Electrochemical Degradation of Reactive Blue 21 and Synthetic Textile Effluent by Using Co$_{47.5}$/C$_{47.5}$-PVC$_5$ Composite Electrode

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Abstract

In this study, cobalt/graphite-polyvinyl chloride (Co$_{47.5}$/C$_{47.5}$-PVC$_5$) composite electrode was fabricated by mechanical alloying technique. The fabricated electrode and graphite rod were used as anode and cathode, respectively, in the decolourisation of aqueous C. I. Reactive Blue 21 (RB21) and synthetic textile effluent, containing a mixture of azo and anthraquinone dyes. The fabricated electrode showed high efficiency in the decolorisation of aqueous RB21 (99.95%) and synthetic textile effluent. This is further confirmed by the high reduction percentage (>75%) of COD and BOD$_5$ for both treated samples. The elemental composition study by using FESEM-EDX showed no significant changes in the composition of elements (C, Co and Cl) in the freshly fabricated electrode and after electrolysis of synthetic textile effluent. This showed that the fabricated electrode has a high mechanical strength and strong binding ability between C and Co due to the use of PVC as a binder.

Keywords: Composite electrode; decolorisation; electrochemical technique; C. I. Reactive Blue 21; synthetic textile effluent

1. Introduction

Synthetic dyes are among the most widely used pollutants in various industries, including textiles, paper, food and cosmetics. In line with the increase in usage by various industries, more than 100000 synthetic dyes with different structures are synthesised and more than 0.7 million tonnes of dyestuffs are produced throughout the year. Synthetic dyes are categorised into several groups, depending on their applications (dyeing method) such as reactive dyes, basic dyes, acid dyes, vat dyes, mordant dyes, and disperse dyes. It also depends on their chemical structure, such as azo dyes, anthraquinone dyes, triphenylmethane dyes, and phthalocyanine dyes.

In the textile industry, only 60%–90% of the dyes used are fixed to textile fibre while the other 10%–40% may remain unfixed to the fibre and will be released into the effluent. This has an adverse effect on aquatic ecosystems due to the presence of synthetic dyes even in small quantities (<1 mg L$^{-1}$). They can be seen with the naked eye and have negatively affected the aesthetic quality and transparency of lakes, rivers, and others. This in turn resulted in the destruction of aquatic ecosystems and the formation of dead deoxygenated zones in seas and oceans. Therefore, the treatment of dye containing effluents is very important to reduce the negative effects on aquatic life.

Various strategies were reported on the treatment of textile effluents. They are classified into biological methods (enzymes and microorganisms), physical methods (filtration, flocculation, and adsorption), and oxidation methods (advanced oxidation and chemical oxidation). However, today the use of electrochemical oxidation technique in textile wastewater treatment is getting more attention as this method does not involve the use of additional chemicals. Previous studies have shown that this technique provided high efficiency in the removal of organic and inorganic pollutants from the effluents. According to Najafpoor et al., this technique requires simple equipment, easy implementation, and on-site treatment in less space.
In the electrochemical treatment of industrial effluents, anode plays an important role as it acts as a site for electrochemical reactions. The material for electrode fabrication plays a major role in determining the efficiency and reactivity of the prepared electrode in an electrochemical reaction. Various electrodes were used in the treatment of synthetic dyes and textile industrial effluents, such as Pt, boron-doped diamond (BDD), and dimensionally stable anodes (DSA). In the current study, metal/graphite composite electrodes were prepared by mixing two different material (metal and graphite) powders with polyvinyl chloride (PVC). It is expected that the electrode performance in the electrochemical reaction will increase as the existence of two different materials in an electrode provides better synergistic effects and active bifunctional catalyst.

The main objective of this study is to investigate the efficiency of Co/C-PVC composite electrode in the decolourisation of aqueous RB21 and synthetic textile effluents. The effect of electrolysis conditions was also examined in the current study by investigating the effect of metal:graphite ratio in the prepared electrode, supporting electrolyte concentration, applied voltage, and electrolysis time on RB21 decolourisation. The surface characterisation of the prepared composite electrode was also performed in this study by using FESEM, EDX, and gas sorption analyser.

