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Effective Chemical Coagulation Treatment Process for Cationic and Anionic Dyes Degradation

Hussein M. Ahmed[a] Mariam E. Fawzy*[b] and Hossam F. Nassar[c]

[a]*Housing and Building Research Center (HBRC), Egypt, Sanitary and Environmental Engineering Institute* (SEI)
[b]*Water Pollution Research Department, National Research Centre, P.Box 12622, Dokki, Giza, Egypt.*
[c]*Environmental Science and Industrial Development Department, Faculty of Postgraduate Studies for Advanced Sciences, Beni-Suef University, 62511 Beni-Suef, Egypt.*

Abstract
Throughout the industrial activities, water consumption is increased, resulting in large amounts of wastewater that must be treated before being discharged into the water streams. Coagulation/flocculation and sedimentation processes are considered as one of the most used chemical treatment methods for removing the majority of water contaminants. Cationic dye of methylene blue (MB) and anionic dye of methyl orange (MO) are common hazardous organic wastewater contaminants that mostly degraded by different chemical coagulants processes. Chemical coagulants act as an auxiliary agent in the coagulation/flocculation-sedimentation process. This study aimed to investigate the effectiveness of combined chemical coagulants of $FeCl_3$/lime in the degradation of cationic and anionic dyes. In this work, kinetics, effect of adsorption parameters such as pH, initial concentration of dyes and the chemicals coagulants doses was studied. At an optimum coagulant dosage of (200/70) mg/L and (70/100) mg/L, and optimum pH ranged from (6.0 - 8.0) for MO and MB, repectively . The achieved removal values for both anionic and cationic dyes using the combined coagulant ($FeCl_3$/lime) were 97.78% and 95.54% for MO and MB, respectively. The maximum adsorption capacity of $FeCl_3$/ lime was calculated from the isotherm at 500 mg/g. This technique was successfully conducted for the treatment of tannery and laundry wastewaters for improving the quality of pollution parameters and investigating the efficiency of the applied treatment technique. The achieved removal efficiencies for tannery and laundary wastewater ranged from 93.9 to 94.4 % for COD, 92.9 to 92.5% for BOD_5 , 93.7 to 92.8% for TSS, and 96.7 to 99.2% for turbidity, respectively.
Keywords: Cationic dyes; anionic dyes; chemical coagulants; auxiliary agent; coagulation/flocculation process; tannery; laundry; wastewater.

1. Introduction

Wastewater generated from industrial activities encompasses numerous amount of contaminants. Textile, dyestuff and tanning industries represent a great sector from Egypt income. Most of the used dyes are complex aromatic compounds, stable and hardly can undergo biodegradation. They cause severe environmental problems if they are discharged without treatment to the aquatic environment as they hinder light penteration and decrease oxygen transfer [1-3]. They consume huge amount of water during their manfacturing and are characterized by intense color, high organic content, suspended particules, bad odor and contaminated by heavy metals [4]. Metal complex dyes are widely used in textile industry such as cobalt, copper and chromium complex with azoligands [5]. They are posing several health problems due to their toxicity and necessary to be treated [6]. Dyes are divided into two main categories based on the surface charge of the dye molecule, cationic as methylene blue (MB), anionic dyes as methyl orange (MO) [6]. The MO and MB are highly toxic, carcinogenic and mutagenic [7-9]. As a result of these pollutants, different treatment methods have been applied such as: electronic adsorption, membrane filtration, chemical oxidation, biological treatment, ion exchange, chemical coagulation (CC) and biological decomposition using different microorganisms[10-12]. The coagulation/flocculation

