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Raw fruit juice processing wastewater treatment using electrochemical coagulation followed by synthesis of CuO Nano sorbents using leaf extract

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Abstract: Stainless steel and aluminium electrode was utilized inside batch electro chemicals coagulations (BECCs) using current densities (CD) for the treatment of fruit juice processing wastewater (FJPW). During ECC, ~65-70% color removal and COD removal of ~55-60% was observed for CD 260 A/m2 at 75 min electrolysis time for both 4SS (four stainless steel) and 4Al (four aluminium) electrodes. In general, 4SS and 4Al electrodes had less influence on FJPW for all CDs. Therefore, to improve the quality of treatment of leftover color and COD by BECC treatment, the batch adsorption studies were conducted as secondary treatment by synthesis of CuO nanoparticles using *Carica papaya*, *Centella asiatica* (CA), *Ocimum sanctum* and 1:1:1 mixture of leaves. An effect of several operating parameters like adsorbent dose, pH, and contact duration on leftover color and COD removal was studied for optimal conditions to treat FJPW. The results showed that ~70% color and ~65% Chemical Oxygen Demand elimination at an optimal condition for adsorbent dosages 0.60 g/L, at pH 8.0 to 8.5 and contact time 40 min for CA and 1:1:1 mixture of leaves. Altogether, BECC - nanosorption, a dual treatment, effectively treated FJPW wastewater with clean water reclamations of up to 90%.

Introduction

Water is an all-purpose solvent that sustains life in all living systems. The availability of fresh water for drinking relies on the endless hydrolytic metrological factor of a few regions or nations. India has shown consistency in displaying high output of agricultural production according to the annual report of 2018-19, Ministry of India's Food Handling Industries (Industries and India). India ranks top inside the globe for producing dairy products and fruits like papaya and mango, second with rice and wheat. The agri-based industries are categorized as dairy, pulp and paper, coffee, oil, textile, sugar, food handling/built-up industry, and many more. The sub-sections that come under food processing industries are fruits and vegetables, dairy, meat and poultry handling, grain, fishery, customer food comprising package food, beverage and package drinking liquid, industries etc. discharges effluent mainly comprising of colored materials, organic matter and dissolved solids. In this study, we have chosen the fruit juice processing industry (non-alcoholic beverages) as a part of the food processing industry for treatment using Batch Electrochemical Coagulation (BECC).

The main parameters of interest in fruit juice processing wastewater (FJPW) are pH, color, solids and COD. After post-harvesting, fruits coming from the marketplace generally contain leaves, twigs, trash and soil. They need systematic wash prior to sending the commencing of the juices extraction process. Inside the washing units, a rotatory brush and a great-speed syringe are used for cleaning the fruit. A wastewater ejecting from the units contains debris and wax with a major-suspended solid. The pressing's units consume 0.830 m^3 water per day and

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the effluent release of wastewater by the processing units has a pH between the range of 5.80 to 6.00, COD in the range of 2800.0 to 2900.0 mg/L and settleable solid in between the range of 27.0 to 28.0 mg/L (Em″ke Horváth-Kerkai Mónika Stéger-Máté, 2012). The effluent wastewater has a pH of 5.00 to 6.00, BOD_5 for 56 - 290 mg/L and settling solid 12 - 20 mg/L from the filtration unit using up to 0.20 to 1.80 m^3 water. Container's and bottles cleanings wastewater account for 50.0 to 300.0 mg/L of BOD_5, solid 700.0 to 850.0 mg/L and pH in the range of 6.0 - 9.0 (Sinha et al., 2012; Diane et al., 2004). The water consumption in the bottle and container cleaning process needs 5 to 20 L/day. Since pilot plants will treat various waste streams of FJPW. The electrochemical coagulation (ECC) technology limits the use of a number of unit operations and unit processes for application in domestic wastewater treatment and industrial wastewater treatment facilities cutting off the initial capital costs to a minimum. It also allows us to arrive at a small cost and space footprint, exercising complete control of the design of the units.

Recent studies have shown that using different electrode configurations gives promising results for treating wastewater effluent released from the food processing industry. The present study attempts to eliminate COD from ECC using aluminium and iron electrodes to treat fruit juice wastewater. The results were obtained 52.4% removal using Al electrodes at pH 6.0, CD 200 A/m^2 at 25 min ET and 61.3% COD removal using Fe electrodes at CD 200 A/m^2 at 60 min ET. Al-Shannag et al. (2014) studied Batch ECC treatment for Baker's yeast factory wastewater achieving 85% removal of COD at pH 7.0, stirrer speed 300 rpm, CD 40 A/m^2, ET 60 min using Al electrodes in bipolar series. Dindas et al. (2018) have reported COD removal of 50% at CD 15 mA/cm^2, 180 min ET using iron electrodes for cake industry wastewater. There is very sparse research in the open literature on the treatment of food processing wastewater using bipolar ECCs. Hence, the researchers' objective was to agree to study an electro chemical's degradations level by utilizing 4SS (four stainless steel) and 4Al (four aluminium) electrodes to treat FJPW. Since the electrodes and their combinations failed to treat FJPW using BECC effectively, secondary treatment for complete removal of color and COD from partially treated FJPW was carried using adsorption of synthesized CuO nanoparticles by extracting leaves of *Carica papaya* (CP), *Centella asiatica* (CA) and *Ocimum sanctum* (OS). In India, CP, CA and OS are abundantly available and can be regenerated and used as a coal for further energy recovery. Synthesis of nanomaterials on hard substrates serves as 'Nano sorbent' with higher adsorptions capability due to the larger outer surface dimension compared with traditional adsorbents like granular activated carbon (Katubi et al., 2021).

The following chemical reactions occur During the ECC process (equation 1-4). Here M shows an electrode material and n shows the number of electrons. The general reactions during the ECC process are shown through equations (1) - (4) with M as an electrode material and n-numbers of electrons. In a bipolar configuration, a metal ion produced near the anode face reacts with a hydroxyl ion produced near the cathode face to make metal hydroxides in the wastewater.