2. Experimental

2.1. Chemicals

All the chemicals used were of analytical research (AR) grade. Tin (Sn), copper (Cu), cobalt (Co), and aluminium (Al) powder with 99.9% purity were purchased from Aldrich. Sodium chloride (NaCl) solution, which acts as a supporting electrolyte in the electrolysis process, was purchased from R & M Chemicals. In this study, C. I. Reactive Blue 21 (RB21), C. I. Reactive Blue 19 (RB19), C. I. Reactive Violet 5 (RV5), and C. I. Reactive Red 198 (RR198) (Figure 1) were used as synthetic dyes and purchased from Dylon. Besides, polyvinyl chloride (PVC) and graphite powder (C) were obtained from BDH Ltd. whereas tetrahydrofuran (THF) was obtained from Systerm.

2.2. Preparation of Metal/Graphite-PVC Composite Electrode

The anode was prepared by mixing 0.475 g of metal powder (Sn, Cu, Al, or Co) with 0.475 g of graphite (C) powder (M:C is 50:50 (wt. %), in which M = metal) and 0.05 g of PVC as a binder by using a mechanical alloying technique (MAT). The ratio of metal and C powders to PVC was 95:5 PVC (wt. %). Then, 4 mL of THF was used to dissolve the PVC. The mixture was stirred until homogenous and oven dried at 100 °C for 2 h. The mixture was placed in a stainless-steel mould of 1 cm diameter and pressed at 104 kg cm–2. The pellet obtained (approximately 1.5 g) was then connected to a silver wire with silver conducting paint (Sigma-Aldrich) and sealed in a glass rod. Subsequently, epoxy resin (Devcon) was applied to cover the silver wire connecting surface. The metal/graphite-PVC composite electrode was used in the decolourisation of RB21 solution.

2.3. Preparation of Aqueous RB21 and Synthetic Textile Effluent

In this study, two types of samples were used, namely aqueous RB21 and synthetic textile effluent. The RB21 solution...
solution was prepared by dissolving a certain amount of RB21 in deionised water. Synthetic textile effluent was prepared by dissolving equal amount of RB21, RB19, RV5, and RR198 in tap water along with the other chemical additives, as described by Verma et al.\textsuperscript{23}

2. 4. Decolourisation of Aqueous RB21 and Synthetic Textile Effluent

The electrolysis of aqueous RB21 was performed by using a two-electrode system, which consisted of an anode (metal/graphite-PVC composite electrode) and a cathode (graphite rod electrode), with NaCl solution as a supporting electrolyte. Prior to electrolysis, both anode and cathode were rinsed with distilled water and a small amount of acetone. A direct current (DC) power supply (TTi PSU Bench CPX 400) and stirrer hotplate with magnetic bar were used throughout the electrolysis process. The electrochemical cell used was a simple and unidivided cell made of Pyrex glass with a capacity of 250 mL. The electrodes were placed vertically and parallel to each other in the electrochemical cell, with a constant gap between electrodes at approximately 20 mm. The electrolysis of synthetic textile effluent was carried out by using similar procedures, as described above. The same anode from the previous electrolysis of aqueous RB21 was used in the electrolysis of synthetic textile effluent.

2. 5. Optimisation of Electrolysis Parameters for the Decolourisation of Aqueous RB21

Optimisation of electrolysis parameters was carried out by optimising the ratio of metal and C in the prepared electrode, supporting electrolyte concentration, electrolysis time and applied voltage. For the optimisation of metal and C ratio in the prepared electrode, the ratio and mass of metal, C, and PVC are summarised in Table 1. The procedure for preparation of anodes is similar as mentioned in Section 2.2.

2. 6. Instrumentation

To observe the decolourisation level of aqueous RB21 and synthetic textile effluent, the sample solution was characterised by using an UV-Vis (Perkin Elmer Lambda 35) spectrometer in the range of 200–900 nm by using 10 mm quartz cuvettes. The surface properties of the electrode were determined by using gas sorption analyser (ASAP 2020 V4.010). Brunauer-Emmett-Teller (BET) method was used to determine the surface area of the electrode. BJH model was used to calculate the pore size. Surface morphology of the electrode was observed by using Field Emission Scanning Electron Microscope (FESEM) (Leo Supra 50 VP). The elemental composition of prepared electrode was determined by using Energy Dispersive X-ray (EDX) spectrometer. The size and shape of the particles were observed by using a transmission electron microscopy (TEM) (Philips CM12-12796) with an accelerating voltage of 100 kV. Samples were prepared on carbon-coated copper grids covered with a polyvinyl formal polymer by adding a drop onto the grid and evaporating the solvent (ethanol) in ambient condition.

