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Synthesis of Meso Active Carbon & Fenton oxidation for Removal of Copper and Environment Impact of Electroplating Wastewater, Kinetic Study

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Abstract

Heavy metals are one of the most serious environmental pollutants in water; they caused serious damage to animals and human lives. The electroplating industry generates a high portion of the effluents, which are highly toxic and can be considered a dangerous material pollutant. The current investigation contracts to remove Cu (II) from electroplating industrial wastewater as well as eliminate environmental impact of that effluent. The wastewater was characterized by low pH (3.2), high chemical oxygen demand (COD, 650), ammonia (4.72), total suspended solids (TSS, 312), TKN (13), TDS (3500) and Cu (1200). As a result, the layout and functionality of treatment plants require careful handling of the wastewater generated by the electroplating industry. Traditional treatment processes for that waste remain ineffective in meeting the necessary boundaries of the national regulatory standard. Meanwhile, such wastewater contains resistant and toxic compounds that require extensive work. The present work used Fenton's reactions and/or meso-active carbon for the treatment of the final electroplating effluent and removal of Cu as a substitute for traditional treatment procedures. The prepared Meso active carbon was characterized by different techniques as XRD, BET-surface area and FT-IR. The obtained results reveal that, cu removal present 91%, BOD 98%, COD 82%, TSS 78%, TDS 54%, TS 40%, TKN 87%, ammonia 97%. The results indicated the good quality of the treated effluent with Permissible values for wastewater and can be reused for irrigation wood trees.

Keywords: Electroplating Industry, Meso Active Carbon, Fenton oxidation, Electroplating wastewater.

Introduction

Industrial effluent containing heavy metals is mostly generated by various metal industries, as that produces from pesticides, metal surfaces, electroplating, metal surface treatment, mining, fertilizer, tanneries, batteries, thermoplastics, and pigments [1 - 3]. In addition, milling, etching, anodizing-cleaning, conversion-coating and electrolysis depositions [4]. The production of printed circuit boards (PCBs) is a noteworthy additional source of heavy metal wastes. The most popular resistant over plates are made of tin, lead, and nickel solder. The production of inorganic pigments, which results in pigments containing chromium compounds and cadmium sulfide, the petroleum refining, which produces conversion catalysts contaminated with nickel, vanadium, and chromium, the photographic process, which results in film with high concentrations of silver and ferro cyanide, are additional sources of the metal wastes [5]. The above chemical industry produce large amounts of heavy metal-containing effluent as Zinc, copper, nickel, mercury, cadmium, lead chromium, vanadium, platinum, silver, and titanium are regarded as hazardous metals that should be particularly avoided while treating wastewater.

Each of these industries generates a significant amount of residues, sludge, and wastewaters that fall under the category of hazardous wastes that need to be thoroughly treated. Particularly in developing nations, these sectors release wastewater and heavy metals into the environment either directly or indirectly. They tend to accumulate in living organisms because they are poisonous and non-biodegradable. As a result, they contribute to a wide range of illnesses. Thus, to improve the water quality, it is now necessary to treat industrial wastewater that contains heavy metals [6].

Heavy metals, which are hazardous to living things at relatively low concentrations and have a tendency to either biologically magnify or accumulate in plant and animal systems, are among the metals that should be particularly taken into consideration while treating industrial wastewaters. Because of these negative impacts, the discharge of wastes containing heavy metals into water bodies or on land is a major concern. Consequently, industrial complexes are currently the main sources of pollution in the environment. Generally speaking, metals from wastewater need to be precipitated or otherwise bound to an insoluble state using adsorbents or other technologies [7-9].

Over time, several systems have been developed to heavy metals extraction from wastewater used in industrial processes. The most significant technological advancement is flocculation/coagulation, precipitation; ion exchange, electrochemical reactions, and membrane technology are further common conventional chemical techniques [10 -16]. The biosorption procedure has shown to be far more efficient and less expensive than any of the chemical approaches [17].