*Corresponding authors E-mail addresse: mariamemadeldin@hotmail.com (Mariam E. Fawzy)
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process is characterized by being practically cost–effective, simple, efficient and does not release toxic substances [12-14]. There are many types of chemical coagulants including organic, inorganic, and polymers. Inorganic materials such as aluminum salts, lime and iron salts, are the most widely used when added to water producing inorganic hydroxides.
Inorganic coagulants are cheap, available and effective in removing differenent contaminantes. The choice of coagulant depends on wastewater characterization, type of particulate to be removed, quantiy of wastewater, cost, sludge treatment, and the quality of effluent required [12,15]. Coagulation/flocculation is an instantenous process accomplished by adding coagulants into wastewater. Consequently, rapid cleavage or aggregation of particles or rearrangement takes place. This is carried out through four stages: 1- electrical double layer condensation, 2-adsorption and charge neutralization, 3- precipitation, and 4- adsorption and interparticle bridging [15-16]. The coagulation and flocculation mechanisms depends on the type of charge of suspended solids in wastewater. Where, if the suspended solids have the same charge of surface then a repulsion force will be established when they come close to each other. Consequently, the treatment process could not be completed [9,10,15]. However, the treatment process could be carried out efficiently through the presence of the coagulant chemicals (CC). Since, by the addition of CC to the suspended solids will carry the same charge, and this results in the neutralization of the non-sediment solids and the small suspended particles will stick to each other forming larger particles (flocs) capable of sedimentation [9,15].
Moreover, the particles of small masses will collide to produce larger masses to increase the size of the particles until the macro flocs are formed and ready for precipitation [15]. Iron salts are widely used in water treatment. Where, by using iron salts in water treatment, a soluble ferric hydroxide is produced that could be used easily in a wide range of pH [17,18].
There are several advantages of using ferric chloride to be used as a coagulant for water treatment in removing turbidity, color, organic contaminants and relatively cheap [17,19]. The coagulation reaction is most effective at a lower pH values arround 5.0 when ferric chloride is used to remove color and organic contaminants [20,21].The lime is one of the most commonly used chemicals for pH adjustment and water stabilization. Lime is characterized by its low cost and higher density [11].

Tannery wastewater

Tanneries manufacturing plants are typically characterized as contaminant intensive industrial complexes which generate widely varying and high-strength colored wastewaters. Tannery wastewater containes high contents of organic and inorganic matters as nitrogenous compounds, chromium, sulfides, suspended solids and dissolved solids. Tannery wastewater could be treated via several techniques including physical, chemical , biological or combination of these methods. The goal of any tanneries wastewater treatment is to reduce the organic matter, solids, nutrients, color and other water quality parameters as BOD_5, COD, TDS and turbidity [9,22]. Song et al [23] use alum and ferric chloride for treatment of tannery wastewater and achieve 85-85% for color removal, 30-37 % COD, 38-46% TSS and 74-99% of chrmomium. While, Ekran et al [24] obtain a high removal rates of TOC ranged from 60.8-75.6% using the same coagulants with 100% removal of total chromium.

Laundry rinsing water

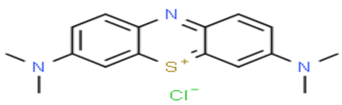
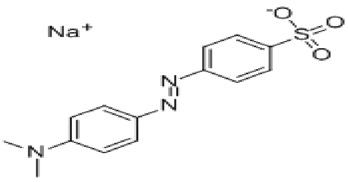
Laundry waters usually accounts for more than half consumption of the daily domestic water in most countries. Rinsing water represents the major part of laundry water. Due to human activities such as sweat, and dust during the day, the clothes become dirty so the water is used for washing, and removing the dirties. Laundry rinsing waters are comparatively clean and are suitable for cleaning up and reuse. The main components of the rinse water are powdered detergents including surfactants and dyes [25]. The process of reuse rinsing water is an effective procedure for saving water for higher priority uses [26,27]. Camila et al [26] use an integrated coagulation/flocculation/sedemintation coupled with membrane sepration for laundry wastewater treatment and achieved satisfactory removal rates of turbidity, color, surfactants, TDS and COD 99.1%, 98.4%, 71.7%, 55% and 70%, respectively.
In this work, attention is directed towards the degradation of both cationic and anionic dyes represented in MB and MO. Chemical coagulation process using cost-effective coagulants of ferric chloride aided with lime ($FeCl_3$/ lime) were studied. Batch adsorption studies were carried out to study the adsorption parameters including the effect of pH, initial dyes concentration and dose of chemical coagulants on the removal of both cationic and anionic dyes. Moreover, Apply such combined technique of coagulation/flocculation for the treatment of tannery wastewater and laundry rinsing water. Meanwhile, carrying out the analysis of water quality parameters of influent and effluent of those wastewater including (pH, turbidity, TDS, TSS, COD, BOD_5, phosphate and chromium) to identify the efficiency of coagulation/flocculation technique for the treatment of wastewater and the possibility of reuse.