2. 7. Analytical Measurement

Decolourisation of aqueous RB21 was determined based on the original concentration of RB21 ($c_i$) and RB21 concentration after electrolysis process ($c_t$) by measuring absorbance at the wavelength of 624 nm in the Vis region of RB21. Measurement of RB21 absorbance was performed by using UV-Vis spectrophotometer. Decolourisation was calculated in percentage (%) as in the following equation:

$$\text{Decolourisation (\%)} = \left( 1 - \frac{c_t}{c_i} \right) \times 100\% \quad (1)$$

The absorbance versus RB21 concentrations graph in the range of 10 to 110 mg L$^{-1}$ is a linear graph referring to the following equation:

$$\text{Absorbance} = 0.015c + 0.033 \quad (R^2 = 0.996) \quad (2)$$

Where $c$ represents the concentration of RB21 solution in mg L$^{-1}$ unit.

2. 8. Reduction of COD and BOD$_5$

Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD$_5$) were performed on an aqueous RB21 and synthetic textile effluent before and after electrolysis by using the prepared electrode. Standard methods

\begin{table}
\caption{The composition ratio and mass of Co, C, and PVC for the preparation of Co/C-PVC electrodes.}
\begin{tabular}{|c|c|c|c|c|}
\hline
Electrode & Co:C ratio (%) & Mass of Co (g) & Mass of C (g) & Mass of PVC (g) \\
\hline
Co$_{95.0}$/C$_{0.0}$-PVC$_5$ & 100:0 & 0.950 & – & 0.05 \\
Co$_{66.5}$/C$_{28.5}$- PVC$_5$ & 70:30 & 0.665 & 0.285 & 0.05 \\
Co$_{47.5}$/C$_{47.5}$- PVC$_5$ & 50:50 & 0.475 & 0.475 & 0.05 \\
Co$_{28.5}$/C$_{66.5}$- PVC$_5$ & 30:70 & 0.285 & 0.665 & 0.05 \\
Co$_{0.0}$/C$_{95.0}$- PVC$_5$ & 0:100 & – & 0.950 & 0.05 \\
\hline
\end{tabular}
\end{table}
508B and 507 were used for the COD and BOD₃ analyses, respectively, as described by the American Public Health Association (APHA 1981).²⁴

2. 9. Statistical Analysis

The data were expressed as mean ± standard error (SE) with at least three times replication. The statistical analysis was carried out by using Statistical Package for Social Sciences (SPSS) Version 17.0 with one-way ANOVA. The data obtained were considered as statistically significant when the value of \( p < 0.05 \).

3. Results and Discussion

3. 1. Preliminary Experiment

Four types of metal/graphite-PVC composite electrodes were prepared and used in the preliminary experiment to investigate the efficiency of the prepared electrodes in the decolourisation of RB21 solution. This was to identify the best metal-graphite mixture that could give a maximum decolourisation of aqueous RB21. The results in Figure 2 show that maximum decolourisation percentage (85.09%) of RB21 is obtained by using Co₄⁷.⁵/C₄⁷.⁵-PVC₅ electrode compared to other metal/graphite-PVC composite electrodes. This showed that the mixture of Co and C in the Co₄⁷.⁵/C₄⁷.⁵-PVC₅ electrode showed the best synergistic effect with a maximum decolourisation percentage as compared to other electrodes. Therefore, this electrode will be used in the optimisation of electrolysis parameters for the decolourisation of aqueous RB21.

3. 2. Optimisation of Electrolysis Parameters for the Decolourisation of Aqueous RB21

Figure 3a shows the percentage of decolourisation on RB21 by using Co/C-PVC electrodes with different Co:C ratios (100:0, 70:30, 50:50, 30:70, 0:100). The electrode with a composition ratio of 50:50 (known as Co₄⁷.⁵/C₄⁷.⁵-PVC₅ electrode) exhibited the highest percentage of decolourisation, which was 85.27% as compared to other electrodes. This showed that the ratio of Co and C in the electrode provided better efficiency for RB21 removal. The composition ratio of 100:0 and 70:30 (known as Co₉₅.⁰/C₀.₀-PVC₅ and Co₆₆.₅/C₂₅.₅-PVC₅ electrodes, respectively) gave almost equal percentage of decolourisation (84.8% and 82.5%, respectively) as the decolourisation percentage obtained for 50:50 ratio. However, the use of more Co powder in both electrodes can increase the operating costs. Therefore, the electrode with a 50:50 ratio (Co₄⁷.⁵/C₄⁷.⁵-PVC₅ electrode) was considered as an optimum electrode based on the highest RB21 decolourisation percentage achieved in this study with less Co used in the preparation of the electrode.