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Agricultural byproducts, such as agro tree wood that has been converted into activated carbons, are inexpensive and unconventional adsorbents. These adsorbents are significant to remove of organics and heavy metals from industrial and municipal wastewater. Citrus trees have the highest sorption capacity among these inexpensive adsorbents [18]

On the other side, chemical techniques can add to the environmental pollution burden, as an advanced oxidation process (AOPs). One of the most effective techniques for oxidizing organics in water is the Fenton process, which is also frequently used to remove or eliminate stubborn organic components from industrial and municipal water [19]. The oxidation methods (AOPs) use a combination of strong oxidizing agents (e.g. H_2O_2 , O_3) with catalysts (transition metal ions) and/or irradiation (e.g. ultraviolet, visible) [20]. The dissociation of the H_2O_2 molecule causes the in-situ formation of high oxidation species, hydroxyl radicals, which is the cause of this reactivity. Hydroxyl radicals are incredibly reactive and non-selective oxidants, so it disintegrates all organic materials in solution [19]. In Fenton's oxidation process, an organic substrate is given to an aqueous solution in a very acidic medium together with hydrogen peroxide and ferrous sulfate. These results in a complex redox reaction, as shown by the following equation: -

$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2$	\longrightarrow	$Fe^{3+} + OH^{-} + OH$	(1)
RH + 'OH		$R' + H_2O$	(2)
$R' + H_2O_2$	\rightarrow	ROH + 'OH	(3)
$OH + H_2O_2$	\rightarrow	$HO_2 + H_2O$	(4)
$R' + O_2$	\rightarrow	ROO'	(5)
$R' + Fe^{3+}$	\longrightarrow	$R^+ + Fe^{2+}$	(6)
Fe^{2+} + $\cdot \mathrm{OH}$	\longrightarrow	$Fe^{3+} + OH^{-}$	(7)
$\mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O}_2$	\longrightarrow	$\mathrm{Fe}^{2+} + \mathrm{H}^{+} + \mathrm{HO}_{2}^{-}$	(8)
$\mathrm{Fe}^{3+} + \mathrm{HO}_2$	>	$\mathrm{Fe}^{2+} + \mathrm{O}_{2}\mathrm{H}^{+}$	(9)
2HO ₂ ·	\longrightarrow	$H_2O_2 + O_2$	(10)

Therefore, the present study was dedicated to finding satisfactory solution to eliminate or remove the effects of the environment impact caused by the discharging of electroplating effluent without proper treatment. This wastewater was chosen since copper is most heavily laden and polluted effluent. Fenton oxidation method and/or prepared MAC (from agricultural waste) were applied as a substitute for traditional expensive chemical and biological processes.

2. Materials and Methods

2.1 Chemicals and reagents

All chemicals used were high-grade analytical reagents, which used through this work. The chemical reagents used including, Hydrochloric acid (HCL, 99.0 %, Merck, Germany), Sulphuric acid (H₂SO₄, 98%, Merck, Germany), NaNO₃ (99.99%, Merck, Germany), KMnO₄ (99.5%, Germany), Sodium Hydroxid (NaOH, 99.90 %, Merck, Germany), Hydrogen Peroxide (H₂O₂, 30%, Merck, Germany, are obtained from sigma Aldrich without further purification. An agriculture waste was aggregate from lemons trees and disintegrated well.

2.2 The sampling site

Most of the electroplating industries are located mainly in the October City, factory region. Currently, these industries' wastewaters are released untreated straight into the home sewer system. The infrastructure and sewage systems in this region have so severely degraded and been harmed. Because of this toxicity, the traditional wastewater treatment plant was unable to meet the national regulatory standards. To carry out the current inquiry, a comprehensive sampling procedure was created to gather composite samples every two weeks from a manhole of certain nearby electro plating businesses. Every composite sample is a representation of an effluent discharge. The wastewater's physico-chemical properties were determined according to the APHA, 2017 [21].

2.3 Integrated treatment system

Research has been done on an integrated system for treating tannery wastewater that uses Fenton's reagent for wet hydrogen peroxide catalytic oxidation (WHPCO), Scheme (1).



Scheme 1: Experimental configuration of the Fenton process treatment stages (WHPCO)