2. Materials and methods

2.1 Preparation of synthetic dyes

Methylene blue (MB) and Methyl orange (MO) were purchased from LOBA Chemie, India. Table (1) shows the chemical formula and the characteristics of MB and MO [1,2,8,]. Stock solution of MO and MB solution was prepared by dissolving an accurately weighed amount of dyes 1.0 g (PCE-BSK 310 Instruments UK), in 1.0 L of the deionized water system (DWs) (Millipore system, GER).
A Stock solution of dyes (1.0 g/L =1000 mg/L of dyes). The working solutions were obtained by diluting the stock solution of MB and MO (10, 100, 200, 300, 400, and 500 mg/L).

Table (1): Chemical characteristics of dyes

Methyl orange (MO)	
Chemical formula	 $C_{14}H_{14}N_3NaO_3S$
Absorption wavelength (λ) (nm)	464
Type of dye	Anionic
Molecular weight (M_{wt}) (g/mol)	327.33
Methylene blue (MB)	
Chemical formula	 $C_{16}H_{18}N_3SCl$
Absorption wavelength (λ) (nm)	664
Type of dye	Cationic
Molecular weight (M_{wt}) (g/mol)	373.90

2.2 Chemical coagulation/ Flocculation of dyes
Jar test procedure was used for chemical coagulation process using Jar-Test system, (Thermo Fisher Scientific, US) to determine the optimum dose of coagulants and the optimum pH for each dye. Two experimental runs has been carried out for each dye (MO and MB). All experiments were conducted by mixing 500 mL of sample. The samples were rapidly mixed at 300 rpm for 30 sec and then addition of coagulants ($FeCl_3$/ lime) were immediately added followed by flocculation at 40 rpm for 20 min, and allowed to settle for 30 min for flocs formation [29]. After each run siphon is used to collect the samples from each beaker.

2.2.1 Determination of the optimum dose of coagulants
Coagulant dosage is one of the most important parameters that must be considered in the coagulation /flocculation process. Insufficient dosage and overdosing leads to inefficiency of the chemical treatment process. Therefore, the optimum dose must be determined to minimize the costs and to achieve the best removal effieciency. Inorder to determine the optimum dose of coagulants, a series of $FeCl_3$ solutions were prepared (1.0, 10, 30, 70, 100, and 200 mg/L) with a constant dose of lime (CaO). While, changing the pH from (1.0, 3.0, 6.0, 8.0, and 10) ± (0.2) by sodium hydroxide (NaOH 1.0 N, 40g/L) or HCl (1.0 N, 36.5 %) solution. This was confirmed by measuring the concentrations of MO and MB and calculation of the percentage removal. The procedure was repeated after the determination of the optimimum dose of $FeCl_3$ for each dye. Then a series of lime were prepared (1,10, 30, 70, 100 and 200 mg/L) with changing the pH. The supernatant and the sludge were collected and analysed after each run.

2.2.2 Effect of initial dye concentration
A series of diffent concentration of MB and MO were prepared (10, 100, 200, 300, 400, and 500) mg/L and examined at the pre-determined optimum doses of ($FeCl_3$/lime).