Figure 3b shows the effect of the supporting electrolyte concentration on the decolourisation of RB21 solution. The supporting electrolyte (NaCl solution) was added in the electrochemical system to modify the electrochemical conductivity and facilitate the electrical current flow.²⁴ The presence of chloride ions from the addition of NaCl can lead to active oxidant formations, such as chlorine, hypochlorous acid, and/or hypochlorite, depending on the pH (Equations 3–5). These active oxidants are beneficial in the oxidation of organic pollutants at the anode or/and in bulk solution (Equation 6).⁸

\[
\begin{align*}
2 \text{Cl}^- & \rightarrow \text{Cl}_2 + 2 \text{e}^- \quad (3) \\
\text{Cl}_2 + \text{H}_2\text{O} & \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (4) \\
\text{HOCl} & \rightarrow \text{H}^+ + \text{OCl}^- \quad (5) \\
\text{Organics} + \text{OCl}^- & \rightarrow \text{intermediates} \\
& \rightarrow \text{CO}_2 + \text{Cl}^- + \text{H}_2\text{O} \quad (6)
\end{align*}
\]

As shown in Equations 3–6, the increased NaCl concentration has increased the electrogenerated OCl⁻ anions. This electrode corrosion was also due to the presence of OCl⁻ ions in the electrolysis solution. This was reported
by several researchers in previous studies\textsuperscript{26−28} According to Galvan-Martinez et al.,\textsuperscript{26} OCl\textsuperscript{−} ions are corrosive to some elements. This resulted in the corrosion of Co\textsubscript{47.5}/C\textsubscript{47.5−PVC\textsubscript{5}} electrode surface after electrolysis of RB21 by using NaCl electrolytes. Therefore, 0.5 mol L\textsuperscript{−1} was considered as an optimum concentration of NaCl for the decolourisation of RB21 with 85.09\% of RB21 decolourisation percentage.

The effect of electrolysis time on the decolourisation percentage of RB21 was investigated in the range of 15 min to 90 min. The increase in electrolysis time from this study showed an increased decolourisation percentage of up to 93.67\% (Figure 3c). Due to the increase in generation of OCl\textsuperscript{−} ions in the bulk solution resulting from the longer electrolysis time, better RB21 decolourisation efficiency was obtained as compared to a shorter electrolysis time. Electrolysis by using 60 min to 90 min leads to the electrode damage and corrosion of anode materials into the bulk solution. Due to the anode corrosion, precipitate was formed at the end of the electrolysis process and mixed with the electrolysis product. At 45 min, the electrode showed its ability to decolourise the aqueous RB21 without the formation of precipitate at the end of the electrolysis. Therefore, 45 min was considered as an optimum electrolysis time, with 86.87\% of RB21 decolourisation percentage.

The decolourisation efficiency was significantly affected by the applied voltage which was studied in the range of 1 V to 20 V. In Figure 3d, increasing the applied voltage from 1 V to 20 V increased the percentage of RB21 decolourisation after 45 min of electrolysis from 56.20\% to 99.95\%, respectively. Again, this was due to the increased generation of OCl\textsuperscript{−} species by the application of high value of applied voltage. Therefore, 20 V of applied voltage was considered as an optimum value of applied voltage based on the complete decolourisation of RB21 obtained in Figure 3d.

3.3 Decolourisation of Aqueous RB21

Figure 4 shows the UV–Vis spectra obtained for 50 mg L\textsuperscript{−1} of RB21 in 0.5 mol L\textsuperscript{−1} NaCl by using the optimum electrolysis parameters as obtained in the previous Section.
(3.2). The initial spectra (0 min) showed the appearance of three peaks at the wavelength of 339 nm in the UV region, and 624 nm and 663 nm in the visible region. The peak at 663 nm exhibited maximum absorption and was selected for subsequent study.\cite{29,30} The spectra obtained after 45 min of electrolysis showed the disappearance of all peaks after the electrolysis process. This suggested that the complex structure of RB21 was completely destroyed by the electrochemical process, and a colourless solution was produced after the electrolysis.

