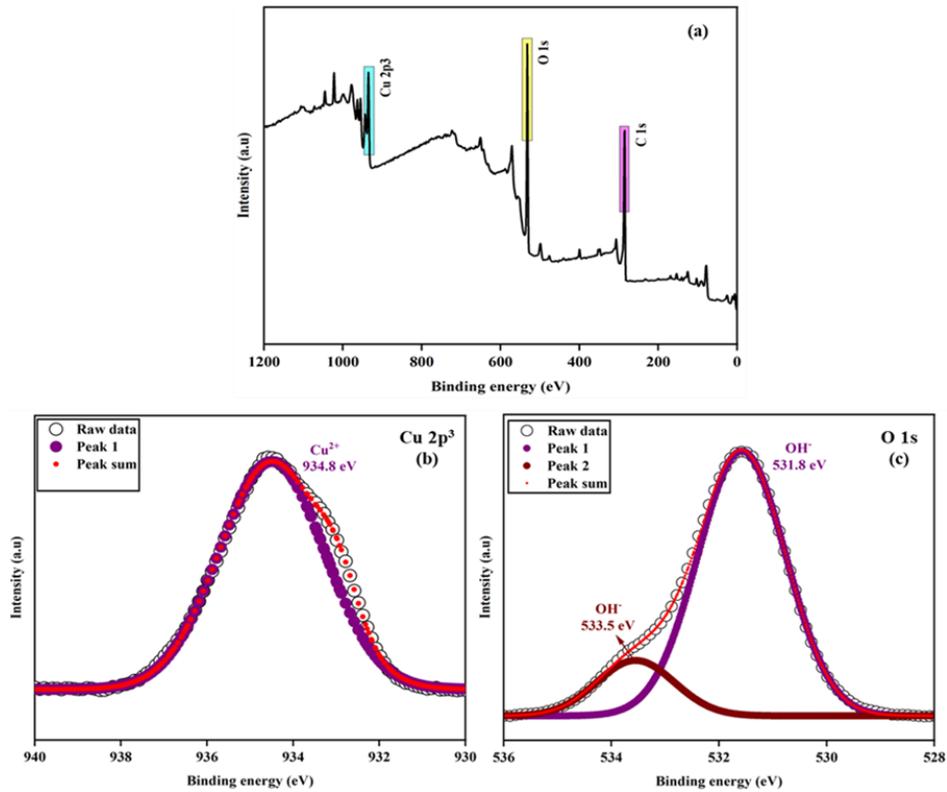


Fig. 11. XPS analysis spectrum of sludge obtained from Cu-Al electrodes (a) survey spectrum (b) Cu 2p³ (c) O 1s

larger binding energy peak at 533.5 eV is attributable to the hydroxyl oxygen atoms and seems to be relatively broadened when compared to the peak at a lower binding energy of 531.8 eV. This gives an evident formation of cuprous oxide, $\text{Cu}(\text{OH})_2$ [108-109].

4. Conclusions

In this work, the efficiency in the removal of colour, COD, BOD, and other parameters was investigated for the textile effluent using two sets of electrode materials. For Al-Cu electrodes, high removal occurred at pH 4, 10 V, and a reaction time of 30 min (98.42%) whereas for Cu-Al it was observed at pH 7, 10 V, and 30 min (95.12%). Only insignificant changes in the removal efficacy were observed in both experiments. The SEM micrographs exhibits the hydroxide flocs for both the electrodes. The better electrocatalytic dissolution on copper was confirmed from EDX, on uniform and less dissolution of copper whereas more aluminium dissolution in both the cases. The XPS analysis proved the formation of the hydroxide and its type along with the valence state of the metals. The other parameters such as TSS, TDS, TOC, and phenolic compounds were also eliminated in an efficient way in both conditions. But the energy and electrode consumption were less when copper was used as anode. Similarly, the operational cost was also minimum while comparing with Al-Cu electrodes. Similar results were found in HPLC, indicating high removal of components. Due to the minimum operational cost of copper as an anode, it promises to be the efficient electrode material for high removal efficiency.

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References

[1] P. Zucca, C.M.B. Neves, M.M.Q. Simoes, M.G.P.M.S. Neves, G. Cocco, E. Sanjust, *Molecules*. 21 (2016) 964.