2.4 Fenton Reaction method

The electroplating effluent was treated by the jar-test device in a room temperature using Fenton reaction. Prior to starting, the pH of the effluent was adjusted to 3.0 ± 0.10 by adding 0.10 N H₂SO₄. For the duration of the batch experiment, the ideal dosage of the Fenton reagents, specifically H₂O₂ and Fe²⁺, was established. The highest dose of Fe²⁺ catalyst, 4.0 g/L, was added after many doses of H₂O₂ ranging from 0.50 to 12 g/L were introduced initially. The latter was added to each jar and mixed slowly (at 100 rpm) after being added at a high speed of 200 rpm. The ideal dose of H₂O₂ was determined by letting the reaction run for 60 minutes. More than pH 10, Fenton reactions cannot occur.; Therefore, before the chemical characterization, 1.0 M NaOH was injected at a high speed for 5.0 minutes for raising the pH to more than 10 and to remove excess H₂O₂. Because the flocculation phase comes next, the mixing speed was lowered to 30 rpm for 20 minutes. The system was paused at zero speed for sixty minutes to allow sedimentation to occur. To find the perfect dose of Fe²⁺ catalysts, the same experimental procedure was performed using a fixed quantity of the determined optimal dose of H₂O₂. The Fe²⁺ dosages under examination varied from 0.49 to 4.0 g/L[19].

2.5 Preparation of meso-activated carbon

Two consecutive procedures were used to prepare the activated carbon samples from Lemons tree: pre-carbonization at 400 $^{\circ}$ C and chemical activation. An air-tight graphite crucible containing the cleaned Lemons tree was heated to 400 $^{\circ}$ C for four hours. After the pre-carbonized material was placed in an airtight crucible, it was activated using ortho phosphoric acid (H₃PO₄) in a ratio of 1: 2.3 (carbon: H₃PO₄). After that, a temperature programmer was used to heat the material to 800°C at a rate of 5 °C per minute. The temperature was then sustained at this level for one hour before cooling. Ultimately, the excess phosphorus compounds were removed from the activated carbon by washing it in hot water until the wash water reached pH 7. Samples of activated carbon that had been cleaned were dried at 110 °C to obtain the final product. To get microporous/mesoporous composites, the samples were heated to 800°C activation temperatures; these composites were designated as MAC800, [22].

2.6 Analytical methods

By observing the quality of the raw wastewater and the treated wastewater from each stage of the process, the effectiveness of the treatment was assessed. The physico-chemical examination encompassed: the pH & total suspended solids (TSS) as physical parameters, chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), oil & grease, sulfides (S²), represent the chemical organic loads, the total phosphorus (TP), and total Kjeldahl nitrogen (TKN), represent the nutrient loads. All the analyses were carried out according to the APHA, 2017 [21].

2.7 Instruments and characterization techniques

Thermo Fisher Scientific, an American scientific provisioner, and Atomic Absorption Spectrophotometer (AAS) with graphite furnace for measuring extremely low concentrations were the two instruments used in this study. The AAS was also connected to a personal computer. Additionally, a deionized water system (Millipore GER), a digital electronic balance (PCE-BSK 310 Instruments UK), and a drying oven (Fisher Scientific Equipment, an American provider of scientific supplies) were utilized. The samples' pH values were determined with a pH meter (AD110, ADWA, Hungary). Thermo Fisher Scientific (UK) offers Fourier-transform infrared spectroscopy (FT-IR); thermo Fisher Scientific (US) offers orbital shakers; COD digestor (with auto time-controlled, MAC, India); BOD5 incubator (Airco, India); UV-Vis T70+ Spectrophotometers (PG Instruments, UK company); Thermo Fisher Scientific (UK) offers incubator; HORIBA (USA) offers portable multi-parameter water quality measurement; Kjeldahl Digestion instrument (ESEL, India), XRD, surface area, and PerkinElmer Spectrum GX were utilized in this work to characterize the produced materials' surfaces and structures.

2.8 Adsorption studies

The investigation primarily focuses on the adsorption and desorption processes, thoroughly examining the kinetics and isotherms involved. Adsorbent dose and contact duration were two operational parameters whose impact on adsorbent adsorption effectiveness was investigated. Measurements were made of the impact of contact time, adsorbent amount, and removal efficiency (R%) as well as the adsorption capacity (q max, mg/g) of adsorbents[23,24]. The samples were used to

calculate the R%, or the quantity of metals adsorbed on a given amount of adsorbent qe (mg/g) (11,12) [25].

$$R\% = \frac{Co - Ce}{Co} \times 100 \tag{11}$$

$$q(mg/g) = \frac{(Co - Ce)V}{m}$$
(12)

Where Co represents the initial concentration (mg/L), Ce represents the concentration following adsorption (mg/L), R% is the removal effectiveness, qe is the quantity of pollutants adsorbed on a certain amount of adsorbent (mg/g), m is the dose of adsorbents (g), and V is the volume of sample (liter).