At anode/anode face:

$$Metal_{(s)} \rightarrow Metal^{n+}_{(aq)} + n^- \quad \ldots\ldots(1)$$

$$2.0H_2O \rightarrow 4.0H^+ + O_2 + 4e^- \quad \ldots\ldots(2)$$

At cathode face:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \quad \ldots\ldots(3)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \ldots\ldots(4)$$

Zema et al. (2019) has confirmed that Sustainable monitoring systems for citrus remnants must still be properly standardized and improved for the citrus manufacturing sector's existence and growth; several of these systems would enable converting this raw material into useful assets. The systematic incorporation of technology was critical to the performance among the most advanced CPWW monitoring systems on a wide scale and procedures to retain by-products like- flavonoids, pectin, and aromatic water along with those directing for manufacturing the "major" product as orange juice.

Anjum et al. (2019) described all possible expansions in nano-technology for wastewater treatment and discoursed use of numerous nanomaterial types in wastewater treatment methods. The first is nano adsorbents, including carbon nanotubes, zinc oxide, graphene, activated carbon,

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manganese oxide, ferric oxides, titanium oxides, and magnesium oxide which are commonly used to remove heavy metals from wastewater. Secondly, nano-catalyst, including photocatalysts, electrocatalysts, Fenton-oriented catalysts, and chemical oxidants, were seen in the ability to remove all inorganic and organic pollutants. Thirdly, carbon nanotubes membrane, electro-spun nanofiber, and hybrid nano-membrane have been utilized to effectively remove dyes, heavy metals, and foulant. Lastly, the potential for water disinfection was addressed by combining nanoscience with biological systems like algal membrane bioreactors, anaerobic digestions, and microbial fuel cells.

Jing et al. (2020) explained the modern sign that Electrocoagulation was an auspicious process for treating and reprocessing mineral treating wastewater. Guided for sewage treatment in sectors like manufacturing, foods, and petrochemistry, electrocoagulation (EC) was used for the 1st time in the literature for investigating their effectiveness in the wastewater treatment from a Pb/Zn sulfide mineral flocculation project via the primary Chemical oxygen demand with 424.290 milligram/Litre as well as its impact for water reuses. The findings suggested that the Electrocoagulation method could create additional possibilities for reusing mineral's processing sewage. The given research added to our understanding of how the mining industry deals with wastewater and is useful for both environmental and economic terms. The present study is an attempt to optimize the process for the treatment of wastewater generated by the fruit juice processing unit by using electrochemical coagulation followed by the synthesis of CuO nano sorbents from leaves extract (Atri et al., 2023).

Methodology

Design

The electrochemical reactors (ECR) were designed and fabricated using organic glass to have a cuboidal shape by the efficient volumes for 1.5 Litre. Metal sheets 1mm thick were cut off from stainless steel (SS 304 grade) and aluminium (Al) sheets to rectangular shapes with 150 x 140 x 130 mm dimensions and 1 mm thickness. The electrodes were placed in parallel having 20.0 meter^2/meter^3 surface areas per volume (SA/V) from the inter-electrodes arrangement for 10.0 millimeters maintained in the ECR by a lead copper wire connected with a Direct Current energy supplying unit using crocodile clips in bipolar mode. A digital magnetic stirrer (REMI 2MLH) set at a rotation speed of 400 rpm was used to stir the bulk solution in the ECR during treatment inductively. Electrode plates are cleaned for scaling and oxide onto their exterior by means of 15.0 percent HCl acid, washed spending purified water, dehydrated and formerly used for BECC experiments after each use.

Sample

The chemicals required for water quality parameters like $K_2Cr_2O_7$, $KMnO_4$ and Sodium Molybdite (Na_2MoO_4), were analyzed using methodical reagents ranking procured from HiMedia laboratory at Mumbai in India. The Chemical Oxygen Demand and another contaminant/pollutant were removed from raw FJPW by applying the BECC experiment, which was carried out at an ambient temperature of 25–28°C using a 4SS and 4Al electrode. The First experimental set, 4SS electrodes followed by 4AI electrodes, was used. The ECC-treated samples (about 2 to 3 mL) were collected at predetermined intervals during an experiment, cleaned over by Whatman-42.0 grade filter papers, and analysed for various water quality parameters. All BECC experiment runs lasted for 60-75 min of electrolysis time (ET).

Instrument

Parameters to detect water quality are analyzed by utilizing numerous instruments and equipment next to the procedure inside a APHA guideline (Baird et al., 2017). pH indication is calculated by utilizing in Lab WTW pH-meters (Model: H400, Mettler Toledo, India), colored via Platinum-Cobalt's process and Chemical Oxygen Demand through locked reflux process utilizing digester units (Model: DRB 200, HACH, USA). An electric transmission and all dissolving solid values were dignified by utilizing MH Digital-TDS/EC's meter. Nitrate, phosphate, and sulphate were measured using UV-Visible spectrophotometer (Model: UV-VIS VARIAN 50 BIO, USA). The synthesized CuO nanoparticle was considered from Scanning Electron

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Microscopes (SEMs) (Model: SU3500, Hitachi, Japan) and UV-ViS at 200 to 600 nm absorption range. The confirmation of CuO nanoparticles formed was obtained from Energy Dispersive X-Ray's Analysing (EDAXs) spectrums.

Data Collection

Sample formation and characterization of raw FJPW

FJPW used in the experiments was collected from a local non-carbonated beverages and energy drinks production private limited company. In each sampling, 20 - 25 L of raw untreated wastewater was collected from the equalizations tanks just before entering an effluent treatment plant (ETPs) and stored in the polymer cans in preservation. The first raw FJPW feature utilized for a BECC is displayed in Table 1.

