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MODELING OF TEXTILE WASTEWATER ELECTROCOAGULATION VIA ADSORPTION ISOTHERM KINETICS

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Abstract

This study has been carried out to determine the feasibility of COD adsorption on iron coagulant by EC process, and to find a mathematical model using kinetic isotherms. Experiments were carried out to treat a high strength wastewater of textile industry located in Al-Hilla-Iraq using a batchwise mode. A well-rounded range of current density was tested and the COD removal percent has reached a maximum value of 85.2 under c.d. of $20 mA/cm^2$. It was attempted to fit the experimental data with the popular adsorption isotherms Langmuir, Freundlich and Temkin, hense the mechanism of adsorption with the effect of individual parameters on the efficiency of electrocoagulation have been critically examined. Two well-known coagulant mechanisms were modeled with the kinetic equations utilizing the result from experiments relative to EC of COD removal for five set of experiments. It has been found from the present analysis that the adsorption isotherm with iron (II) and iron (III) hydroxides combined to generate hydroxo cationic-anionic complex of green rust mechanism, can be described by Langmuir isotherm equation which gives a preferable fit of experimental data than the Freundlich and Temkin isotherm model equations.

الخلاصة :

أجريت هذه الدراسةِ لتحديد ملائمة أستخدام تقنية التخثر الكهروكيمياوي لأمدصاص متطلب الأوكسجين الكيمياوي بوجود فطب حديدي ، ولإيجاد نموذج رياضي يحاكي موديلات حركية الأمدصاص المعروفة . التجارب نُفّذتْ بطريقة الوجبات لمُعَالَجَة مياه صناعيةِ متدفقة مِنْ الشركة العامة للصناعات النسيجية-الحلة-العراق . أستخدم مدى واسع مِنْ كثافةِ التيار ووجد أن الحد الأقصى لأزالة متطلب الأوكسجين الكيميائي هو 85.2% تحت $20mA/cm^2$كثافة تيار . لتحديد كفاءة تقنية التخثر الكهروكيمياوي تم ربط النتائج التجريبيةِ لأزالة متطلب الأوكسجين الكيميائي من المياه الصناعية الملوثة مع ثلاث موديلات شائعة تفسر حركية الأمدصاص بثبوت درجة الحرارة وهي لنكمور و فرندلج و تميكن وبافتراض تكون نمط محدد من المادة المخثرة في العملية الكهروكيمياوية. حيث أن هنالك آليتان معروفتان تم أعتمادهما لتحديد نوع المادة المخثرة المتكونة شُكّلتَا المعادلاتِ الحركيّةِ المستنبطة لتفسير تقنية التخثر الكهروكيمياوي وفق موديل الأمدصاص المقترح. وُجِدَ مِنْ هذا التحليلِ أن ألية تكون معقد هايدروكسي لأيونات الحديد الثنائي والثلاثي لتكوين مادةِ الصدأِ الخضراءِ كمادة ممدصة يُمْكِنُ أَنْ تُوْصَفَ بمعادلةِ لنكمور لتفسير طريقة الأمدصاص والتي تَعطي أفضل اتفاق مع نتائج التجارب مقارنة مع معادلتي فرندلج و تميكن .

Key words: Electrcoagulation, COD removal, Adsorption isotherms, model.

INTRODUCTION :

EC technique is an electrochemical technology for the treatment of water and wastewater uses an electrochemical cell, where a dc voltage is applied to the electrodes corroded to generate a coagulant, and the electrolyte is usually water effluents. Electrocoagulation is an efficient treatment process for various type of wastes such as soluble oils, liquid from food, textile industries, cellulose and effluents from paper industry (Calvo et al., 2003). According to Can et al., (2006) EC has been proposed in recent years as an effective method to treat various wastewaters such as landfill leachate effluent from restaurant, saline wastewater, tar sand and oil shale wastewater, textile wastewater, urban wastewater, laundry wastewater, tannery wastewater, nitrate and arsenic bearing wastewater and chemical-mechanical polishing wastewater.