3. Results and Discussion

Heavy metals and related organic compounds can present an environmental risk if not correctly treated. They have the potential to cause various problems such as impacting human health, disrupting ecosystems and diminishing the visual appeal of water bodies, and so on. This article focuses solely on using MAC and chemical oxidation based on AOPs as a presented study for treatment of electroplating effluent.

3.1 Characterization of the prepared MAC

Over the last twenty years, researchers around the world focused on the treatment of wastewater using various methods. One of the most processes is the adsorption due to its adaptable design, minimal treatment byproducts, simple maintenance, high efficiency, and potential for reuse, affordability, ease of use, and resistance to biological substances in water environments. As a result, adsorption has become the most commonly employed method for remediation. [26,27]. Activated carbon (AC) made from agricultural waste has become popular because it is cost-effective and it has excellent adsorption capabilities.

Porous activated carbons are commonly used as good adsorbents in a wide range of industrial applications for the purposes of gas separation, removal, and recovery etc. [28, 29]. The structure of pores and the chemical composition of the surfaces play important factors in the determination of the adsorption properties of activated carbons. Adsorption technologies greatly benefit from the influential role of porous carbon materials[30]. The Meso active carbon was prepared from agriculture waste, which aggregate from lemons trees and disintegrated very well.

3.2 The structure and morphology of MAC:

3.2.1 X-ray diffraction

The XRD pattern of MAC shows a strong peak centered at $2\theta = 11.7^{\circ}$, corresponding to the (0.01) interlayer spacing of 7.43, together with a small one at 42° due to the (200) plane, Figure (1). The attained data indicates that the natural graphite was converted to MAC matrix in angstrom size.



Figure (1): XRD Pattern of MAC

3.2.2 IR studies

The presence of oxygen-containing functions for MAC and its structural alterations were examined using FT-IR spectroscopy, as shown in Figure (2). The distinctive peaks of the FT-IR spectrum of MAC are seen at 3346 cm⁻¹, along with absorbed water molecules at 3346 cm⁻¹, aromatic C=C (1615 cm⁻¹), carboxy C-O (1417 cm⁻¹), epoxy C-O (1217 cm⁻¹), alkoxy C-O (1049 cm⁻¹), stretching C-O-C (850 cm⁻¹), and surface OH groups.





3.2.3 The BET surface area

Figures (3, 4) show the measured and reported pore size distribution curves and adsorption-desorption isotherms. The MAC's BET surface area, pore volume, and pore radius values (176 m² g⁻¹, 0.38 cm³ g⁻¹, and 19.1 Å) show higher SBET and lower pore volume and radius values. Major capillary condensation steps are visible in the MAC desorption isotherms within the 0.45–0.95 relative pressure range, Figure (4).



Figure (3): BET results its corresponding pore size distribution curve of MAC



Figure (4): MAC desorption isotherms within the relative pressure range.

Parameter	Unit	Concentration
pН		3.20
COD	mgO ₂ /L	650
BOD	mgO ₂ /L	320
TSS	mg/L	312
TKN	mg/L	13
Ammonia	mg/L	4,72
EC	µs/cm	12.60
TDS	mg/L	3500
Cu	mg/L	1200

The sample shows those mean values for ten samples.

3.4 Fenton Reaction Treatments

3.4.1 Effect of the dosage of ferrous sulfate

The effect of different dosages of ferrous sulfate (FeSO₄) was carried out for the treatment processes at time 1 hour. The samples' pH was adjusted to about (3.0-4.0) units using 0.1 N H₂SO₄. Table (2) represents the weight and volume of the produced sludge. Based on the removal efficiency of COD, weight, and volume of sludge, The ideal dose of FeSO₄ for completing the remaining experimental research was determined to be 1.0 g/L. Figure (5) illustrates how adding FeSO₄ at varying concentrations (ranging from 0.3 to 1.0 mg/L) altered the sludge properties and the removal efficiency of COD. During the addition of FeSO₄, a constant concentration of calcium oxide (1.0 g) and hydrogen peroxide (2.0 g) were added simultaneously. The concentration of COD reduced from 650 mg/L to 67 mg/L and Cu from 1200 mg/L to 91 mg/L at the dose of 1.0 mg/L of the FeSO₄. The SVI of the produced sludge in all cases shows a good settled sludge [32] 0.7 ml is better.