[2] K.K. Samanta, P. Pandit, P. Samanta, S. Basak, *Water in Textiles and Fashion*, Woodland Publishing, 2019, pp. 41-59.

[3] M.A. Uqaili, K. Harijan (Eds), *Energy, Environment and Sustainable Development*. Springer Science and Business Media, New York, 2011.

[4] International Recommendations for Industrial Statistics, Iris Business Services (India) Private Limited, 2008.

[5] T. Seyedi-Chokanlou, S. Aghabeygi, N. Molahasani, F. Abrinaaei, *Iran. J. Catal.* 11 (2021) 49-58.

[6] A. Rostami-Vartooni, A. Moradi-Saadatmand, M. Bagherzadeh, M. Mahdavi, *Iran. J. Catal.* 9 (2019) 27-35.

[7] S. Ghattavi, A. Nezamzadeh-Ejhieh, *Compos. B.* 183 (2020) 107712.

[8] A. Tenenbaum, J. David, *Environ. Health Perspect.* 106 (1998) A235.

[9] C.E. Gurnhan, *Industrial Waste Control*, Academic Press, New York, 1965.

[10] D. Prabakar, S.K. Suvetha, V.T. Manimudi, T. Mathimani, G. Kumar, E.R. Rene, A. Pugazhendhi, *J. Environ. Manage.* 218 (2018) 165-180.

[11] C.R. Holkar, A.J. Jadhav, D.V. Pinjari, N.M. Mahamuni, A.B. Pandit, *J. Environ. Manage.* 182 (2016) 351-366.

[12] S.N. Singh, *Environmental Science and Engineering*, Springer, 2014, pp. 367.

[13] C.M. Carlliel, S.J. Barclay, C. Shaw, A.D. Wheatley, C.A. Buckley, *Environ. Technol.* 19 (1998) 1133-1137.

[14] A. Bafana, S.S. Devi, T. Chakrabarti, *Environ. Rev.* 19 (2011) 350-371.

[15] R.G. Saratale, G.D. Saratale, D.C. Kalyani, J.S. Chang, S.P. Govindwar, *Bioresour. Technol.* 100 (2009) 2493-2500.

[16] E.A. Clarke, R. Anliker, In *Handbook of Environmental Chemistry*, (Eds) O. Hutzinger. Springer-Verlag, Heidelberg, 1980, pp. 181-215.

[17] K.T. Chung, S.E. Stevens, *Environ. Toxicol. Chem.* 12 (1993) 2121-2132.

[18] N. Puvaneswari, J. Muthukrishnan, P. Gunasekaran, *Indian J. Exp. Biol.* 44 (2006) 618-626.

[19] G. Zaalishvili, E. Lomidze, O. Buadze, T. Sadunishvili, P. Tkheldze, G. Kvesitadze, *Int. Biodeterior. Biodegrad.* 46 (2000) 133-140.

[20] S. Parmar, S. Daki, S. Bhattacharya, A. Shrivastav, *Development in Wastewater Treatment Research and Processes*, Elsevier, 2022, pp. 175-193.

[21] A. Garg, K.L. Bhat, C.W. Bock, *Dyes Pigm.* 55 (2002) 35-52.

[22] M.S. Tsuboy, J.P.F. Angeli, M.S. Mantovani, S. Knasmuller, G.A. Umbuzeiro, L.R. Ribeiro, *Toxicol. In Vitro.* 21 (2007) 1650-1655.