Effluents with sturdy color and high COD are common in chemical process industries such as textile, paper, leather and mineral processing industries. In textile processing industries, dyeing and finishing are the two most important process operation which consumes large amount of water and generates considerable amount of wastewater which contains strong color, suspended particles, high pH and high COD and BOD. (Chithra et al., 2008) observed that the percent of COD reduction is significantly influenced by the initial dye concentration, pH and current density. The adsorption isotherms of Langmuir and Temkin were used to check the adsorption kinetics, and they found that the adsorption isotherm with hydroxo cationic complexes can be described by the Langmuir equation which gives the better fit of the experimental data than the Temkin equation. The electrolysis voltage is one of the most important variables. It is strongly dependent on the current density, the conductivity of the water/wastewater to treat, the inter-electrode distance, and the surface state of electrodes. A model involving terms of activation overpotential, concentration overpotential and ohmic drop of the solution resistance has been proposed by Vik et al. (1984). Although electrocoagulation has been available for more than a century, nowadays the design of an industrial electrocoagulation unit is still mainly based on empirical knowledge due to the lack of available models (Xueming Chen et al., 2002). They found two mathematical models, one applicable to non-passivated aluminum electrodes and the other to passivated aluminum electrodes were established and verified. With these models the total required electrolysis voltage of an electrocoagulation process can be calculated.

Dyes used in the textile industry are mostly synthetic and are derived from petroleum-based intermediates (Chithra and Balasubramanian 2010). They concluded that the electrocoagulation of textile effluent follows pseudo second order kinetics and the reaction rate constant is influenced by current density, pH and initial effluent concentration. Also they modeled the electrocoagulation results using adsorption isotherm and found that Langmuir isotherm model match satisfactorily with the experimental observations.

Arsenic contaminants are generated from various industries such as steel making, electroplating, leather tanning, and industrial operations that involve the processing of ferrous and nonferrous metals (Parga et al., 2009). They carried out experiments to determine the feasibility of arsenic adsorption on iron species by EC process using the Langmuir's isotherm and to find the thermodynamic parameters such as ΔH°, ΔS°, and ΔG°. The results of this study indicate that arsenic can be successfully adsorbed on iron species by electrocoagulation process. Based on Langmuir's isotherm analysis, the adsorption capacity was determined to be 4.24 mmol/gm for arsenic. Balasubramanian et al. (2009) modeled adsorption isotherm kinetics for arsenic removal from aqueous solutions by means of electrocoagulation through response surface methodology.

The objectives of the present study are to establish a theoretical models regarding the effect of current density and the required operation time of electrolysis in the electrocoagulation process and to verify the COD removal experimental data from a local textile wastewater with Langmuir, Freundlich and Temkin adsorption isotherms.

MECHANISM OF COD ELECTROCOAGULATION :

COD (Chemical Oxygen Demand) is a measure of the amount of the oxygen used in the chemical oxidation of inorganic and organic matter present in wastewater. COD is also an indicator of degree of pollution in the effluent, and of the potential environmental impact of the discharge of wastewater in water bodies. COD results do not necessarily correlate to BOD because the chemical oxidant may react with substances that bacteria do not stabilize. Although BOD and COD are not specific compounds, they are considered as conventional pollutants under the federal Clean Water Act, and also they have been widely used by regulatory agencies worldwide to gauge overall treatment plant efficiencies (Hector et al. 2005).

By using an iron anode the $Fe(OH)_n$ formation with n = 2 or 3 is released at the anode. Simplified oxidation and reduction mechanisms at the anode and cathode of the iron electrodes are represented as follows (Daneshvar et al., 2003; Larue et al., 2003; Daneshvar et al., 2006, Chithra et al, 2008, Parga et al, 2009):

Mechanism 1(a) (basic wastewater):

Anode : $Fe(s) \rightarrow Fe^{2+}_{(aq)} + 2e^-$ (1)

$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$ (2)

Cathode : $2H_2O_{(l)} + 2\,e- \rightarrow H_{2(g)}\uparrow + 2OH^-_{(aq)}$ (3)

Overall : $Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)}\uparrow$ (4)

Mechanism 1(b) (acidic wastewater):

Anode : $4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^-$ (5)

$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+_{(aq)}$ (6)

Cathode : $8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)}\uparrow$ (7)

Overall : $4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)}\uparrow$ (8)

According to Larue and Vorobiev (2003), the generation of iron hydroxides $Fe(OH)_n$ is followed by an electrophoretic concentration of colloids (usually negatively charged) in the region close to the anode. The produced ferrous ions hydrolyze to form monomeric hydroxide ions and polymeric hydroxide complexes that depend on the pH of the solution. The polymeric hydroxides, which are highly charged cations, destabilize the negatively charged colloidal particles allowing their aggregation and formation of flocs.