Figure (5): Efficiency of FOR for removal of COD and Cu at different FeSO₄ doses

Dose of FeSo ₄	Sludge Vol.	Sludge weight
g/L	ml/L	G
Raw	0.0	0.0
0.20	11	0.45
0.40	14	0.50
0.70	16	0.50
1.00	17	0.50
1.20	17	0.60
1.50	17	0.60

Table (2):	sludge volume a	nd weight at FO	OR treatment	process a	at different]	FeSO ₄	dose

3.4.2 Dosage of Hydrogen peroxide

The treatment was conducted using the optimum $FeSO_4$ dosage of 1.0 mg/L. Table (3) and Figure (6) present the COD concentration at various hydrogen peroxide dosages. The concentration of COD was in compliance with the national regulatory standard for treated effluent discharge to the sewage system at all hydrogen peroxide doses [31]. This might be explained by the extremely oxidative hydroxyl radical species that are produced when the H_2O_2 molecule dissociates. When it comes to the oxidation and disintegration of organic materials in solution, hydroxyl radicals are incredibly reactive and non-selective oxidants.

It was observed that the volume and weight of the sludge were not affected by increasing the dosage of hydrogen peroxide from 1.5 to 3 g/L as an indication of no extra precipitation as indicated in Table (3) and Figure (6). This may be attributed to the constant added dose of ferrous sulfate and calcium oxide. Due to economic reasons, the dose of 1.5 g of hydrogen peroxide was chosen to be the optimum dose. The mechanism of AOPs action is based on production of extremely reactive hydroxyl radicals (HO•) in a suite of powerful, non-selective oxidants. Free radicals that are produced as a result target the organic substance and aid in its breakdown in the reaction media. The breakdown of organic compounds by highly active free radical (HO•), with almost all organic compounds quickly and without preference. Compared to traditional oxidants, they show quicker rates of oxidation reactions and have an oxidation potential of 2.33 V [18]. After they are generated, hydroxyl radicals can attack organic compounds via the electron transfer equation (15), radical addition equation (13), and hydrogen abstraction equation (14). Fenton's reactions were thought to be an effective wastewater treatment method.

$R + HO \bullet$	>	ROH	(13)
R + HO∙		$R \bullet + H_2O$	(14)
Rn + HO•	>	$Rn-1 + OH^{-}$	(15)

R is used to characterize the organic compound (pollutants) that is responding in the equations.

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Figure (6): Efficiency of FOR for removal of COD and Cu at different H₂O₂ dose Table (3): Following of FOR at different H₂O₂ doses on sludge volume index and sludge weight

Dose of H ₂ O ₂ (g/L)	Sludge Vol. (ml/L)	Sludge weight (g)
0.50	15	0.50
1.00	17	0.55
1.50	17	0.60
2.00	19	0.70
2.50	19	0.70
3.00	19	0.70

3.4.3 The dosage of Calcium oxide

Calcium oxide was used as a conventional treatment for effluent to adjust the solution's pH and also, to precipitate the residual dissolved metals. Table (4) shows the increase of the dosages of calcium oxide from 1.0 to 5.0 mg/l lowers the COD content and raises pH. It was observed that the residual H_2O_2 volatilized at higher pH values. As a result, the COD demand resulting from excess H_2O_2 was decreased [33–36]. At the optimum conditions, which were 1.50 g of hydrogen peroxide and 0.90 g/L of ferrous sulfate, the impact of calcium oxide dosages was investigated. The effectiveness of the Fenton reaction in treating copper-containing wastewater is displayed in Table (4). The pH is raised and the COD concentration is lowered by increasing the calcium oxide dosages from 1.0 to 5.0 g/L. Higher pH levels were found to cause the residual H_2O_2 to volatilize. The optimum dosage of calcium oxide was determined to be 2.0 g/L, as shown in Figures (7).



Figure (7): Efficiency of FOR treatment with different CaO doses for removal COD and Cu

Dose of CaO	Sludge Vol	Sludge weight
g/L	ml/L	G
0.50	13	0.50
1.00	16	0.55
1.50	16	0.60
2.00	16	0.60
2.50	17	0.65
3.00	18	0.65
4.00	19	0.70
5.00	20	0.70
6.00	22	0.80

Table (4): Following of Sludge Volume and weight at FOR treatment at different CaO doses

3.4.4. Performance of the treatment process

Figure (8) show the main characteristics of the treated wastewater at the optimum operating conditions and reflect the Fenton reaction's ability to treat wastewater at optimum conditions of operation. Meanwhile, the average COD, TKN, EC, TDS, TSS and Cu removal rate reached (70.76, 76.92, 48.80, 49, 63, and 91.25) %. The pH increases from 3.2 to 7.8.