3.4. Decolourisation of Synthetic Textile Effluent

Optimum electrolysis conditions obtained in Section 3.2 were also applied in the decolourisation of synthetic textile effluent. This was to determine the efficiency of Co_{47.5}/C_{47.5}-PVC composite electrode in the degradation of various types of structurally different dyes and other pollutants. Figure 5 shows the UV-Vis spectra obtained for synthetic textile effluent before and after electrolysis. For untreated effluents (0 min), three peaks were observed at the wavelengths of 337 nm in the UV region, and 626 nm and 667 nm in the visible region. After 45 min of electrolysis with an applied voltage of 20 V in the presence of 0.5 mol L^{-1} of NaCl as a supporting electrolyte, the previous peaks completely disappeared. The colour of dyes mixture solution changes from blackish blue to colourless solution at the end of the electrolysis. It proved that the electrochemical treatment by using Co_{47.5}/C_{47.5}-PVC$_5$ electrode was able to degrade the pollutants contained in the effluent.

3.5. Reduction of COD and BOD$_5$

The results for COD and BOD$_5$ analyses of treated and untreated aqueous RB21 and synthetic textile effluent are summarised in Table 2. In addition to the colour removal, the electrochemical treatment by using the Co$_{47.5}$/C$_{47.5}$-PVC$_5$ electrode could also significantly reduce the COD and BOD$_5$ (Table 2). Table 2 also shows that the removal percentages of COD and BOD$_5$ for the synthetic textile effluents were lower than for the RB21 solution. This was due to the presence of more organic and inorganic compounds in synthetic textile effluents that created more challenging conditions for the COD and BOD$_5$ removal, resulting in lower COD and BOD$_5$ removal percentage than for the aqueous RB21.

| Sample               | Analysis     | Untreated   | Treated     | Removal (%) |
|----------------------|--------------|-------------|-------------|-------------|
| RB21 solution        | COD (mg L$^{-1}$) | 182.4 ± 7.1 | 15.5 ± 8.5  | 91.5 ± 6.0  |
|                      | BOD$_5$ (mg L$^{-1}$) | 56.8 ± 6.7  | 10.7 ± 8.3  | 81.2 ± 5.7  |
|                      | pH           | 6.6         | 6.3         | -           |
| Synthetic textile effluent | COD (mg L$^{-1}$) | 753.0 ± 5.5 | 89.8 ± 5.0  | 88.1 ± 6.2  |
|                      | BOD$_5$ (mg L$^{-1}$) | 81.6 ± 4.2  | 19.1 ± 7.9  | 76.6 ± 4.8  |
|                      | pH           | 12.3        | 11.9        | -           |

Table 2. COD, BOD$_5$, and pH of untreated and treated 50 mg L$^{-1}$ RB21 solution and synthetic textile effluent by using Co$_{47.5}$/C$_{47.5}$-PVC$_5$ electrode. ([NaCl] = 0.5 mol L$^{-1}$, E = 20 V, t = 45 min).
According to Chatzisymeon et al., two mechanisms are involved in oxidation of pollutants by an electrochemical technique, namely direct anodic oxidation and indirect anodic oxidation. For direct anodic oxidation, pollutants are absorbed on anodic surfaces and destroyed by anodic electron transfer reactions. Indirect anodic oxidation involves the use of electrogenerated oxidants, such as Cl₂, OCl⁻, OH⁺, O₃ and H₂O₂. The effect of NaCl presence on mineralisation of RB21 and synthetic textile effluent can be explained by referring to the following equations (Equations 7–10).

\[
\begin{align*}
\text{H}_2\text{O} + M + \text{Cl}^- &\rightarrow M[\text{ClOH}^+] + \text{H}^+ + 2 \text{e}^- \quad (7) \\
R + M[\text{ClOH}^+] &\rightarrow M + \text{RO} + \text{H}^+ + \text{Cl}^- \quad (8) \\
\text{H}_2\text{O} + M[\text{ClOH}^+] + \text{Cl}^- &\rightarrow M + \text{O}_2 + \text{Cl}_2 + 3 \text{H}^+ + 4 \text{e}^- \quad (9) \\
\text{H}_2\text{O} + \text{Cl}^- &\rightarrow \text{HOCl} + \text{H}^+ + 2 \text{e}^- \quad (10)
\end{align*}
\]

In the presence of NaCl, anodic water discharge resulted in the formation of chlorohydroxyl (ClOH⁺) radicals on the anode surface (M) (Equation 7) which then oxidized the organic matter (R) (Equation 8). Furthermore, molecular O₂ and free Cl₂ can be formed by the reaction between H₂O and ClOH⁺ radicals on the anode surface (Equation 9). Then, the resulting Cl⁻ ions will react with water to form OCl⁻ ions (Equation 10). The presence of large amount of electrogenerated OCl⁻ ions in the bulk electrolysis provided better mineralisation efficiency (COD and BOD₅ reduction) as these electrogenerated species are beneficial in the degradation of organic pollutants in both samples.