2.2.3 Adsorption isotherms
Adsorption process is one of the most effective widely used technologies. Throughout the modeling of experimental adsorption isotherm, the adsorption mechanisms could be predicted. The isothermal models were applied to figure out the adsorption data. The amount of dye adsorbed at equilibrium q_e (mg/mg) is given by equation (1):

$$qe = \frac{(Co - Ce)v}{m} \quad (1)$$

where C_o is the initial dye concentration (mg/L), C_e is the dye concentration at equilibrium (mg/L), V is the volume of the used dye solution (L), and m is the mass of the adsorbent used (mg). The Langmuir model is based on the assumption that the surface is uniform with no interactions between adsorbed molecules and that, it has defined adsorption sites [16,30]. This model considers that adsorption takes place through the formation of an adsorbate monolayer and leads to the equation (2),

$$\frac{1}{qe} = \frac{1}{qm\,.KL} \cdot \frac{1}{Ce} + \frac{1}{qm} (2)$$

Freundlich isotherm is an empirical equation that assumes that the adsorption surface becomes heterogeneous during the adsorption process [7]. The Freundlich isotherm is expressed as shown in equation (3).

$$Ln\ qe\ \frac{1}{n} Ln\ Ce + Ln\ Kf \quad (3)$$

2.3 Case studies

Bench scale experiments were carried out for the treatment of real tannery and lanundry wastewaters collected from a manufacturing plant and a residential household, respectively located in Cairo, Egypt. The characterization of wastewaters were depicted in Tables (2-3). Application of coagulation/ flocculation followed by sedimentation was studied using $FeCl_3$ aidded with lime. The coagulants dose tested were 10/10, 10/100 and 10/150 mg/L.

Table (2): Characterization of tannery wastewater

Pollutants	Unit	Results
pH	unit	3.10
TDS	mg/L	9490
Turbidity	NTU	1150
TSS	mg/L	3189
COD	mg/L	4250
BOD_5	mg/L	2620
Phosphate	mg/L	2.15
Total chromium	mg/L	1240

**Average of 6 samples*

Table (3): Characterization of laundry wastewater

Pollutants	Unit	Results
pH	unit	7.9
TDS	mg/L	850
Turbidity	NTU	712
TSS	mg/L	720
COD	mg/L	1180
BOD_5	mg/L	530
Phosphate	mg/L	2.9

**Average of 6 samples*

2.4 Analysis

The physico-chemical characteristics of raw wastewaters and treated effluents were analysed. The testing prameters includes pH, turbidity measured by turbidity meter (Hanna meter), total dissolved solids (TDS) is determined by Hanna TDS/COND meter, chemical oxygen demand (COD) by COD digester instrument, MAC, India, the concentration was measured using UV-Vis T70+ Spectrophotometers (PG Instruments, UK Company), biological oxygen demand (BOD_5) using BOD_5 incubator (Airco, India), total chromium by (Atomic absorption spectrometer (AAS) equipped with graphite furnace to measure the low concentration (Thermo Fisher Scientific American provision of scientific). Total suspended solids measured gravimetrically after sample filtration using GF/C filter paper as shown in equation (4), Phosphate (PO_4^{3-}) was measured by stannous chloride method and the concentration was measured using spectrophotometer. All the testing parameters, unless otherwise specified, were carried out according to the Standard Methods for the Examination of Water and Wastewater [31].

$$\text{Total suspended solids } (TSS)\ mg/L = \frac{(\text{W2} - \text{W1})}{\text{the volume of sample mL}}\ x\ 1000 \quad (4)$$

Where; W_1 is the weight of filter paper before dried residue (mg) and W_2 is the weight of filter paper after dried residue (mg).

The removal efficiency (R%) of dyes were adsorbed at equilibrium time is illustrated in equation (5) [32]:

$$R\% = \frac{Ci - Ce}{Ci}\ x\ 100 \quad (5)$$

R % is the removal efficiency, C_i is the initial concentration, and C_e is the equilibrium concentration (mg/L).