Figure (8): The main characteristics of the treated wastewater at the optimum operating conditions* * The optimum operating conditions are 1.20 g/L FeSO₄, 2.00 g/L H₂O₂ and 4.00 g/L for CaO

3.4.5. Inhibition of H₂O₂ residual

To stop the residual effect of H_2O_2 , other types of reducing agents were applied, including MnO_2 , SnO, Fe powder, and sod thio-sulfite. In this case, the percentage of COD will increase due to the existence of residual H_2O_2 , which will provide an inaccurate COD measurement. As can be seen in Table (5), the results show that MnO_2 is the best, followed by SnO and Fe powder. Even because sod thiosulfate has a strong reducing property, the COD increased more than the original material, so the results were not what were anticipated. This can be described in terms of the redox system, in which the presence of leftover Fe²⁺ traces together with sodium thiosulfate forms a redox reaction that results in the production of a free radical as shown by equation (16):-

$$Fe^{2+} + Na_2S_2O_8 \qquad \longrightarrow \qquad Fe^{3+} + SO_4^{--} + SO^{4--} \qquad (16)$$

According to the above equation of redox system, it yields a free radical which increases COD percentage.

Reducing agent	COD after treatment
SnO	220
Fe powder	260
MnO ₂	90
$Na_2S_2O_8$	1000
COD before treatment	nt 650 PPm

Table (5): Elimination of H₂O₂ residual by different categories of reducing agents

3.5. Application of MAC for Copper Removal

In general, the carbonization and activation processes are the two processes that make up the production of MAC. The aim of the carbonization process is to pyrolyze the precursor at a moderate temperature (between 250 and 400° C) while an inert gas is flowing through it, producing a material with a high carbon content (char). However, the activation procedure is used to improve the surface area by promoting pore growth inside the char. Initiation By removing less ordered, loosely bound carbonaceous material; the gaps between the elementary crystallites are cleaned during the activation process. The porous structure, with a large internal surface area, is made up of fissures within and parallel to the graphite planes, the spaces between elementary crystallites, and the consequent channels across the graphitic areas [36]. Prior to carbonization, chemical activation entails adding inorganic additions, metallic chlorides like zinc chloride or phosphoric acid, to the precursor [37]. ZnCl_{2 inclusion} can result in carbons with well-developed meso- and microporous structures. The pore volume and active carbon surface area were successfully enhanced by KOH activation [38]. The characterizations of the prepared MAC were performed above.

3.5.1 Effect of contact time at different doses





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Time (min)	Cu (ppm), 0.1/100mL	Cu (ppm), 0.12/100mL	Cu (ppm), 0.15/100mL	Cu (ppm), 0.2/100mL
10	1150	1120	1050	1010
20	1020	995	960	930
30	970	950	910	905
45	820	795	770	740
60	690	650	630	560
80	550	530	490	450
100	410	380	370	370
120	390	370	345	310
150	385	360	330	290
180	385	360	330	290
240	385	360	330	290

3.5.2 Kinetic Model Analysis of copper removal by MAC

In the present work kinetics reactions of first- and second- order were used to study the removal of copper kinetics by MAC. The following linear equations (17 and 18) govern the reaction kinetics: First-order reaction kinetics:

$$\log \frac{\mathrm{Ct}}{\mathrm{C0}} = K1.t \tag{17}$$

Second order reaction kinetics:

$$\frac{\mathrm{t}}{\mathrm{Ct}} = K2.t \qquad (18)$$

The kinetic rate constants for first- and second-order reaction kinetics are denoted as k1 and k2, respectively. The variable t represents the reaction time. Figure (10) shows the kinetics models of copper removal from wastewater by MAC. The relation between log $\left(\frac{Ct}{Co}\right)$ and t. The correlation coefficients (R²) of the pseudo-first-order kinetic model are linear but the pseudo-second-order kinetic model non-linear , the correlation coefficients (R²) of the pseudo-second-order and first orderis given in Figure (10). The results showed that the overall rates of removal of copper, by MAC were controlled by physic-sorption properties. [39]. The Correlation coefficients (R²) Parameters of pseudo-second-order model is =0.9015 but pseudo-first-order model parameter is 0.942. Besides, the value of R² about 1 in pseudo-first-order confirms that the adsorption kinetics is controlled by this order and that there is a strong interaction between adsorbent and adsorbate. The kinetics of copper removal from wastewater at different time fitted with first order model.