Mechanism 2 (acidic and basic wastewater)

$Fe + 6H_2O \rightarrow Fe(H_2O)_4(OH)_{2(s)} + H_{2(g)}\uparrow$ (9)

$Fe + 6H_2O \rightarrow Fe(H_2O)_3(OH)_{3(s)} + 1.5H_{2(g)}\uparrow$ (10)

In the appropriate conditions, iron (II) and iron (III) hydroxides combine in the following proportion to generate Green Rust, GR (Parga et al., 2009):

$x\,Fe(OH)_{3(aq)} + (6-x)Fe(OH)_{2(aq)} \rightarrow x\,Fe(OH)_3\,.(6-x)Fe(OH)_{2(s)}$ (11)

EC can be considered as an accelerated corrosion process. GR is recognized as an important intermediate phase in corrosion of Fe^0. GR's are layered Fe(II)-Fe(III) hydroxides having a pyroaurite-type structure consisting of alternating positively charged hydroxide layers and hydrated anion layers. Results of many studies (Gomes et al., 2007, Parga et al., 2005) have shown that GR's conform to a general chemical composition and stoichiometry, that can be represented with the general formula:

$[Fe^{II}_{(6-x)}\,Fe^{III}_{x}\,(OH)_{12}]^{x+}[(A)_{x/n}\cdot yH_2O]^{x-}$

where x ranges from 0.9 to 4.2, A is an n-valent anion (typically CO_3^{2-}, Cl^{-}, or SO_4^{2-} and y denotes the varying amounts of interlayer water (typically y ranges from 2 to 4 for most GR's.

EXPERIMENTAL SET UP

The electrocoagulator cell used was 1500 ml glass reactor with upper Teflon cover contain two glands for electrodes fixation and equipped with magnetic stirrer without temperature control. The electrolysis time was established of 60 minutes using DC power supply of 30 V and a current controlled through rheostat. Five current densities of 4, 8, 10, 12 and 20mA/cm^2 were tested at ambient temperature 25°C ±1. The cell arrangement can studied the effect of the EC process on COD removal using two variables: current density (mA/cm^2), and EC operation time (minutes).

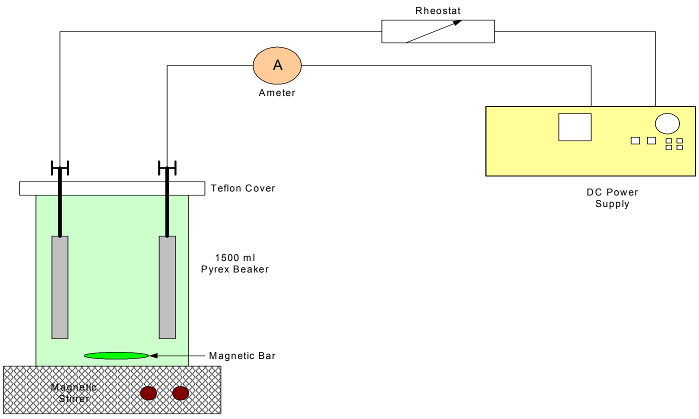

Fig.1 Scheme of experimental set

EQUIPMENTS AND PROCEDURES

A laboratory scale electrochemical setup made up of glass beaker cell, electrodes and other accessories were arranged as in (Fig.1). However, in each run, 1 liter of sample was used to treat by electrocoagulation process. Two electrodes of iron with surface area of 20 cm^2. The separation between the anode and the cathode was kept at 5 cm (Fadil Othman et al., 2006). The solution in the reactor was stirred by a magnetic plate stirrer with Teflon bar at a rotating velocity of 500 rpm (HP-3000). Controlled direct current was supplied by a DC power supply (ATTEN DC power supply type APR 3002A of 0-30V). The current was kept invariant in each test by a rheostat (Wheatstone Type 2755-Japan) and measured by an ammeter (Aswar DT830D). The effects of textile wastewater COD removal efficiencies were studied with different current densities. The electrical potential was held constant for each run, being fixed at 30 volts. COD measurements were according to the Standard Methods for Examination of Water and Wastewater (APHA, American Public Health Association 2000). The calculation of COD removal efficiencies after electrocoagulation treatment were performed using the following formula (Carneiro et al., 2003):

$$C_R\,(\%) = [(C_0 - C)/C_0] \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

Where C_R is contaminant removal, C_0 and C are concentrations of wastewater before and after electrocoagulation.