The sludge volume index (SVI) refers to the amount of sludge settled after chemical coagulation process. It is a critical operational parameter to determine the settleability of sludge needed to design the wastewater treatment plant. The samples are allowed to settle for 30 min to observe the settling condition of sludge (SVI) and after 30 min of settling the sludge moved downwards by gravity force. The volume of sludge continued to decrease until a time that it remained unchanged. The amount of sludge obtained at all experiments was measured by Imhoff funnel, amount of SVI was determined at 30 min settling and calculated as in equation (6) [10].

$$SVI\ \% = \frac{\text{Settled sludge volume after 30 minutes } (\frac{\text{ml}}{\text{L}})}{\text{total suspended solids}(\frac{\text{mg}}{\text{L}})}\ x\ 100 \quad (6)$$

3. Results

3.1 Effect of coagulant dosage

The effect of different coagulant doses on dye removal were depicted in Figures (1 and 2). Optimum doses of coagulants ($FeCl_3$ /lime) for MO and MB removal were (200/70) mg/L and (70/100) mg/L, respectively. It is obvious that, increasing the concentration of $FeCl_3$ and lime improves color removal rates. The use of $FeCl_3$ alone resulted in an average removal rates of 74% for MB and 79% for MO degradation. However, the combination of lime with $FeCl_3$ improves the removal rates by 19.5% for both MB and MO. Also, the produced sludge is more compact and stable. The overall % R rates of MO and MB reached 95.5% and 93.5%, respectively. The R% increased up to their optimum values as the dose of coagulants increase. At dosages beyond the optimum, the removal rates decrease due to the destabilization of coagulation process takes place [17,33, 34].

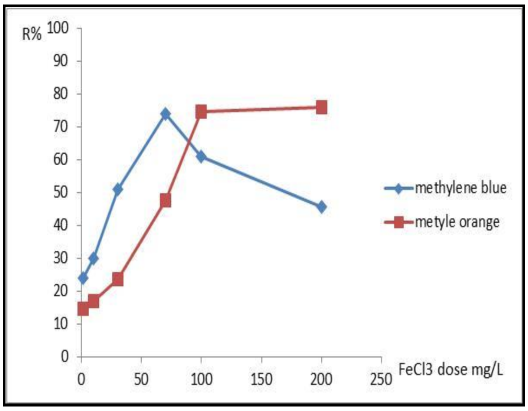


Figure (1): Effect of ferric chloride dose on MO and MB removal

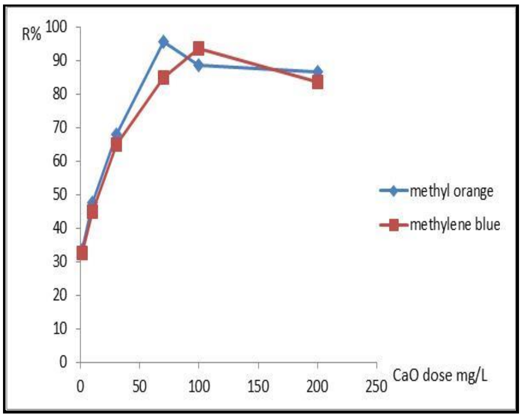


Figure (2): Effect of lime dose on MO and MB removal

3.2 Effect of initial dye concentration

The effect of initial dye concentration on MO and MB removal were studied at different concentrations ranging from 10 mg/L to 500 mg/L. Figure (3) shows that the % R of MO and MB decreases with an increasing initial concentration of dyes [4,26,35]. The results shows that increasing the MO concentration droped the % R from 94% to 40%. While, for MB increasing the concentration droped from 72% to 42.4%. Therefore, aqueous dye solution with initial MO concentration = 200 mg/L was appropriated for all the adsorption studies to verify equilibrium accomplishment [4,11,27].