Figure (10): Kinetic study treated effluent using different time of active carbon at different doses 3.6. Comparison study at Performance processes on removal of Copper



Figure (11): Comparison of different treatment methods for removal of pollutants from wastewater at active carbon and Fenton reaction

	Wastewater characterization	Residual concentration of pollutants		Removal efficiency of opuntia (%)	
Test		Fenton	Active Carbon 2.0g/L	Fenton	Active Carbon 2.0g/L
COD(mg/L)	650	190	120	71	82
BOD ₅ (mg/L)	320	12	7	96	98
TSS(mg/L)	312	116	69	63	78
TDS(mg/L)	35000	18000	16000	49	54
TS(mg/L)	30000	23000	18000	23	40
ECµs/cm	12.60	6.5	6.1	48.80	52
TKN(mg/L)	13	3	1.7	77	87
Ammonia	4.72	0.89	0.12	81	97
Cu(mg/L)	1200	105	290	91	76

Table (7): The comparison of different treatment methods for removal of pollutants from wastewater

Table (8): C	Comparison o	of adsorp	otion efficie	encies of a	some selected	adsorbents
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Adsorbents	Adsorbents	Q max (mg/g)	Reference
Untreated rice husk	Direct dyes	2.4	[40]
Activated rice husk	Direct dyes	4.3	[40]
Red-mud	Ni ⁺²	0.0018	[41]
Peanut Hulls	Fe ⁺³ and Cu ⁺²	79.28 and 96.58 mg/g for Fe^{+3} and Cu^+	[42]
Zeolite derived from fly ash	Cu ⁺²	14.7	[43]
Ag nanoparticle-loaded activated	Cu ⁺²	60	[44]
carbon (Ag-NP-AC)			
Iron oxide coated eggshell powder	Cu ⁺²	6.7	[45]
Chitosan	Cu ⁺²	62.4	[46]
AC from citrus tree	Ni^{+2} , Pb^{+2} and	58.13 for Ni ⁺² , 69.82 for Pb ⁺² and 60.6	[47]
	Co ⁺²	for Co ⁺²	

3.7 Adsorbents' cost (Visibility study)

Table (9) presents the cost analysis of employing Fenton and activated carbon as efficient ways to remove contaminants from wastewater, based on the preparation procedure utilized in this study. According to the cost study, the generation of activated carbon and Fenton takes 3.5 kWh/m³ of specific energy and 0.035 m³ of water. The amount of money required to produce 0.1 kg of adsorbent is 0.177, or 3.535 Egyptian Pounds. Compared to other adsorbents like activated carbon or other adsorbents, which are manufactured from natural waste materials at a priceless cost, this is regarded as having a very poor value [40]. Adsorption is not only an economical way to handle dangerous pollutants like heavy metals, but it also doesn't produce any secondary byproducts and is safe for the environment. The following formula was used to determine the cost: The price of ingredients plus the cost of electricity used equals the cost of 0.1 kg of adsorbents. Therefore, the cost of producing 0.1 kg is equal to 0.035 + 3.5 = 3.535 L.E.

Table (9): Material and energy consumption for production of 0.1 kg of adsorbents

Process	Water consumption* (m ³)	Electricity consumption* (kWh)
Washing	0.002	-
Drying at 105 ^o C (24h)	-	2
Crushing and sieving	-	0.5
Washing	0.0015	-
Total Consumption	0.0035	2.5
Cost	0.035	3.5

*In Egypt, the cost of 1 m^3 of water for industrial use = 10.0 L.E

*In Egypt, the cost of 1 kWh of electricity for industrial use = 1.45 L.E

Conclusion

The obtained results reveal that the copper removal by percent (91) by AOPs technique and by treating with meso-active carbon is (76%). Meanwhile, the average COD removal rate reached 82%. Treatment with meso-active carbon confirmed that the toxicity of the wastewater was highly reduced and improved, as well as, it was considered very low-cost compared to other methods. This study provides a solution of the potential of agro wastes as adsorbing material and the recent technological advances adopted by researchers in producing of AC. The use of this technology is commercially feasible serve as the foundation for the control of these harmful priority pollutants.

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