Several EC batch experimental runs were performed in the laboratory. Initially wastewater was rigorously stirred for 5 minutes by stirrer for homogenization of sample. Then a specific current density was applied for various time periods (ranging from 5 minutes to 60 minutes). Treated wastewater samples were collected after settling for predetermined time to estimate the effect of EC treatment time on removal efficiency COD. The sample was allowed to settle for 60 minutes after treatment so that the flocs (coagulates) that were formed during electrocoagulation may settle. In each experimental run, after settling, about 50 ml supernatant sample was collected for laboratory analysis.

ELECTROCOAGULATION KINETICS

The pollutant is generally adsorbed at the surface of the flocs (coagulant) generated electrochemically. Critical analysis of the electrocoagulation of pollutants reveals that there are two separate processes taking place, i.e. electrochemical process through which the metal coagulants are generated and physio-chemical process through which the effluents are adsorbed on the surface of the coagulants (Chithra and Balasubramanian, 2010). The removal of pollutant is similar to conventional adsorption except the generation of coagulants. The electrode consumption can be estimated according to Faraday's Law and the amount of coagulant generated can be estimated stoichiometrically (Parga et al., 2009):

$$W = \frac{(D.t.M)}{z.F} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad (13)$$

where *W* is the amount of the electrode dissolved (g/cm^2), *D* the current density (A/cm^2), *t* the time (seconds), *M* the relative molar mass of the electrode, z the number of electrons in the redox reaction, and *F* Faraday's constant (96500 coulombs). At equilibrium a relationship exists between the concentration of the pollutant species in solution and the concentration of pollutant species in the adsorbent (i.e. the amount of species adsorbed per unit mass of adsorbent). The amount of pollutant (COD) at equilibrium on iron species N_e (mg/g) was calculated from the following equation (Kumar et al., 2010, Malakootian et al., 2011):

$$N_e = V.(\frac{C_0 - C_e}{W}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. \quad (14)$$

Since the amount of coagulant can be estimated for a given time, the pollutant removal can be modeled by adsorption phenomenon. During electrocoagulation the insoluble metal hydroxides removes pollutants by surface adsorption.

ADSORPTION ISOTHERMS

It is assumed that the pollutant can act as a ligand to bind a hydrous iron in situ formed gelatinous precipitate, it is further attempted to extend the adsorption isotherm models for pollutant removal by Langmuir, Freundlich and Temkin models (Chithra et al., 2008, Kumar et al., 2010, Malakootain et al., 2011, Zohre Shahryari et al., 2010):

LANGMUIR ISOTHERM

The Langmuir isotherm assumes monolayer deposition of adsorbate on homogenous adsorbent surface (coagulant). It is well known that the Langmuir equation is intended for a homogeneous surface. The mathematical expression of Langmuir isotherm is given as:

$$N_e = (\frac{N_{Max} K_L C_e}{1 + K_L C_e}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad (15)$$

where N_e is the solid phase adsorbate concentration in equilibrium (mg/g), N_{max} the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), C_e the concentration of adsorbate at equilibrium (mg/l), and K_L the Langmuir constant (l/mg). Equation (15) can be rearranged to a linear form:

$$\frac{C_e}{N_e} = \frac{1}{N_{Max}K_L} + \frac{C_e}{N_{Max}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

Accordingly, a plot of C_e/N_e vs. C_e should produce a straight line with a slope of $1/N_{max}$ and intercept of $1/(K_L N_{max})$.

FREUNDLICH ISOTHERM

It is empirical model relating the adsorption intensity of the sorbent towards adsorbent. The isotherm is adopted to describe reversible adsorption and not restricted to monolayer formation. The mathematical expression of the Freundlich model is represented by:

$$N_e = K_F\, C_e^{\frac{1}{n}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

K_F is Freundlich constant that indicate the adsorption capacity of the adsorbent (l/gm) and n is an empirical constant related to the magnitude of the adsorption driving force.