Table 1. Physio-chemical characteristics of raw/actual fruit juice processing wastewater

S. No.	Characteristic	Units	Parameter's Values
1	Electrical Conductivity (EC)	mS/cm	1.10-1.40
2	Color	PCU	900-1100
3	pH	-	6.67-7.14
4	Total Solid (TS)	mg/L	220-370
5	Total Alkalinity (TA) as $CaCO_3$	mg/L	740-880
6	Total Suspended Solid (TSS)	mg/L	680-1020
7	Total Hardness (TH) - $CaCO_3$	mg/L	280-340
8	Chlorides	mg/L	900-1400
9	Total Dissolved solid (TDS)	mg/L	2990-3630
10	Biological oxygen demands (BOD_5)	mg/L	278-296
11	Chemical oxygen demands (COD)- mg/L of O_2	mg/L	1100-1210
12	COD/BOD	Ratio	3.95-4.08
13	Nitrate	mg/L	115-148
14	Phosphate	mg/L	105-120
15	Sulphate	mg/L	7-7.5
16	Cl^-/SO_4^-	Ratio	125-185

Adsorbent material

Fresh leaves of *Carica papaya* (CP), *Centella asiatica* (CA) and *Ocimum sanctum* (OS) were collected locally from Bengaluru, India and are systematically washed away numerous times to remove dirt material. Further CP, CA and OS were used as nanosorbents to treat treated FJPW.

Preparation of extract for phytochemical analysis

The collected leaves were washed using distilled water, dried and crushed into a fine powder (0.2 – 0.5 mm particle range). 10 g of powdered leaves were soaked overnight into 100.0 ml of distillate water each, stirring till 30 minutes and after that, centrifugation for 10 minutes at 2000 revolution per minute. Supernatants were filtered by utilizing Whatman filter paper No.1 and filtered solutions were used to determine phytochemical analysis. Important phytochemical constituents like alkaloids, flavonoids, phenols, reducing sugar, tannins and amino acids were present in all the three leaves samples.

Preparation of leaf extract for the synthesis of CuO nanoparticles

Based on phytochemical analysis results, all three CP, CA and OS leaves were selected for the synthesis. The leaf was washed systematically with distillate water, cleaned, desiccated in a dark room doe 5 – 6 days and then crushed into fine powder. In this study, four samples were synthesized for the analyses **1.** CP, **2.** CA, **3.** OS, and **4.** 1:1:1 mixture of all three leaves. The synthesis was carried out using 5 g powdered leaves, weighed, and each plant's powdered leaves were mixed thoroughly and taken in 1:1:1 ratio. The powdered leaves (5 g) are boiled in 50.0 ml of double distillate water for 5 to 7 minutes. The mixtures were cool at room temperature and filtered through a Whatmann's filter papers and the extracts were stored on 4^0C as a stock for preparing CuO nanoparticles.

Synthesis of CuO Nanoparticles

Twenty-five (25) ml aqueous leaf extractions were added with 100.0 ml of 1.0 mM cupric sulfate solution, agitated, and incubated for 24 hrs. The color change indicates the formation of CuO nanoparticles. CuO nanoparticles using OS and the mixture of leaves extract indicated by color changing

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from blue to dark brown. For CP and CA, the color changed from light blue to pale brown and to brown precipitation, respectively. By repeated centrifugations on 8000 revolutions per minute for 15 minutes, the extracted materials were washed in double distillates water, the supernatant was discarded and sediment was collected, dry in an oven with 110.0°C for 3 - 4 hours and stored for future use.

filter paper filtration before being analyzed at the prescribed time intervals. The sample CP, CA, OS, and a 1:1:1 mixture of each, were used as inexpensive nanosorbents in a batch adsorption study to investigate the effects of pH on removing residual colors and Chemical Oxygen Demand. In a conical flask, Batch's adsorption test was demonstrated, and the pH of the wastewaters was adjusted using NaOH and HCl. Conical flasks

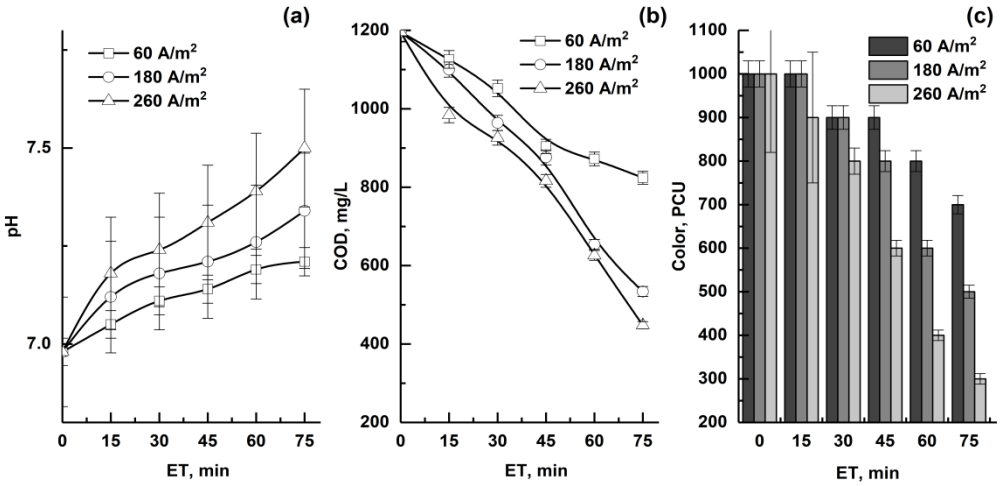

Figure 1. (A) pH, (B) COD and (C) Colour Removal using 4SS Electrodes as A Function of CDs 60 – 260 A/M2 Up To 75 Min ET

To study the optimum condition for the synthesis of CuO nanoparticles, the experiments were carried out at various concentrations of cupric sulfate using 1, 3, 5, and 7mM concentrations at pH 4, 5, 6, 7 and 8. Using 0.10 Normal sodium hydroxides and 0.10 Normal hydrochloric acids, the pH of the reaction mixture was adjusted and the effect on these parameters was monitored by UV-ViS spectrophotometer.