3.6. Characterisation of Co₄₇.₅/C₄₇.₅-PVC₅ Electrode

Figure 6 shows the FESEM micrograph obtained from the morphological study of freshly prepared Co₄₇.₅/C₄₇.₅-PVC₅ composite electrode and after electrolysis of synthetic textile effluent by using 20 V applied voltage and 45 min electrolysis. Figure 6a shows the distribution of Co and C in the electrode can be seen clearly and are mixed quite well. However, the surface of the electrode slightly changes after electrolysis of RB21 solution in Figure 6b.

Figure 6. FESEM micrograph of Co₄₇.₅/C₄₇.₅-PVC₅ electrode (a and c) fresh and (b and d) after electrolysis of synthetic textile effluent by using (a and b) 1000x and (c and d) 5000x magnification. ([RB21]₀ = 50 mg L⁻¹; [NaCl] = 0.5 mol L⁻¹; t = 45 min; E = 20 V).
This is due to the degradation of the pollutant that occurred on the surface of the electrode. FESEM micrograph in Figure 6d shows a significant change in the surface of the electrode as compared to the freshly prepared electrode in Figure 6c. The surface of the electrode was no longer smooth as compared to the freshly prepared electrode.

In addition, the surface of the prepared electrode showed the existence of voids that were not filled by the element and PVC. The presence of voids in the surface was very important as it increased the porosity characteristic of the electrode for a better electrochemical reaction. Figure 6c and 6d show the presence of voids in the surface of each electrode before and after electrolysis, respectively. The presence of voids in the electrode surface after electrolysis showed that this electrode can be used for further electrolysis process without reducing its efficiency. TEM micrograph of freshly fabricated Co47.5/C47.5-PVC5 powder in Figure 7 indicated that the mixture formed agglomerate of different shapes. The Co particles can be identified due to their almost regular shape while the C was formed in an irregular shape as demonstrated in Figure 7.

The elemental composition of Co47.5/C47.5-PVC5 electrode was determined by using the EDX analysis and the results are presented in Table 3. The results obtained proved that the prepared electrode contained C, Co, and Cl. The presence of Cl elements was due to the use of PVC as a binder in the fabricated electrode. The composition of C for both samples (fresh and after electrolysis) was higher as compared to the Co due to the presence of polymeric carbon chain in PVC. Additionally, no significant changes were indicated by the weight percentage of each element in the fresh electrode and after the electrolysis of synthetic textile effluent. The difference in weight percentage may occur if the precipitate resulted after the electrolysis of synthetic textile effluent. The resulting precipitation was due to the corrosion of anode materials. However, no precipitate was obtained after the electrolysis of synthetic textile effluent. It can be concluded that PVC acts as a good binder agent between C and Co elements inside the electrode.

The surface area and pore size of fresh Co47.5/C47.5-PVC5 powder and after electrolysis of synthetic textile effluent were analysed by using Brunauer-Emmett-Teller (BET) method. The surface area of fresh Co47.5/C47.5-PVC5 and after electrolysis was 2.45 m² g⁻¹ and 6.89 m² g⁻¹, while the pore size was 12.53 to 9.19 nm, respectively. The increased surface area and reduced pore size of the Co47.5/C47.5-PVC5 powder after electrolysis were due to the adsorption of compounds on a solid surface. However, no significant difference was shown by the results obtained from the surface area and pore size of Co47.5/C47.5-PVC5 powder (p > 0.05). The results obtained were consistent with the observations made based on the FESEM micrographs. The pore sizes obtained from this study for freshly prepared Co47.5/C47.5-PVC5 and after electrolysis of synthetic textile effluent were referred to A mesopore type, as mentioned by Chen et al. 34

4. Conclusions

The Co/C-PVC electrode with a composition ratio of 50:50 (known as the Co47.5/C47.5-PVC5) was considered to be the best metal/graphite-PVC composite electrode because it gives the highest decolourisation percentage of aqueous RB21. Optimum electrolysis conditions for the decolourisation of aqueous RB21 by using Co47.5/C47.5-PVC5 powder were determined.