- [23] A. Stammati, C. Nebbia, I.D. Angelis, A.G. Albo, M. Carletti, C. Rebecchi, F. Zampaglioni, M. Dacasto, *Toxicol. In Vitro.* 19 (2005) 853-858.
- [24] Y. Juang, E. Nurhayati, C. Huang, J.R. Pan, S. Huang, *Sep. Purif. Technol.* 120 (2013) 289-295.
- [25] G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I. Banat, R. Marchant, W. Smyth, *Appl. Microbiol. Biotechnol.* 56 (2001) 81-87.
- [26] S. Ahmadzadeh, M. Dolatabadi, *Environ. Earth Sci.* 77 (2018) 1-11.
- [27] S. Ahmadzadeh, M. Dolatabadi, *J. Mol. Liq.* 254 (2018) 76-82.
- [28] D.T. Moussa, M.H. El-Naas, M. Nasser, M.J. Al-Marri, *J. Environ. Manage.* 186 (2017) 24-41.
- [29] S. Ahmadzadeh, A. Asadipour, M. Pournamdari, B. Behnam, H.R. Rahimi, M. Dolatabadi, *Process Saf. Environ. Prot.* 109 (2017) 538-547.
- [30] C.T. Wang, W.L. Chou, Y.M. Kuo, *J. Hazard. Mater.* 164 (2009) 81-86.
- [31] S. Barisci, O. Turkyay, *J. Water Process. Eng.* 10 (2016) 56-66.
- [32] D.D. Nguyen, H.H. Ngo, W. Guo, T.T. Nguyen, S.W. Chang, A. Jang, Y.S. Yoon, *Sci. Total Environ.* 563-564 (2016) 549-556.
- [33] M. Kobya, F. Ulu, U. Gebologlu, E. Demirbas, M.S. Oncel, *Sep. Purif. Technol.* 77 (2011) 283-293.
- [34] Y. Kuroda, Y. Kawada, T. Takahashi, Y. Ehara, T. Ito, A.Z.Y. Kono, K. Yasumoto, *J. Electrostat.* 57 (2003) 407-415.
- [35] N.F. Nielsen, C. Anderson, *Electrostatic Precipitation*, 2009, pp. 111-118.
- [36] T.H. Kim, C. Park, J. Yang, S. Kim, *J. Hazard. Mater.* 112 (2004) 95-103.
- [37] P. Durango-Usuga, F. Guzman-Duque, R. Mosteo, M.V. Vazquez, G. Penuela, R.A. Torres-Palma, *J. Hazard. Mater.* 179 (2010) 120-126.
- [38] M.C. Wei, K.S. Wang, C.L. Huang, C.W. Chiang, T.J. Chang, S.S. Lee, S.H. Chang, *Chem. Eng. J.* 192 (2012) 37-44.
- [39] B.K. Korbahti, K. Artut, C. Gecgel, A. Ozer, *Chem. Eng. J.* 173 (2011) 677-688.
- [40] C.L. Yang, J. McGarrah, *J. Hazard. Mater.* 127 (2005) 40-47.
- [41] A.K. Golder, N.H. Hridaya, A.N. Samanta, S. Ray, *J. Hazard. Mater.* 127 (2005) 134-140.
- [42] M.S. Secula, I. Cretescu, S. Petrescu, *Desalination.* 277 (2011) 227-235.
- [43] U.B. Ogutveren, N. Gonen, S. Koparal, *J. Environ. Sci. Health A.* 27 (1992) 1237-1247.
- [44] M.Y.A. Mollah, S.R. Pathak, P.K. Patil, M. Vayuvegula, T.S. Agarwal, J.A.G. Gomes, M. Kesmez, D.L. Cocke, *J. Hazard. Mater.* 109 (2004) 165-171.
- [45] P. Kalivel, R.P. Singh, S. Kavitha, D. Padmanabhan, S.K. Krishnan, J. Palanichamy, *Ecotoxicol. Environ. Saf.* 201 (2020) 110858.
- [46] H. Srikantha, M. Shivaswamy, S. Mahesh, *Water Sci. Technol.* 82 (2020) 1467-1483.
- [47] J.L. Trompette, *Colloids Surf. A Physicochem. Eng. Asp.* 648 (2022) 129196.
- [48] M. Ince, *Sep. Sci. Technol.* 48 (2013) 515-522.
- [49] M.K.N. Mahmud, M.A.Z.M.R. Rozainy, I. Abustan, N. Baharun, *Procedia Chem.* 19 (2016) 681-686.
- [50] T. Tamiji, A. Nezamzadeh-Ejhieh, *J. Taiwan Inst. Chem. Eng.* 104 (2019) 130-138.
- [51] E. Zarei, M.R. Jamali, J. Bagheri, *Iran. J. Catal.* 8 (2018) 165-177.
- [52] R.A. Mirzaie, F. Hamed, *Iran. J. Catal.* 5 (2015) 275-283.
- [53] A. Ehsani, R. Asgari, A. Rostami-Vartooni, H.M. Shiri, A. Yeganeh-Faal, *Iran. J. Catal.* 6 (2016) 269-274.
- [54] T. Tamiji, A. Nezamzadeh-Ejhieh, *Mater. Chem. Phys.* 237 (2019) 121813.
- [55] A. Ehsani, M. Hadi, E. Kowsari, S. Doostikhah, J. Torabian, *Iran. J. Catal.* 7 (2017) 187-192.
- [56] M.A. Sadik, *Adv. Chem. Engineer. Sci.* 9 (2019) 182-193.
- [57] J.A. Aguilar-Torrejon, P. Balderas-Hernandez, G. Roa-Morales, C.E. Barrera-Diaz, I. Rodriguez-Torrez, T. Torres-Blancas, *SN Appl. Sci.* 5 (2023) 118.
- [58] H. Zazou, H. Afanga, S. Akhouairi, H. Ouchtak, A.A. Addi, R.A. Akbour, A. Assabbane, J. Douch, A. Elmchaouri, J. Duplay, A. Jada, M. Hamdani, *J. Water Process. Eng.* 28 (2019) 214-221.
- [59] C.E. Barrera-Diaz, P. Balderas-Hernandez, B. Bilyeu, *Electrochemical Water and Wastewater Treatment*, 2018, pp. 61-76.
- [60] A.S. Koparal, U.B. Ogutveren, *J. Hazard. Mater.* 89 (2002) 83-94.