Data Analysis

Following the synthesis of adsorbents, batch adsorptions were studied to determine how pH, contact time, and adsorbent dose affected the removal of color and COD from partially treated FJPW. The adsorption test for each batch was carried out at room temperature. Initially, 100 ml of treated FJPW sample was taken in a conical flask for batch adsorption tests. The adsorbents were added, and the desired pH and contact time (CT) were maintained. To ensure the equilibrium is reached, batch adsorption experiments were conducted over a 2-hour CT period at a constant speed of 120 ± 5 rpm, pH 5, and room temperature of 27 ± 0^0C. The wastewater samples underwent 42-grade Whatman's

containing 100 ml of wastewater sample were filled, sealed with cotton plugs, and stored in a water bath shaker set to agitate at a speed of 130 to 150 rpm. After each run, wastewater samples were examined and analyzed for colors and COD removals using an optimal dose of 0.5 g/L CA as an adsorbent. The studies with the other three nanosorbents, CA, OS, and 1:1:1 mixture, were conducted repeatedly.

Result

The initial characterization of FJPW was analyzed and the batch ECC was carried out using 4SS and 4Al electrodes at applied voltages of 12, 18V and 24V with corresponding CDs of 60, 180 and 260 A/m^2.

Influence of current density on 4SS electrodes on FJPW

The effect of CD treating FJPW was explored over a cell voltage of 24, 18 and 12 V having equivalent to CD range 60 – 260 Ampere/m^2 for wastewater having initial characteristics pH_o: 6.98, $Color_o$: 1000 PCU, COD_o: 1196 mg/L and agitation speed: 400 rpm.

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Figure 1 represents pH values, COD and color removal for 4SS electrodes at CDs 60 − 260 A/m^2 and 75.0 minutes ET. pH for a bulk's solutions in 4SS electrodes were increased only by 0.5 to 0.7 pH units as the ET increased because OH^- ions partially buffered ferric hydroxide forms. The pH of the solution was 6.98, which increased to pH 7.21, 7.34 and 7.56 for 60, 180 and 260 A/m^2 at 75 min ET as shown in Figure 1 (a). CD 60 A/m^2 show less Chemical Oxygen Demand elimination in 824 milligram/Litre at 75 min ET from its initial value 1196 mg/L because low-charge M^+ ions have no power for picking negatively charged colloidal particle inside the solutions for forming floc precipitate (Oncsik et al., 2014). Figure 1(b) shows COD degradation during electrolysis using 4SS plate electrodes for CDs 180 and 260 A/m^2 at 75 min ET, recording maximum COD removals of 534 mg/L (55%) and 448 mg/L (62.5%). While using 4SS electrodes, the COD removals were inconsistent and showed lesser removal efficiency at 75 min ET. Since, the treatment efficiency is mainly affected by charge loading at optimum ET, there was not much charge loading observed in treatment and there was a generation of liniment-type layers over an anode on neutral pH. Figure 1 (c) shows ECC degradation curves for color using 4SS electrodes. At CD 60 A/m^2, the color removal was less, showing the values of 700 PCU. As the electrolysis proceeds, color removals were less and in turn, the system added color during the experimental run in CDs 180 A/m^2 and 260 A/m^2 showing color of 500 and 300 PCU at 75 min ET. This is because Fe dissolution results in a larger volume of sludge and makes the solution murkier (Golder et al., 2007). In general, 4SS electrodes had less influence on FJPW at all the CDs showing <70% removal efficiency in color and <55% in COD removal. For the entire experimental runs using 4SS, sponge a black-green color gel designed on an ECR, at a top or edge of the electrode near a negative end since iron oxides deposit onto a positive part of SS electrode face (Li et al., 2013). Fighting corrosion is large, whereas via SS electrode over an anode faces recognized near great chlorides values (900 - 1100 milligram/L) inside raw FJPW. Likewise, zone corrosions were detected though by means of 4SS electrodes in combination with more active sites on the face of the electrodes.

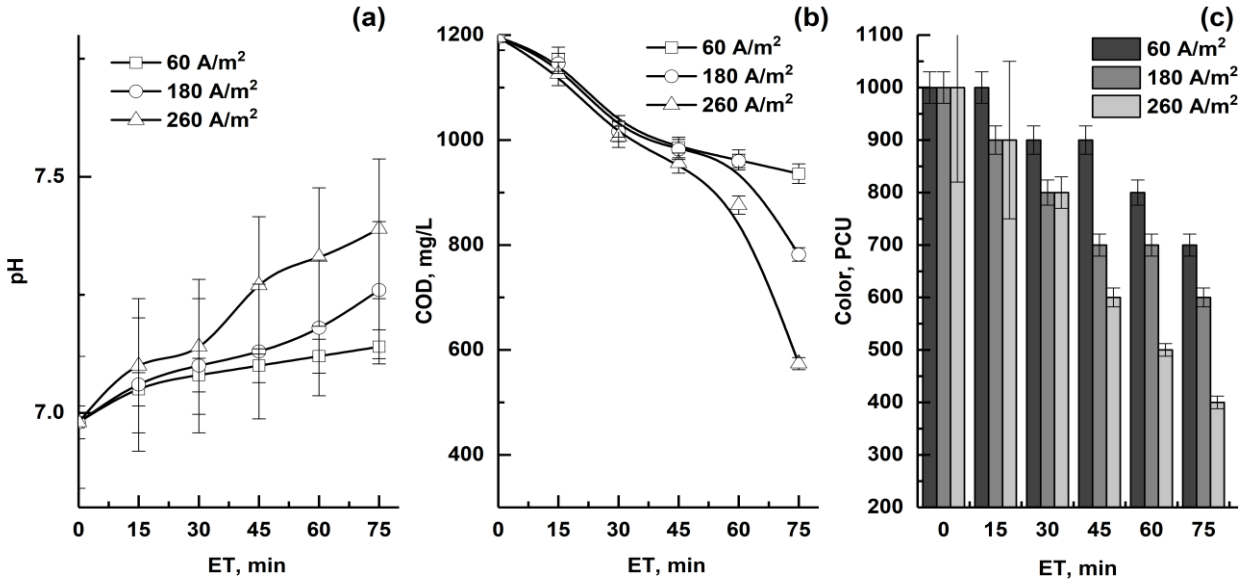

Figure 2. (a) pH, (b) COD and (c) Colour removal for 4Al electrodes as a function of CDs 60, 180 and 260 A/m2 up to 75 min ET