The Freundlich isotherm can be rearranged to give a linear form:

$$Ln(N_e) = Ln(K_F) + \frac{1}{n} Ln(C_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

Accordingly, a plot of Ln N_e vs. Ln C_e should produce a straight line with a slope of $1/n$ and intercept of Ln K_F.

TEMKIN ISOTHERM

The Temkin isotherm describes the behavior of adsorption system on heterogeneous surface, and represented as follows:

$$N_e = \frac{RT}{b_0} Ln(K_T C_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

Equation (19) can be expressed in a linear form as:

$$N_e = BLn(K_T) + BLn(C_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

Where $B=RT/b_0$, and B is a constant related to adsorption heat, and K_T is the equilibrium binding Temkin constant (l/gm) corresponding to maximum binding energy. A plot of N_e vs. $Ln(C_e)$ enables to determine the constants B and K_T.

RESULTS AND DISCUSSION

Experiments were carried out in a batch electrochemical reactor at various current density of 4, 8, 10, 12, and 20 mA/cm^2 with iron electrode as sacrificial anode using the textile wastewater of a plant located in Al-Hilla Iraq. All the experiments were carried out under potentiostatic conditions covering a range of electocoagulation operating time of 5, 10, 20, 30, 40, 50 and 60 minutes electrolysis conditions and results are presented in Figure (2). The variation of percentage COD removal with the process time is given in Figure (2). It can be ascertained from Figure (2) that the percentage COD removal increases with an increase in the process time for iron anode. The rate of percentage COD removal is sharp at the beginning of the process and approaches monotonical situation beyond 30 minutes of process time. It can be noticed that more than 90% of COD has been removed within 30 minutes of the coagulation time and the percent of COD removal increases with an increase in the applied current density. This can be explained that at high current density, the extent of anodic dissolution of Fe metal increases, resulting in great amount of precipitate for the removal of pollutants. However, the initial COD and pH are 1140 mg/l , 4.52 respectively and the final pH value of the treated wastewater is slightly basic (7.6 ± 0.2) which is within the allowable limit.

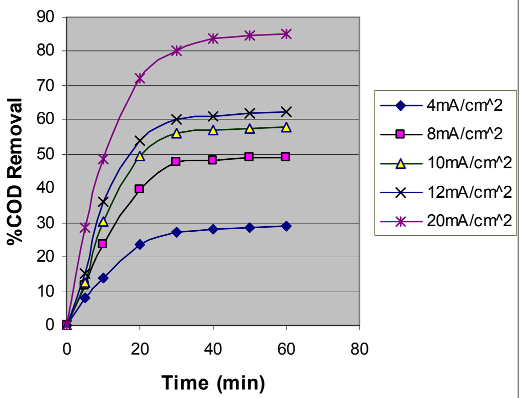

Fig.2 Variation of %COD Removal with Current Density and Electrolysis Time

A comparison of the electrocoagulation kinetic for the treated textile wastewater based on Langmuir, Freundlich and Temkin isotherms can be predicted depending upon the type of adsorbent material and the mechanism of electrocoagulation. As W is the mass of corroded iron and W_{ad} is the mass of adsorbent produced, that can be assumed constant for a given current density, so the total mass of coagulant produced within the electrolysis time (60 minutes) can be also estimated depending on current density with the application of equations (13) and (14), and the molar mass difference between the dissolved Fe^0 and the produced coagulant.

ELECTROCOAGULATION KINETIC BASED ON FE(OH)$_3$ FORMATION MECHANISM

The variation of the dissolved mass of Fe^{2+} per unit area of electrode during 60 minutes of electrolysis time with the tested current density is explained in table (1).

Table (1) The variation of the Fe(OH)$_3$ adsorbent mass with current density

C.D. mA/cm^2	4	8	10	12	20
W_{ad} (gm)/cm^2	0.00798	0.0159	0.0198	0.0238	0.0399

The COD amount that adsorbed on iron adsorbent can be expressed by N_e which represents the milligrams of adsorbate per gram of coagulant adsorbed. Table (2) explain the amount of COD adsorbed on Fe(OH)$_3$ coagulant.