- [61] P.R. Kumar, S. Chaudhari, K.C. Khilar, S.P. Mahajan, *Chemosphere*. 55 (2004) 1245-1252.
- [62] P.K. Holt, G.W. Barton, C.A. Mitchell, *Water Sci. Technol.* 50 (2004) 177-184.
- [63] C.Y. Hu, S.L. Lo, W.H. Kuan, Y.D. Lee, *Water Res.* 39 (2005) 895-901.
- [64] C. Tsouris, D.W. Depaoli, J.T. Shor, M.Z.-C. Hu, T.-Y. Ying, *Colloids Surf. A Physicochem. Eng. Asp.* 177 (2001) 223-233.
- [65] C. Comninellis, G. Chen, *Electrochemistry for the Environment*. Springer, New York, 2009, pp: 566.
- [66] G. Chen, *Sep. Purif. Technol.* 38 (2004) 11-41.
- [67] M. Kobya, O.T. Can, M. Bayramoglu, *J. Hazard. Mater.* 100 (2003) 163-178.
- [68] S.H. Lin, M.L. Chen, *Water Res.* 31 (1997) 868-876.
- [69] J.S. Do, M.L. Chen, *J. Appl. Electrochem.* 24 (1994) 785-790.
- [70] J. Zhu, H. Zhao, J. Ni, *Sep. Purif. Technol.* 56 (2007) 184-191.
- [71] E. Bazrafshan, A. Mahvi, M.A. Zazouli, *Iran. J. Health Sci.* 2 (2014) 16-29.
- [72] D.T. Moussa, M.H. El-Naas, M. Nasser, M.J. Al-Marri, *J. Environ. Manage.* 186 (2017) 24-41.
- [73] I. Ali, M. Asim, T.A. Khan, *Int. J. Environ. Sci. Technol.* 10 (2013) 377-384.
- [74] N. Daneshvar, A.R. Khatee, N. Djafarzadeh, *J. Hazardous Materials*, 137 (2006) 1788-1795.
- [75] N. Drouiche, S. Aoudj, M. Hecini, N. Ghaffour, H. Lounici, N. Mameri, *J. Hazard. Mater.* 169 (2009) 65-69.
- [76] C. An, G.H. Huang, Y. Yao, S. Zhao, *Sci. Total Environ.* 579 (2017) 537-556.
- [77] A.K. Verma, *J. Water Process Eng.* 20 (2017) 168-172.
- [78] A. Akyol, *Desalination*. 285 (2012) 91-99.
- [79] A.H. Essadki, M. Bennajah, B. Gourich, C. Vial, M. Azzi, H. Delmas, *Chem. Eng. Process.: Process Intensif.* 47 (2008) 1211-1223.
- [80] M.M. Emanjomeh, M. Sivakumar, *J. Environ. Manage.* 90 (2009) 1663-1679.
- [81] A. Eslami, M. Moradi, F. Ghanbari, F. Mehdipour, *J. Environ. Health Sci. Eng.* 11 (2013) 31.
- [82] M. Kobya, E. Gengec, E. Demirbas, *Chem. Eng. Process.* 101 (2016) 87-100.
- [83] V. Kuokkanen, T. Kuokkanen, J. Ramo, U. Lassi, *Green Sustain. Chem.* 3 (2013) 89-121.
- [84] S.M. Safwat, A. Hamed, E. Rozaik, *Sep. Sci. Technol.* 54 (2018) 183-194.
- [85] E.A. Vik, D.A. Carlson, A.S. Eikum, E.T. Gjessing, *Water Res.* 18 (1984): 1355-1360.
- [86] N.M. Mahmoodi, A. Dalvand, *Desalination Water Treat.* 51 (2013) 5959-5964.
- [87] M. Tir, N. Moulai-Mostefa, *J. Hazard. Mater.* 158 (2008) 107-115.
- [88] W. Den, C. Huang, H.C. Ke, *Ind. Eng. Chem. Res.* 45 (2006) 3644-3651.
- [89] B.K. Korbahti, A. Tanyolac, *Ind. Eng. Chem. Res.* 42 (2003) 5060-5065.
- [90] D. Rajkumar, K. Palanivelu, *Ind. Eng. Chem. Res.* 42 (2003) 1833-1839.
- [91] G. Roa-Morales, E. Campos-Medina, J. Aguilera-Cotero, B. Bilyeu, C. Barrera-Diaz, *Sep. Purif. Technol.* 54 (2007) 124-129.
- [92] A.S. Naje, S. Chelliapan, Z. Zakaria, S.A. Abbas, *Int. J. Electrochem. Sci.* 10 (2015) 5924-5941.
- [93] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, *Colloids Surf. A Physicochem. Eng. Asp.* 211 (2002) 233-248.
- [94] A.S. Mohammed, A. El-Gendi, K.M. El-Khatib, S.H. Hassan, *Water, Energy, Food Environ. J.* 2 (2021) 41-53.
- [95] P. Kupittayanant, W. Kinchareon, *J. Anim. Vet. Adv.* 10 (2011) 2631-2638.
- [96] C.D. Zhu, Z.H. Wang, B. Yan, *J. Comp. Physiol. B.* 183 (2013) 1005-1013.
- [97] B. Pelster, M. Egg, *J. Exp. Biol.* 221 (2018) 163709.
- [98] A. Mudhoo, D.L. Ramasamy, A. Bhatnagar, M. Usman, M. Sillanpaa, *Ecotoxicol. Environ. Saf.* 197 (2020) 110587.
- [99] R. Patil, M. Zahid, S. Govindwar, R. Khandere, G. Vyavahare, R. Gurav, N. Desai, S. Pandit, J. Jadhav, *Development in Wastewater Treatment Research and Processes*, Elsevier, 2022, pp. 173-198.
- [100] M.M. Hossain, M.I. Mahmud, M.S. Parvez, H.M. Cho, *Environ. Eng. Res.* 18 (2013) 157-161.