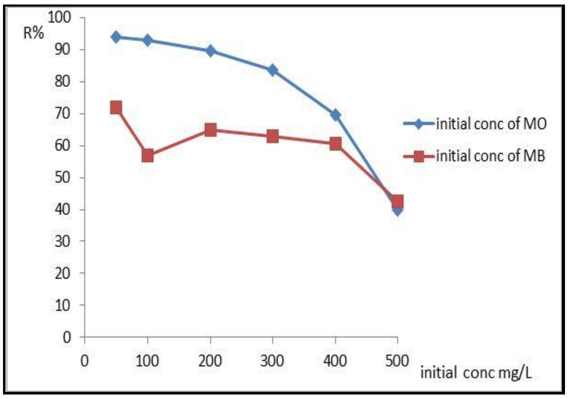


Figure (3): Effect of initial concentration on MO and MB removal

3.3 Effect of pH on dye removal

The pH is responsible for the hydrolysis step in the coagulation process. A series of soluble hydrolysis species are formed with the addition of metal salt coagulants. These species can be either positively or negatively charged depending on the pH value [10,29]. The effects of pH on MB and MO removal using $FeCl_3$ aided with lime are illustrated in Figure (4). The combination of $FeCl_3$ with lime resulted in the formation of $Ca(OH)_2$ and $Fe(OH)_3$ which were able to accept both cationic methylene blue and anionic methyl orange. The results revealed that dyes achieve the highest performance at pH ranged from 1.0 to 10. The optimum pH value recorded that gives the maximum degradation efficiency for MO dyes was pH (1.0 – 6.0), the dye molecules colloid and aggregates with the coagulant and then precipitate.

The removal of MO using $FeCl_3$ and lime increased when pH increased from 1.0 to 6.0, then the removal is decreased at pH > 6.0. The highest percentage removal of MO degradation obtained at pH 6.0 was 95.5%. While, lower pH (1.0-6.0) produces positively charged species as shown in the equations (7,8) [1,6,11, 36].

$$\mathrm{Ca(OH)2 + 2NaOH \rightarrow Na2CaO3 + 2H2O} \quad (7)$$

$$\mathrm{Fe(OH)3 + NaOH \rightarrow NaFe(OH)4} \quad (8)$$

On the other side, the highest percentage removal of MB degradation was achieved at pH 8.0 and reached 94%. The MB is a cationic dye that prefers to bind to negatively charged surface [37,38]. Therefore, the surface charge of coagulants acts as charge neutralization for binding with the methylene blue. When coagulants bound with methylene blue the compounds are rather unstable and leading to breakage at the weaker strength bond. So the de-colorization took place fastly [6,17,28].

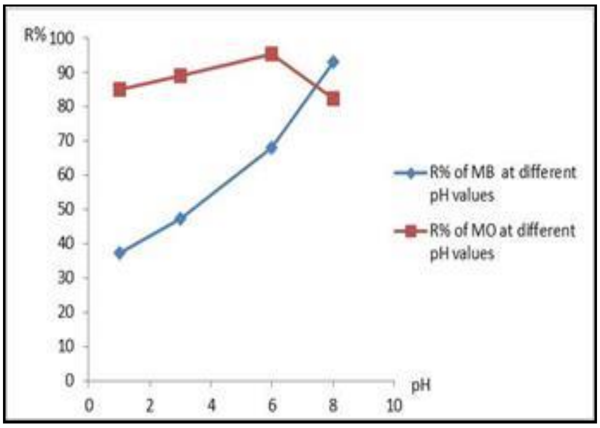


Figure (4): Effects of pH value on MB and MO removal using $FeCl_3$ aided with lime

3.4 Adsorption isotherm

Table (4) summerized the adsorption isotherms with correlation coefficients. The values R^2 of MO and MB for Langmuir isotherm were 0.998 and 0.912 respectively, which is higher than that obtained from Freundlich isotherms [4,6,30]. This indicates that Langmuir isotherm fully describes the nature and the sorption mechanism of MO and MB by chemical coagulation process. The maximum adsorption capacity calculated from Langmuir isotherm was 1428 mg/g for MO. The result obtained from $1/n$ at 25 ºC was (2.9 and 1.4) for MO and MB, respectively, the favorable n values are ($1.0 < n < 10$), where $n > 1.0$ indicates cooperative adsorption [24,40]. Figures (5-6) show Langmuir and Freundlich's models for the degradation of MO and MB by chemical coagulation process.