| Element | Before electrolysis | After electrolysis |
|---------|---------------------|---------------------|
|         | Weight (%) Atomic (%) | Weight (%) Atomic (%) |
| C       | 77.37 93.96 | 75.25 91.38 |
| Co      | 19.96 4.94 | 21.23 6.25 |
| Cl      | 2.67 1.10  | 3.52 2.37 |

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Table 3. Elemental composition of Co47.5/C47.5-PVC5 electrode before and after electrolysis of RB21 solution. ([RB21]₀ = 50 mg L⁻¹; [NaCl] = 0.5 mol L⁻¹; t = 45 min; E = 20 V).
PVC$_5$ composite electrode was by using 20 V of applied voltage for 45 min of electrolysis time in the presence of 0.5 mol L$^{-1}$ NaCl solution as a supporting electrolyte. Under the optimum electrolysis conditions, 99.95% of RB21 decolourisation percentage was achieved. The Co$_{47.5}$/C$_{47.5}$-edged PVC$_5$ composite electrode also showed high efficiency in the decolourisation of synthetic textile effluent by using similar optimum electrolysis conditions as mentioned above. This was further confirmed by COD and BOD$_5$ analyses, in which a high percentage of decolourisation was achieved for COD and BOD$_5$ analyses of RB21 solution and synthetic dye effluent. The electrode surface characterisation by using FESEM showed no significant changes in the presence of void on the electrode surface before and after RB21 electrolysis. The presence of voids on the electrode surface after electrolysis showed that this electrode can be used for further electrolysis process without reducing its efficiency. The results obtained for elemental composition by using EDX showed no significant changes in the composition of C, Co, and Cl elements in the prepared electrode before and after electrolysis of RB21 solution. This showed a good bonding between C and Co by using PVC as a binding agent.

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6. Conflict of Interest

The authors declare no conflict of interest.