Influence of current density on 4Al electrodes on FJPW

Figure 2 represents pH values, COD and color removal for 4Al electrodes for 60−260 A/m^2 and 75.0 minutes ET. A pH for bulk solutions in 4Al combinations also showed not much increasing trend throughout the ET, as displayed in Figure 2 (a). A pH in a bulk solution in 4Al combinations astonishingly showed lesser pH values than 4SS

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electrodes. This may be because hydrolysis of Al was expected above pH 7 but due to gel formation at the anode (1st electrode), Al3+ ion transfer slowed down the increase in pH (Yılmaz et al., 2018), resulting in lesser treatment efficiency. The pH_o of the solution was 6.98, which increased to pH values of 7.14, 7.26 and 7.39 values at 75 min ET. Figure 2 (b) shows the COD degradation during BECC using 4Al electrodes for CDs 60, 180 A/m^2 and 260 A/m^2 at 75 min ET, recording maximum COD removals of 936, 782 and 574 mg/L at 75 min ET by their first values of 1196 milligram/Litre. The ECC degradation curves for color using 4Al electrode combinations at 75 min ET for 4Al electrodes for CDs 60, 180 and 260 A/m^2 color removal were observed as 700, 600 and 400 PCU as shown in Figure 2 (c). The same trend continued in 4Al electrodes showing ≤ 60% removal efficiencies. Chemical Oxygen Demand and color removal show the declining trends in 4Al electrodes due to dissolutions in Al oxide does not have few flocs inside an ECR in removing like scums.

parameters. Therefore, the electrodes were changed to 2SS-2Al (two stainless steel – two aluminium) and 2Al-2SS (two aluminium– two stainless steel) combinations for the treatment of FJPW with the same operating conditions. Even after a different number of experimental runs, the removal efficiency was < 50% with 2SS-2Al and 2Al-2SS electrodes. Therefore, it was inevitable to adopt the secondary treatment method as adsorption by synthesis of CuO nanoparticles using CP, CA and OS leaves as low-cost nanosorbents.

Effect of Cupric Sulphate on synthesizing CuO nanoparticle

Effects due to cupric sulphate ($CuSO_4$) concentrations over production of copper oxides (CuOs) nanoparticles by utilizing a leaf for CP, CA, OS and 1:1:1 mixture of leaves was analyzed with the help of a UV-visible spectrophotometer. $CuSO_4$ is used as a precursor for CuO's nanoparticle. For synthesis of CuO's nanoparticle utilizing leaves extracts for CP, CA, OS and 1:1:1 mixture of leaves was analyzed for 1mM, 3mM, 5mM and 7mM

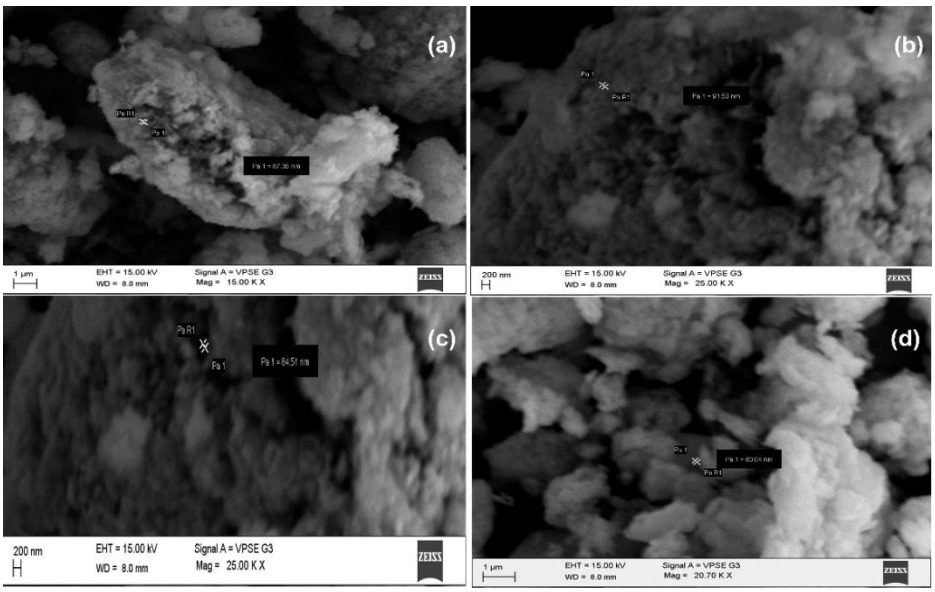

Figure 3. SEM's Image for CuO's Nanoparticle of Leaves Extracts

A major goal for the examination is to remove color, COD and solids pertaining to prescribed standard limits. The analyses were also carried out for total dissolved solids at 75 min ET. The solids removal from both electrodes showed less than 40% removal at 60, 180 and 260 A/m^2. Thus, it was concluded not to conduct other water quality parameters analysis as 4SS and 4Al electrodes are not well suited to remove the main water quality

concentrations. For 1mM concentration of $CuSO_4$ the characteristic UV-ViS bands were observed at 365 nm, 355 nm, 380 nm, and 365 nm respectively. Similarly, for 7mM concentration of cupric sulphate, UV-ViS bands were 380 nm, 370 nm, 395 nm, and 380 nm respectively. It is detected that absorption increased as elevated inside the $CuSO_4$ concentrations. Figure 3 shows the UV spectrum at 7mM concentration of $CuSO_4$ concentration of all

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four leaves extract. Operating conditions: ECR: 1.5 L; Electrode arrangements: bipolar; pH_0: 6.98, $color_o$: 1000 PCU; COD_o: 1196 mg/L; No. of Electrodes: four; agitation speed: 400 rpm

Since, the synthesis of CuO nanoparticles gradually increased as the concentration of $CuSO_4$ and plant extract increased, the 7mM concentration of $CuSO_4$ was found to be optimum. The formation of CuO nanoparticles was observed by the absorption spectra between 380nm - 395nm.