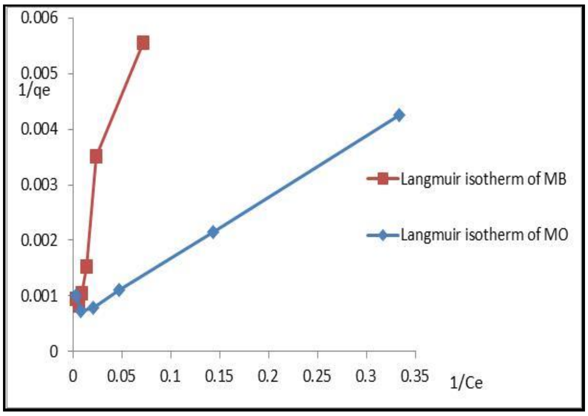


Figure (5): Langmuir isotherm models of MO and MB over chemical coagulation process

3.5 Case studies

3.5.1 Tannery wastewater treatment

Chemical coagulation/flocculation process is a sustainable and effective treatment method for the removal of organic and inorganic contaminants. Application of chemical coagulation using $FeCl_3$ aided with lime resulted in a good quality of effluent as presented in Table (5) and Figure (7). It was noticed that increasing the dose of combined coagulant from 10/10 mg/L up to 10/150 mg/L had an adverse effect on the quality of treated effluent i.e the decrease in % R at 150 mg/L may be attributed to the inhibition of polymeric chain reaction to take place and consequently hindering their combination and flocs formation [13,31,32]. This was assured by our results, the effluent is not clear and contains a high concentration of TSS. At an optimum dose of 10/100 mg/L, the residual values of TDS, turbidity, TSS, COD, BOD and chrmomium were 875 mg/L, 37 NTU, 198 mg/L , 258 mg/L, 185 mg/L and 24.1 mg/L with corresponding percentage removal values of 90.7%, 96.7%, 93.7 %, 93.9% and 97.9%, respectively. The removal of chromium is due to the formation of hydroxide compounds of chromium metals as $Cr(OH)_3$, at pH 8.6. While, complete removal of phosphate ions was achieved as a result of the formation of insoluble ferric phosphate according to the reaction shown in equation (9) [13,34].

$$FeCl_3 + H_3PO_4 \longrightarrow FePO_4 + 3HCl \quad (9)$$

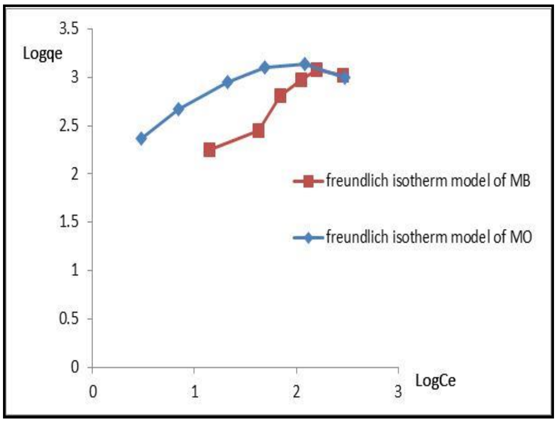


Figure (6): Freundlich isotherm models of MO and MB over chemical coagulation process

3.5.2 Laundry wastewater treatment

The results shown in Table (6) and Figure (8), demonstrates the efficiency of pollutants removal at (10/10) and (10/100) mg/L of $FeCl_3$/lime for laundry wastewater treatment. It is clear that, the optimum dose of coagulants was (10/100) mg/L. The chemical coagulation process produce a very good quality of treated effluent amenable for possible reuse or safe disposal after disinfection. The residual values were, 5 NTU, 33 mg COD/L, 25 mg BOD/L, 19 mg/L TSS.