- [101] B. Merzouk, K. Madani, A. Sekki, Desalination. 250 (2010) 573-577.
- [102] Y. Li, X. Yuan, Z. Wu, H. Wang, Z. Xiao, Y. Wu, X. Chen, G. Zeng, Chem. Eng. J. 303 (2016) 636-645.
- [103] K.K. Garg, B. Prasad, J. Environ. Chem. Eng. 4 (2016) 178-190.
- [104] D. Ghosh, C.R. Medhi, M.K. Purkait, Chemosphere. 73 (2008) 1393-1400.
- [105] T. Picard, G. Cathalifaud-Feuillade, M. Mazet, C. Vandensteendam, J. Environ. Monitor. 2 (2000) 77-80.
- [106] J.T. Kloprogge, L.V. Duong, B.J. Wood, R.L. Frost, J. Colloid Interface Sci. 296 (2006) 572-576.
- [107] J.B. He, D.Y. Lu, G.P. Jin, Appl. Surf. Sci. 253 (2006) 689-697.
- [108] Riyanto, M.R. Othman, Int. J. Electrochem. Sci. 10 (2015) 4911-4921.
- [109] D. Koushik, W.J.H. Verhees, D. Zhang, Y. Kuang, S. Veenstra, M. Creatore, R.E.I. Schropp, Adv. Mater. Interfaces. 4 (2017) 1700043.