However, the maximum results or the synthesis of CuO nanoparticles were obtained at the neutral pH. We can conclude that optimum pH 7 is suitable for CuO nanoparticle synthesis. The same procedures were repeated for CP, CA, OS and 1:1:1 mixture.

Figure 4 shows the UV spectrum at pH 7 of all four leaves extract. Decreasing the OH^- concentration of the extract changes the surface charges on the nanoparticles. Because of this maximizes repulsion or interaction and enhances

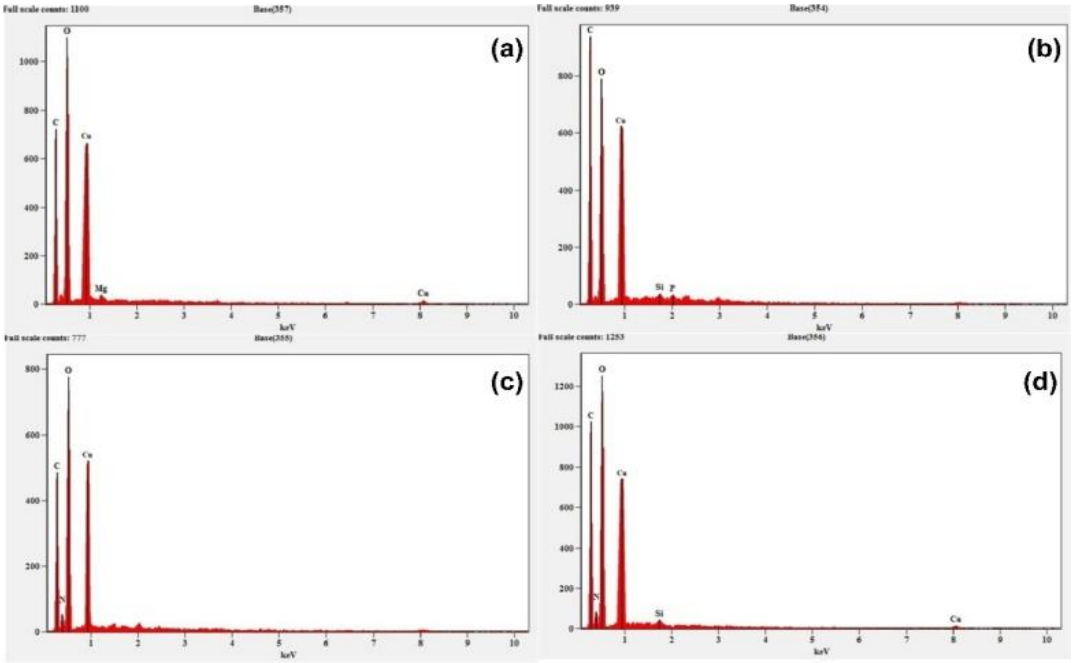

Figure 4. EDAX Image for CuO's Nanoparticle Synthesized by Utilizing Leaves Extracts

Effect of pH on synthesizing CuO's nanoparticle

The maximum synthesizing CuO's nanoparticle was obtained at pH 7. The pH of the solution (50 ml of 7 mM cupric sulphate solution + leaves extract) was 6.7, as shown in Figure. 4.

stability (Hartland et al., 2013). At higher pH, copper ions in solution partly hydrolysed to form bio-organic $Cu(OH)_x$ complex onto a surface over particles (Barakat, 2011).

A SEM's image (Figure S1 – a, b, c and d) clearly

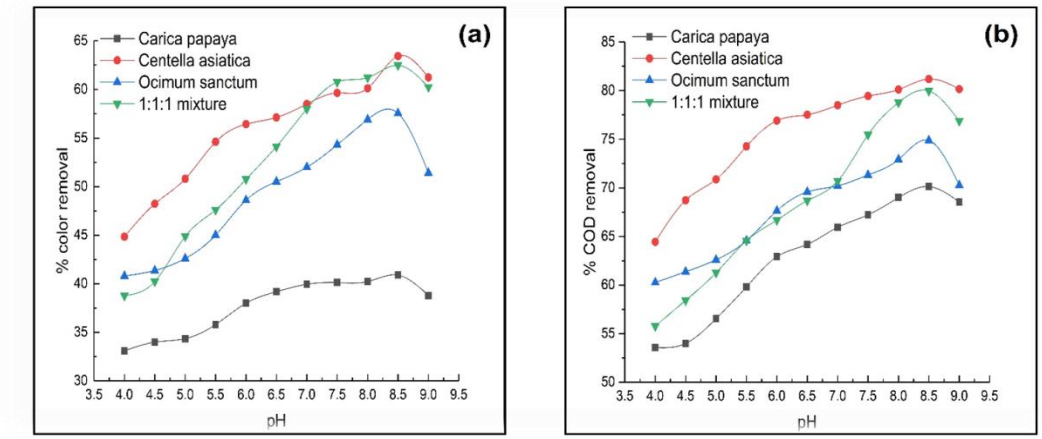

Figure 5. Graphical representation to show the effect of pH on (a) % Colour Removal and (b) % COD Removal using CP (Black), CA (Red), OS (Blue) and 1:1:1 Mixture (Green) as Nano sorbent

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indicated that the formation of CuO nanoparticles from leaves extracts of CP, CA, OS and combination of leaves was within 100nm. The EDAX spectra images (Figure S2 – a, b, c and d) indicate that CuO nanoparticles were synthesized using leaves extract of CP, CA, OS and a combination of leaves.