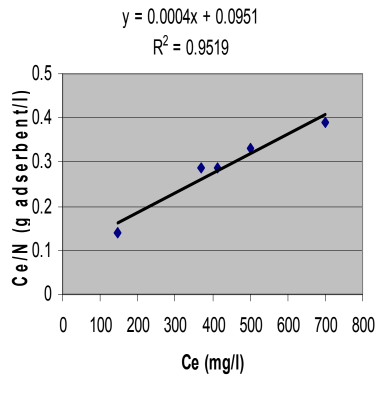

Fig.3 Langmuir Adsorption Isotherm

Table (2) COD milligrams adsorbed on iron species(N_e)

C.D. mA/cm^2	COD,C_e(mg/l)	W (g)	N_e (mg/g)
4	698.95	0.1596	1792.29
8	501.795	0.3182	1518.557
10	412.995	0.3977	1438.282
12	369.375	0.4773	1289.830
29	145.780	0.7983	1051.260

The data of table (2) was subjected to Langmuir, Freundlich and Temkin isotherms, respectively, as explained in figures (3), (4) and (5) where, the isotherm constants and the correlation coefficient for each regression is explained in table (3).

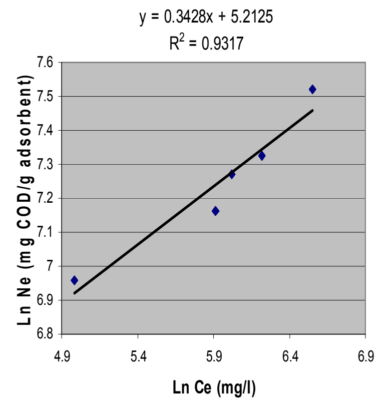

Fig.4 Freundlich Adsorption Isotherm

Table (3) Isotherm constants for adsorption of COD on $Fe(OH)_3$

Langmuir	N_{Max} (mg/g)	K_L (l/mg)	R^2
	2500	0.0042	0.9519
Freundlich	n	K_F (l/g)	R^2
	2.917	183.55	0.9317
Temkin	B	K_T(l/g)	R^2
	471	0.0548	0.8804

Note: n and B are dimensionless constants and R^2 is the correlation coefficient of regressions.

Figures (3), (4) and (5) shows that the COD experimental measurements gives a acceptable fit for both Langmuir isotherm model and Freundlich isotherm model with a acceptable analogous and a linear regression coefficient R^2 of 0.9519 and 0.9317, respectively. It can be noticed that Temkin isotherm model simulation gives a less acceptable analogous for COD experimental measurements with regression coefficient R^2 of 0.8804.

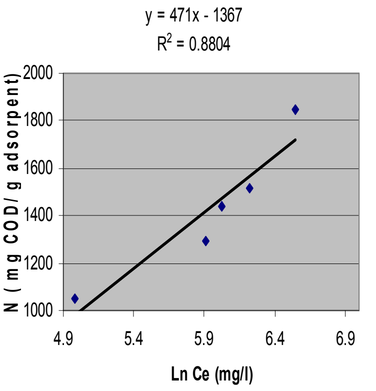

Fig.5 Temkin Adsorption Isotherm

ELECTROCOAGULATION KINETIC BASED ON GR'S FORMATION MECHANISM

The variation of the dissolved mass of Fe^{2+} per unit area of electrode during 60 minutes of electrolysis time with the tested current density is explained in table (4).

Table (4) The variation of the Gr's adsorbent mass with current density

C.D. mA/cm^2	4	8	10	12	20
W_{ad} (gm)/cm^2	0.0401	0.0803	0.1007	0.1204	0.2007

The COD amount that adsorbed on iron adsorbent Gr's can be expressed by N_e which represents the milligrams of adsorbate per gram of coagulant adsorbed. Table (5) explain the amount of COD adsorbed on Gr's coagulant.