Table (4): Langmuir and Freundlich isotherm models for degradation of dyes

Isotherm model	Freundlich isotherm model			Langmuir isotherm model		
Dye	R^2	n	K_F	R^2	q_{max}	K_L
MO	0.735	2.9	189	0.989	1428.6	0.06
MB	0.889	1.4	28	0.912	1428.6	0.009

Table (5): Analysis of tannery wastewater at different doses of FeCl3/lime

$FeCl_3$/lime dose	(10/10) mg/L		(10/100) mg/L		(10/150) mg/L	
Pollutants	**Result**	**%R**	**Result**	**%R**	**Result**	**% R**
pH	4.1	-----	8.6	-----	11.20	-----
TDS, mg/L	6520	99.9	875	90.7	1150	87.9
COD, mg/L	2152	49.3	258	93.9	211	95.03
TSS, mg/L	1950	38.8	198	93.7	150	95.3
BOD_5, mg/L	756	71.1	185	92.9	98	96.3
Turbidity, NTU	856	25.5	37	96.7	237	79.4
Phosphate, mg/L	1.95	9.3	N.D	100	N.D	100
Chromium, mg/L	713	42.5	24.1	97.9	11.5	99.1
SVI, ml/L	100	-----	500	-----	550	-----

**N.D: Not Detected*

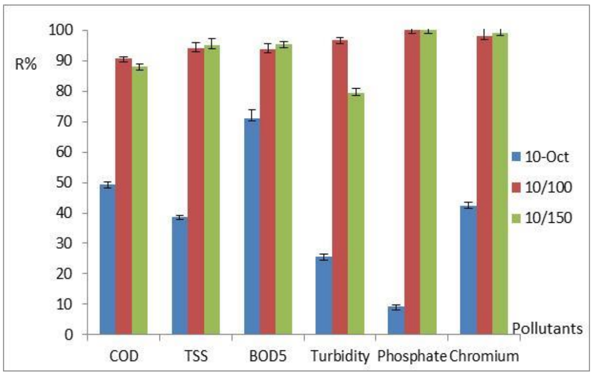


Figure (7): Effect of coagulant dose on the R% of pollutants in tannery wastewater

Table (6): Analysis of laundry wastewater at different doses of $FeCl_3$/lime

$FeCl_3$/lime doses	(10/10) mg/L		(10/100) mg/L	
Pollutants	**Result**	**% R**	**Result**	**% R**
pH	8.7	-----	11.2	----
TDS, mg/L	985	-----	1150	----
COD, mg/L	385	67.3	33	94.4
TSS, mg/L	211	70.7	19	92.7
BOD_5, mg/L	102	80.7	25	92.4
Turbidity, NTU	52	92.7	5.0	99.2
Phosphate, mg/L	1.82	37.2	N.D	100
SVI, ml/L	35	-----	100	-----

**N.D: Not Detected*

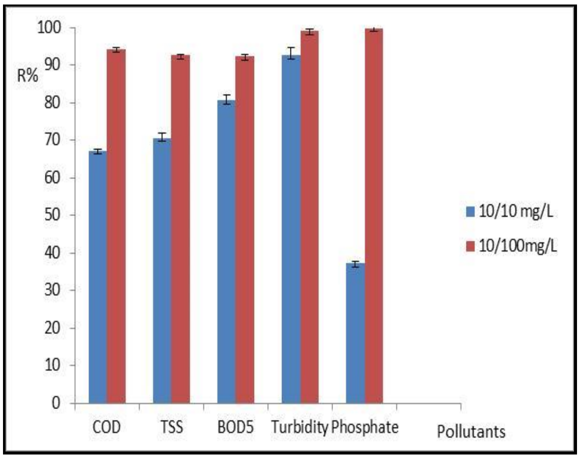


Figure (8): Effect of coagulant dose on the R% of pollutants in laundry wastewater

4. Conclusions

In this study, chemical coagulation/flocculation followed by sedimentation process using combined chemical coagulant ($FeCl_3$/lime) for the degradation of cationic (MB) and anionic (MO) dye were investigated. Moreover, two case studies were studied by the application of the combined CC for tannery and laundry wastewaters to improve the effluent quality. The optimum operating conditions was determined such as pH, dose of coagulants and initial concentration of dyes. The obtained results proved the efficiency of the combined $FeCl_3$/lime that can be used as an effective coagulant for such hardly biodegradable dyes. The optimum dosage of coagulants ($FeCl_3$/lime) were (200/70) mg/L and (70/100) mg/L, respectively.

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