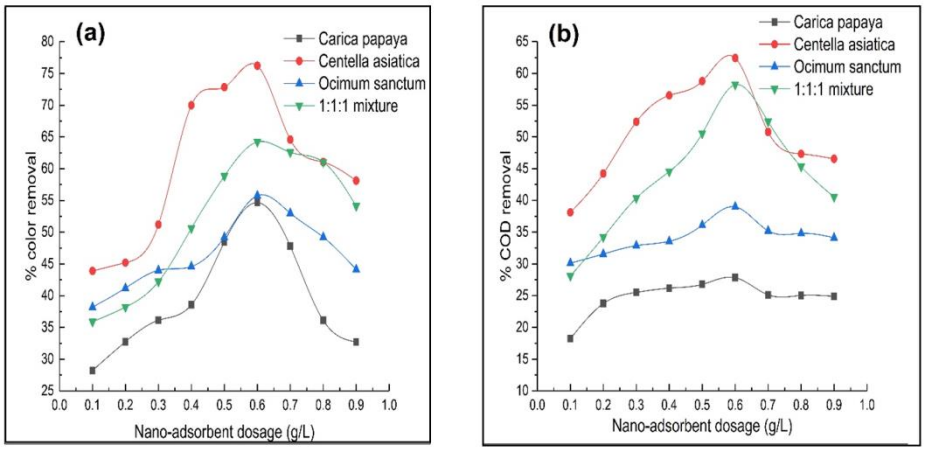

Figure 6. Graphical representation to show the effect of Nano-adsorbent dosage (g/L) on (a) % Colour Removal and (b) % COD Removal using CP (Black), CA (Red), OS (Blue) and 1:1:1 Mixture (Green) as Nano sorbent

The secondary treatment was initiated for the partially treated FJPW by BECC. Since, BECC could remove only ~65 - 70% of color and ~55 - 60% COD removal; ~35% color and 45% COD remained in solution. The leftover color and COD removal was completed by synthesized CuO nanoparticles using CP, CA, OS and 1:1:1 combination of leaves.

Effects of pH for the removing colors and Chemical Oxygen Demand elimination

pH was one of the major operating parameters in the adsorption process (Iftekhar et al., 2018). The partially treated FJPW was adjusted to pH between 4.0–9.00 utilizing 0.10 Normal sodium hydroxides and 0.10 Normal hydrochloric acids to observe a Nano sorbents affinity towards alkaline and acidic region.

Figure 5(a) shows that increased pH displayed increased color, removing efficacy to CA, OS and 1:1:1 mixture. Less color removal efficiency was observed in CP leaves extract because CP leaves are acidic in nature. Like a pH increase, a nanoparticle surface became a positive charge and revolting effects occurred, thus the removal efficacy decreased. Colour removals are great inside an alkaline range between pH range 8 to 8.5 for CA, OS and 1:1:1 mixture nanosorbents. CA obtains the greater color elimination of ~63% and 1:1:1 mixture, whereas 57.54% is for OS and only 41% is for CP nano sorbent. It is found that COD removal did not essentially synchronizes by concurrent color decrease through adsorption.

COD uptake is seen to be lower at extremely high or low pH levels (Ruan et al., 2004). At pH 8.5, the maximum COD removal of almost 80% was observed utilizing CA and a 1:1:1 combination as nano sorbent, as shown in Figure 5(b). A plot demonstrates that the first proportion of COD removal is higher. Adsorption does, however, almost come to an end and reach equilibrium when pH rises. In all four nano sorbents, the removal efficacy begins to decline with a rise in pH values after pH 8.5. The adsorbent surface is more positive at optimal pH, which increases the adsorption rate; this condition was shown in CA at pH 8.5. The maximum COD removal at pH 8.5 was determined to be 74.88% using OS as an adsorbent and 70.12% using CP as an adsorbent. Due to the repulsion between the adsorbent surface and the existence of a partial negative charge on adsorbents, there was a modest drop in adsorption after pH 8.5 (Wang et al., 2020). Adsorption at an alkaline pH resulted in a higher percentage of COD removal than color because the required coagulants produced act with the OH- ions to precipitates that facilitate COD removal by adsorption and flotation.

Effects of adsorbent's dosage on color and Chemical Oxygen Demand elimination

The adsorbent's dosages are among the major operational parameter that determines the capacity of

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the adsorbent to remove the pollutant from wastewater. The nanosorbent dosages varied from 0.1 - 0.9 g/L for secondary treatment of partially treated FJPW. A plot of (a) colours and (b) Chemical Oxygen Demand removals against a dose for CP, CA, OS and 1:1:1 mixture is shown in Figure 6.

Figure 6(a) shows that the highest color removals are obtained on the adsorbent's dosage for 0.60 gram/Liters of all four nanosorbent dosages. The highest color removal of 76.22% was obtained for CA leaves. The active site's number was greater on the lowest adsorbent dosages. By an increase in adsorbent's dosages, particle aggregations occur as an outcome of that removal efficacy increase. Higher and lower adsorbent dosages show fewer color removals by a bulk solution.

removal (62.12% at 0.6 g/L nanosorbent dosage) of the three adsorbents. Similarly, higher COD removal percentages were observed as 26.78%, 36.12% and 58.22% for CP, OS and 1:1:1 mixture, respectively.

It was analyzed that the elimination percentage for colour and COD decreased after 0.6 g/L nano sorbent dosage. This is surmised that tenancy for pore over surfaces for adsorbents and a reduced driving force to transfer mass (Patel, 2019).

Effect of Contact time using CP, CA, OS and 1:1:1 mixture as nanosorbent

The contact time in nanoparticles plays the most important part in most wastewater treatment methods. Figure 7(a) shows colour elimination against connection duration with an operational condition at optimum pH 8.5, an optimum dosage of

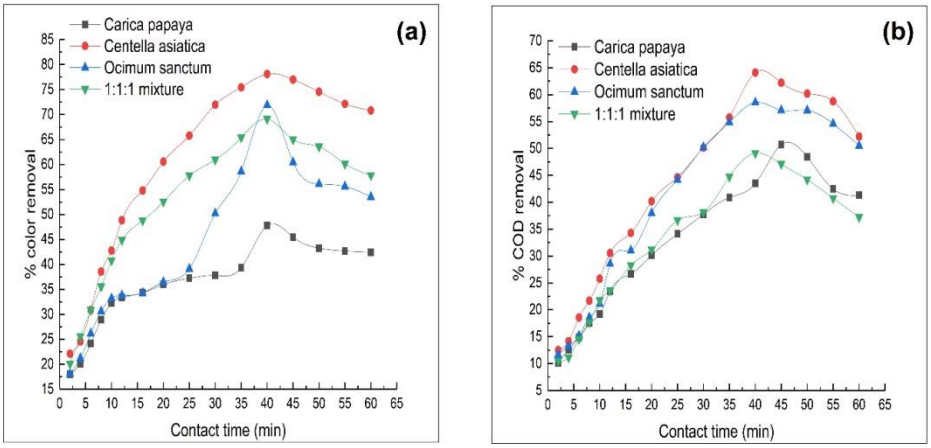

Figure 7. Graphical representation to show the effect of Contact time (min) on (a) % Colour Removal and (b) % COD Removal using CP (Black), CA (Red), OS (Blue) and 1:1:1 Mixture (Green) as Nano sorbent