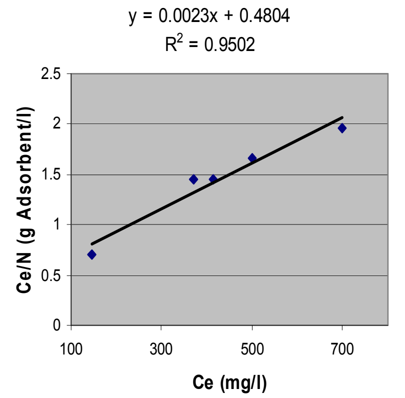

Fig.6 Langmuir Adsorption Isotherm

Table (5) COD milligrams adsorbed on iron species(N_e)

C.D. mA/cm^2	COD,C_e(mg/l)	W (g)	N_e (mg/g)
4	698.95	0.8029	356.27
8	501.795	1.6058	300.91
10	412.995	2.0145	283.94
12	369.375	2.4086	255.59
29	145.780	4.0146	209.04

The data of table (5) was subjected to Langmuir, Freundlich and Temkin isotherms, respectively, as explained in figures (6), (7) and (8) where, the isotherm constants and the correlation coefficient for each regression is explained in table (6):

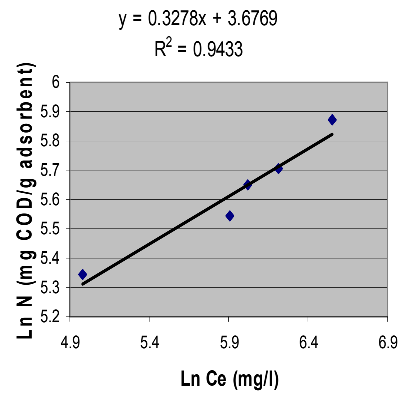

Fig.7 Freundlich Adsorption Isotherm

Table (6) Isotherm constants for adsorption of COD on Gr's

Langmuir	N_{Max} (mg/g)	K_L (l/mg)	R^2
	434.78	0.0048	0.9502
Freundlich	n	K_F (l/g)	R^2
	3.05	39.52	0.9433
Temkin	B	K_T(l/g)	R^2
	88.278	0.0637	0.9004

Note: n and B are dimensionless constants and R^2 is the correlation coefficient of regressions.

Figures (6), (7) and (8) shows that the COD experimental measurements gives a better fit for all of Langmuir isotherm model, Freundlich isotherm model and Temkin isotherm model with a acceptable analogous of a linear regression coefficient R^2 of 0.9519, 0.9317 and 0.9004, respectively. It can be noticed that the COD experimental data approaches to be simulated more precociously with Temkin isotherm model for GR's formation mechanism as compared with $Fe(OH)_3$ formation mechanism .

The variation between the kinetic isotherms which demonstrate the experimental data of COD removal from textile wastewater is due to the variation of the assumption principles for each isotherm. Cosequently Langmuir isotherm assumes monolayer deposition of adsorbate (COD) on homogenous iron coagulant surface, while Temkin considered the effect of heterogeneous iron coagulant /adsorbate (COD) interactions on adsorption isotherm, and the Freundlich isotherm is an empirical model relating the adsorption intensity of adsorbate (COD) towards iron coagulant.

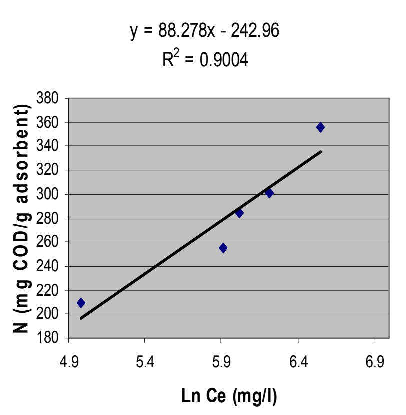

Fig.8 Temkin Adsorption Isotherm

Figures (9) and (10) shows a comparison of Langmuir, Freundlich and Temkin isotherm models prediction from the experimental data of COD removal of textile wastewater with initial COD of 1140 mg/l, iron electrode and pH 4.52.

The two figures indicate that the COD removal experiments data of textile wastewater electrocoagulation process satisfies to large extent and gives a better fit with the Langmuir and Freundlich theoretical models and can be correlated with a regression coefficient of more than 90% for GR's formation mechanism. GR's formation mechanism seems clearly to be more satisfactory than the $Fe(OH)_3$ formation mechanism for COD removal experiments data of textile wastewater electrocoagulation process, while the COD removal experiments data deviate slightly from Temkin isotherm model for the both formation mechanisms with a regression coefficient of 90% or less.

In general, the adsorption isotherm with iron (II) and iron (III) hydroxides combined to generate hydroxo cationic-anionic complex of green rust layers, can be described by Langmuir isotherm equation which gives a better fit of experimental data than the Freundlich and Temkin isotherm model equations.