7. References

1. A. R. Tehrani-Bagha, K. Holmberg, Materials 2013, 6, 580–608. DOI:10.3390/ma6020580
2. N. Ž. Šekuljica, N. Ž. Prlainović, A. B. Stefanović, M. G. Žuža, D. Z. Čičkarčić, D. Ž. Mijin, Z. D. Knežević-Jugović, Sci. World J. 2015, 2015, 1–12. DOI:10.1155/2015/371625
3. V. Lopez-Grima, M. C. Gutierrez, Chemosphere 2006, 62, 106–112. DOI:10.1016/j.chemosphere.2005.03.076
4. N. Nordin, S. F. Mohd Amir, M. R. Yusop, M. R. Othman, Acta Chim. Slov. 2015, 62, 642–651. DOI:10.17344/acsic.2014.1264
5. S. Wijetunga, X. F. Li, C. Jian, J. Hazard. Mater. 2010, 177, 792–798. DOI:10.1016/j.jhazmat.2009.12.103
6. C. R. Holkar, A. J. Jadhav, D. V. Pinjari, N. M. Mahamuni, A. B. Pandit, J. Environ. Manage. 2016, 182, 351–366. DOI:10.1016/j.jenvman.2016.07.090
7. T. Robinson, G. McMullan, R. Marchant, P. Nigam, Bioresour. Technol. 2001, 77, 247–255. DOI:10.1016/S0960-8524(00)00080-8
8. C. A. Martinez-Huitte, E. Brillas, Appl. Catal. B-Environ. 2009, 87, 105–145. DOI:10.1016/j.apcatb.2008.09.017
9. M. Riera-Torres, M. C. Gutierrez, Chem. Eng. J. 2010, 156, 114–120. DOI:10.1016/j.cej.2009.10.006
10. F. Orts, A. I. del Río, J. Molina, J. Bonastre, F. Cases, J. Electroanal. Chem. 2018, 808, 387–394. DOI:10.1016/j.jelechem.2017.06.051
11. J. Luo, Y. B. Wang, D. Cao, K. Xiao, T. Guo, X. Zhao, Chem. Eng. J. 2018, 343, 69–77. DOI:10.1016/j.cej.2018.02.120
12. Z. H. Mussa, F. F. Al-Qaim, M. R. Othman, M. P. Abdullah, J. Latip, Z. Zakria, J. Taiwan Inst. Chem. Eng. 2017, 72, 37–44. DOI:10.1016/j.tjcie.2016.12.031
13. A. A. Najafpoor, M. Davoudi, E. R. Salmani, J. Env. Health Sci. Eng. 2017, 15, 1–11. DOI:10.1186/s40201-017-0273-3
14. M. Jović, D. Stanković, D. Manojlović, I. Andelković, A. Milić, B. Dojićnović, G. Roglić, Int. J. Electrochem. Sci. 2013, 8, 168–183.
15. M. A. Hasnat, J. A. Sañwan, M. S. Islam, Z. Rahman, M. R. Karim, T. J. Pirzada, A. J. Samed, M. M. Rahman, J. Ind. Eng. Chem. 2015, 21, 787–791. DOI:10.1016/j.jiec.2014.04.013
16. N. Nordin, S. F Mohd Amir, Riyanto, M. R. Othman, Int. J. Electrochem. Sci. 2013, 8, 11403–11415.
17. R. Salazar, M. S. Ureta-Zanartu, C. Gonzalez-Vargas, C. D. N. Brito, C. A. Martinez-Huitte, Chemosphere 2018, 198, 21–29. DOI:10.1016/j.chemosphere.2017.12.092
18. S. Alcocer, A. Picos, A. R. Uribe, T. Pérez, J. M. Peralta-Hernández, Chemosphere 2018, 205, 682–689. DOI:10.1016/j.chemosphere.2018.04.155
19. U. Morales, C. J. Escudero, M. J. Rivero, I. Ortiz, J. M. Rocha, J. M. Peralta-Hernández, J. Electroanal. Chem. 2018, 808, 180–188. DOI:10.1016/j.jelechem.2017.12.014
20. D. Rajkumar, B. J. Song, J. G. Kim, Dyes Pigm. 2007, 72, 1–7. DOI:10.1016/j.dyepig.2005.07.015
21. R. El-Palma-Goyes, J. Silva-Agredo, J. Vazquez-Arenas, I. Romero-Ibarra, R. A. Torres-Palma, J. Env. Chem. Eng. 2018, 6, 3010–3017. DOI:10.1016/j.jece.2018.04.035
22. M. R. Cruz-Díaz, E. P. Rivero, F. A. Rodriguez, R. Domínguez-Bautista, Electrochem. Acta. 2018, 260, 726–737. DOI:10.1016/j.electacta.2017.12.025
23. A. K. Verma, P. Bhunia, R. R. Dash, R. D. Tyagi, R. Y. Surampalli, T. C. Zhang, Clean (Weinh). 2015, 43, 767–774. DOI:10.1002/clen.201400256
24. APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Effluents, American Public Health Association, Washington DC, USA, 1981, 525–535.
25. I. A. Sengil, M. Ozacar, J. Hazard. Mater. 2009, 16, 1369–1376. DOI:10.1016/j.jhazmat.2008.04.100
26. R. Galvan-Martinez, M. A. Baltazar, E. Mejia, M. Salaza, A. Contreras, R. Orozco-Cruz, Int. J. Electrochem. Sci. 2018, 13, 9561–9573. DOI:10.20964/2018.10.04
27. S. H. Oliveira, M. A. G. A. Lima, F. P. França, M. R. S. Vieira, P. Silva, S. L. U. Filho, Int. J. Biol. Macromol. 2016, 88, 27–35. DOI:10.1016/j.ijbiomac.2016.03.033
Povzetek
V tej raziskavi smo s tehniko mehanske tvorbe zlitin izdelali kompozitno elektrodo iz kobalta/grafita in polivinilklorida (Co_{47,5}/C_{47,5}-PVC_{5}). Ново elektrodo smo uporabili kot anodo, grafitno paličko pa kot katodo za razbarvanje vodne raztopine C. I. Reactive Blue 21 (RB21) in sintetične tekstilne odpadne vode, ki je vsebovala zmes azo in antrakinonskih barvil. Novoizdelana elektroda je pokazala visoko učinkovitost za razbarvanje RB21 v vodni raztopini (99,95%) in sintetične tekstilne odpadne vode. To smo še nadalje potrdili z visokim deležem zmanjšanja (>75%) KPK in BPK5 pri obeh obdelanih vzorcih. Elementna sestava (C, Co in Cl), določena s FESEM-EDX, ni bila bistveno različna med sveže izdelano elektrodo in po elekrolizi sintetične tekstilne odpadne vode. To je potrdilo visoko mehansko trdnost novoizdelane elektrode in visoko stopnjo vezave med C in Co zaradi uporabe PVC kot veziva.