From the obvious Figure 6(b), the percentages elimination of COD also increases significantly at adsorbent's dosages for 0.60 gram/Litre. The availability of more sorption sites and the increase in the sorption surface led to an increase in the percentage of COD removal (Nayl et al., 2017). The efficacy of COD removal increased during the first five doses, and from then on, the percentage of COD removal declined, which can be attributed to a decrease in the effective adsorptive surface area with dosage and the presence of residual nano sorbent in the solution (Bayuo et al., 2019). When compared to the other three Nano sorbents, CA's ability to adsorb more COD with a given amount of adsorbent resulted in greater efficiency of COD removal. The CA was found to have the highest percentage COD

0.60 gram/Litre with varied association duration. It is obtained that extreme colour removals for 78.2% are attained by using CA nano sorbent in a contract duration of 40 min. The higher and lower contact times showed lesser color removal in all four nano sorbent. This is because of quick adsorption because electrostatic's attractions are monitored from slower contaminant adsorption on nanoparticle surfaces from complexations (Kaur et al., 2023). Both OS and 1:1:1 mixture also showed good color removal efficiencies of ~70%. This is ascribed as at the optimum dosages because an increase in empty place adsorptions and free electron degrades quickly and achieves equilibrium. While using CP, nano sorbent color removal was observed to be less when compared to the other three adsorbents. This is

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because at the point when an exterior active site in adsorbents was enclosed entirely, a degree of adsorption reached an equilibrium bringing less adsorption.

From the Figure 7(b), it is found that at 40 min contact time, high Chemical Oxygen Demand removes efficacy is witnessed for a CA and Chemical Oxygen Demand removals efficiency was observed at 64.2% by the initial's Chemical Oxygen Demand concentrations for 486 milligram/Litre. They could be got by the diagram that at 40.0 minutes CT, the adsorption capacity of the adsorbent was found to be maximum, beyond which there was not much significant increase in an adsorption's capability of an adsorbents. Surmised as this is an equilibriums duration for a batch's adsorptions experiment, adsorptions were not affected away from contact duration for 40.0 minutes (Chowdhury et al., 2009). At 50 min CT, a higher COD removal efficiency was observed, achieving 50% COD removal when using CP as an adsorbent. This phenomenon's likely causes include an adsorptive coagulation mechanism that reached equilibrium at 50 minutes. The maximal COD removal efficiency in OS and 1:1:1 combination was found to be 58.56 and 49.10% at 40 min of contact time, respectively, and afterward, it began to decline. It was evident that the rate of adsorption increases as contact time increases. Adsorption reduces as equilibrium is reached because fewer unoccupied sites are available for adsorption during the initial rapid phase (Robinson et al., 2002). They could be saw by a diagram that on 40.0 minutes for contact time, an adsorptions capability in adsorbents is found to be maximum for CA.

Regeneration of CuO nanosorbents

The regeneration of CP, CA, OS and 1:1:1 mixture as nanosorbents were carried out to validate 3R's (reduce, recycle and reuse) theory. In all four nanosorbents, 25 - 30% CuO was lost after using 5 - 10 cycles of batch adsorption. The nanoparticles were again tested for colour and Chemical Oxygen Demand elimination efficiency. This further reduction of 17% colour elimination and 13% Chemical Oxygen Demand removals efficiencies are observed using CA and 1:1:1 mixture nanosorbents. In contrast, CP and OS showed < 7% color and COD removal efficiencies after 5 - 10 cycles of usage.

Conclusion

The effect of CD treating raw FJPW was explored for CDs 60 – 260 A/m^2 using 4SS and 4Al. During BECC, the color and COD removals were reduced during the experimental run showing color removal by 60 to 70% and COD removal by 62.5% and 52% CD 260 A/m^2 on 75 minutes ET for both 4SS and 4Al electrodes. In general, 4SS and 4Al electrodes had less influence on FJPW for all CDs showing ~65% color and ~55% COD removal efficiency. Therefore, studies were carried out by changing 2SS-2Al and 2Al-2SS electrode combinations for further treatment of FJPW. Even after different experimental runs, the pollutant removals were <50% even with 2SS-2Al and 2Al-2SS electrodes; hence, changing the treatment type and initiating adsorption as a secondary treatment was inevitable. Therefore, this could be determined that ECC treatments are efficient for treating FJPW.

The batch's adsorptions study was done on removing color and COD for partially treated FJPW as secondary treatment using the synthesis of leaves as low-cost nanosorbents such as CP, CA, OS and 1:1:1 combination of leaves. An effect in several operational parameters like pH, adsorbent dose, and CT onto leftover color and COD removal were studied for the optimal conditions to treat FJPW completely. The optimal adsorbent dosages were 0.6 gram/L in color and COD removal at optimum pH of pH 8.5. An optimal interaction duration of 40 min is initiated to at maximum for CA with ~70% color and ~65% COD removal. Therefore, CA and 1:1:1 leaves mixture nano sorbent can eventually be used lower value adsorbents to eliminate color and COD. An overall removal of color and removal using BECC as well as CuO nanosorbents was found to be <90%. This study is presumed useful in bringing color and COD within the prescribed standards and developing the dual treatment by adopting ECC as primary and synthesis of new low-cost nano sorbent as a secondary treatment of different industrial wastewaters.

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Conflict of Interest

The authors declare that the authors have no conflict of Interest among them.

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