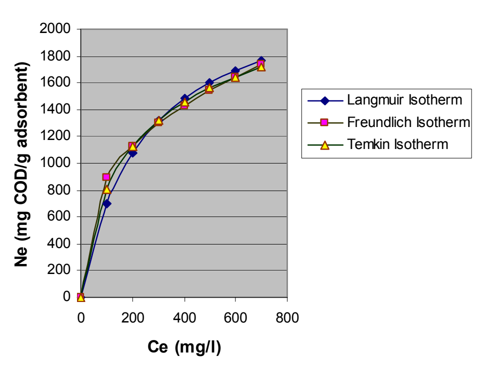

Fig.9 Comparison of Kinetic Models Fe(OH)3

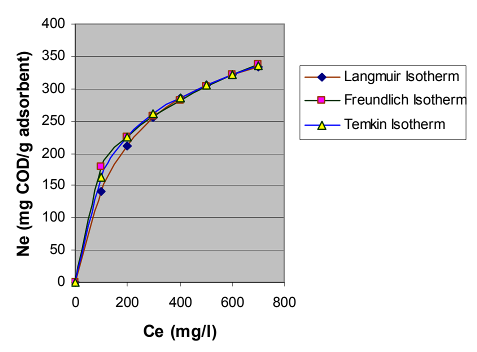

Fig.10 Comparison of Kinetic Models GR's

The following equations represent the suggested Langmuir, Freundlich and Temkin isotherm models for COD removal from textile wastewater by electrocoagulation process.

$Fe(OH)_3$ formation mechanism

Langmuir $$N_e = \frac{9.925\,C_e}{1 + 0.0042C_e} \tag{21}$$

Freundlich $$N_e = 183.55\,C_e^{0.3428} \tag{22}$$

Temkin $$N_e = 471\,Ln(0.0548C_e) \tag{23}$$

GR's formation mechanism

Langmuir $$N_e = \frac{2.078\,C_e}{1 + 0.0048\,C_e} \tag{24}$$

Freundlich $$N_e = 39.52\,C_e^{0.3278} \tag{25}$$

Temkin $$N_e = 88.278\ Ln(0.0637C_e) \tag{26}$$

CONCLUSION

Experiments were carried out to treat a high strength wastewater textile industry located in Al-Hilla-Iraq using a batchwise mode and to determine the feasibility of COD adsorption on iron coagulant with two proposed mechanism for COD removal by EC process using kinetic model isotherms. The electrochemical treatment comprises EC technique using covering a range of current density and electrolysis time operating conditions to remove COD pollutants. The following conclusion can be made:

1.In electrocoagulation of effluent textile wastewater treatment, the percentage COD removal is influenced by the applied current density and the process time. The percentage COD removal increases with an increase in the applied current density and process time for iron anode.

2.The adsorption kinetic for GR's mechanism with the generation of combined hydroxo cationic anionic complex of green rust, can be described by Langmuir isotherm equation which gives a better fit of COD removal experimental data than the Freundlich and Temkin isotherm model equations.

3.The electrocoagulation process was modeled using adsorption isotherm kinetics and it has been observed from the present investigation that Langmuir isotherm model match satisfactorily with the experimental results.

Nomenclature

b_0	constant
B	constant related to adsorption heat
$\%C_R$	contaminant removal percent
C_0	initial COD concentration (mg/l)
C	final COD concentration (mg/l)
C_e	equilibrium COD concentration (mg/l)
C.D.	current density (mA/cm^2)
D	current density (A/cm^2)
F	Faraday's constant (96500 coulombs)
K_L	Langmuir constant (l/mg)
K_F	Freundlich constant (l/gm)
K_T	Temkin constant (l/gm)
M	relative molar mass of the electrode (gm/gmol)
n	empirical constant
N_e	equilibrium amount of adsorbate per unit mass of adsorbent (mg/g)

N_{max} maximum adsorption capacity (mg/g)
R universal gas constant (J/mol k)

t electrcoagulation time (seconds)
T adsorption temperature (K)
V volume of solution (l)
W mass of electrode dissolved (adsorbent) (gm)
W_{ad} mass of adsorbent per unit area of electrode (g/cm^2)

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