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Short Communication

Optimizing $FeCl_3$ in coagulation-flocculation treatment of dye wastes

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Abstract

The aim of the study was to investigate the efficiency of iron chloride in term of color, chemical oxygen demand (COD), TSS and turbidity removal of dye waste. Response surface methodology (RSM) using central composite design (CCD) was employed to analyze and investigate the effects of the independent factors on color, COD, turbidity, and TSS removal as well as the effect on phytotoxicity concentration. The efficiency of the optimal sample removal for dye color, COD, turbidity, and TSS were 91.89%, 85.40%, 98.36%, and 98.66%, respectively was achieved at a fixed pH value (X_1) of 4, iron chloride dosage (X_2) of 2.72 g/L, mixing time (X_3) of 3 min and mixing speed (X_4) of 30 rpm. While the phytotoxicity concentration was 53.05% at the optimal run which considered as not harmful and could be used for irrigation. The finding indicated that the use of iron chloride in coagulation-flocculation has high potential for treatment of dye waste.

Keywords: color removal, wastewater treatment, pigment waste, textile waste

1. Introduction

Globally, several countries are witnessing various environmental pollution, dye wastes such as azo dyes which include textile dyeing and paper printing applications constitute 50% of the industrial color waste in the world (Verma & Madamwar, 2005), which consider as one of the most toxic pollutants of natural water sources. Printing ink center wastes usually contain a high concentration of dissolved colors, organic compounds (Bhayani, 2014; Luo *et al.*, 2014), chemical oxygen demand (COD), turbidity, toxic chemicals and a high temperature (Zayneb *et al.*, 2015), which emphasizes the need to address these type of waste before the disposal stage. At several small printing centres or industries, dyeing wastes are disposed into the drainage with a primitive purification of treatment which led to the deterioration of water quality and obstruct the water treatment processes (Luo *et al.*, 2014). According to Moghaddam, Moghaddam & Arami, (2010), the liquid color wastes of the printing ink center can destroy the aquatic life if not treated before being discharged into natural water sources. Printing wastes prevent the sunlight of penetrating the water surface which could damage the life of the water plants due to the preventing of photosynthesis process (Verma, Dash, & Bhunia, 2012). The presence of inorganic substances (pigments titanium dioxide and carbon black) makes the wastewater inappropriate to reuse due to the soluble excess concentration (Papić, Koprivanac, Božić, & Meteš, 2004).

Nowadays, wastewater treatment and reuse with using low cost and effective methods became very important in the printing ink industry due to the lack of global clean water and the increasingly stringent regulation concerning its disposal (Bhuiyan, Rahman, Shaid, Bashar & Khan, 2016). The composition of dye wastes displaying very low biodegradability because of the huge molecular weight of the compound structure (Gupta *et al.*, 2016). Some of the previous studies have been indicated that more than 10-15% of the dyes used during the production processes are released into the environment directly without any treatment (Bhayani, 2014; Khehra, Saini, Sharma, Chadha & Chimni, 2006) which caused burden to the biological treatment process due to high content of inorganic salt (Ranganathan, Karunagaran, & Sharma, 2007).

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Various techniques have been employed for treating the dyes waste including physical, chemical and biological techniques, where all of them have been achieved and acceptable efficiency of removal reach more than 90% in some conducted studies (Hassaan, El Nemr & Madkour, 2017; Madhav, Ahamad, Singh, & Mishra, 2018; Noman, Al-Gheethi, Talip, Mohamed, & Kassim ,2019, 2020; Šekuljica *et al.*, 2015). Although, the high efficiency of dyes removal of the physical and chemical methods including the conventional membranes, absorption, ozonation, oxidative process, and others, they involve some handicaps as the high cost, suffering from sludge generation, and require a high level of maintenance (Crini & Lichtfouse, 2019). In addition, many studies have emphasized the seriousness of the usage of chemicals in dyes removal which is often instability, generates undesirable by-products due to the utilization of the strong oxidizing agents (H_2O_2, O_3 and Fenton's reagent), besides that there are some dyes are resistant the chemicals agents and require higher dosage (Holkar, Pandit, & Pinjari, 2014; Paz, Carballo, Pérez & Domínguez., 2016; Sivarajasekar & Baskar, 2015). Moreover, Al-Sahari, Al-Gheethi & Mohamed (2020) indicated that the excessive utilization of chemicals could cause secondary pollution.

On the other hand, the biological degradation methods of dyes including the employing of biometals, metabolic pathways or adsorption by microorganisms, biomass and plants-based methods are generally inexpensive, ecosystem friendly, can be applied widely and have less dangerous aspects compared to the physical and chemical methods (Solís *et al.*, 2012). Iron chloride ($FeCl_3$) has known as one of the most effective coagulants due to its high ability to remove dyes and COD under alkaline and acidic conditions (pH 12 or 4) and its high efficiency with a low dosage. Furthermore, the literature has confirmed the superiority of $FeCl_3$ over several of the coagulants currently used in dyes removal processes such as aluminum sulphate (alum) and ferrous sulphate (FeSO4) in terms of the stability time, the performance under different pH and temperature, and the required for overdoses which often cause secondary pollution (Aziz, Alias, Assari & Adlan, 2007; Kumar & Bishnoi, 2017).

2. Materials and Methods

2.1 Sampling of dye wastes of printing ink

The dye wastes were collected from the printing ink center of Universiti Tun Hussein Onn Malaysia (UTHM), Parit Raja, Batu Pahat, Johor, Malaysia. The collected samples were transferred into an ice container to the laboratory and stored at the cooling rooms at 4 °C. The samples were collected from the outside storage tank before subjected to any type of treatment. 30 L of dye water was collected among two weeks to test 30 experimental runs which were designed by Design Expert software 11.1.2.0. Samples were collected daily and kept in the cooling room during treatment process to keep the water quality and maintain it from any change that may occur due to storage process. Safety rules were taken in consideration during samples collection and all samples were collected between 2:00 and 3:00 p.m.

2.2 Experimental setup

The experimental-setup in the present study consisted of preparation of iron chloride ($FeCl_3$), printing ink wastewater samples. The efficiency of iron chloride ($FeCl_3$) in removing color, COD, turbidity and TSS using the jar tests (coagulation-flocculation process) was investigated. The central composite design (CCD) in duplicates was used to study the coagulation-flocculation optimization based on pH, iron chloride ($FeCl_3$) dosage, mixing rate and mixing speed.

2.3 Preparation of iron chloride

The Iron (III) chloride ($FeCl_3$) (99.9% purity) used in the current research was produced by "Science Company". The product identified as ferric chloride, anhydrous, comes in black powder form. The use of $FeCl_3$ was very carefully due to its fast interaction with air. Therefore, the coagulant $FeCl_3$ was took out from the bottle fast and the container was closed directly to maintain the container content. The iron chloride container was stored at 24±1 ºC

2.4 Optimization of color, COD, turbidity and TSS removal

The best operating treatment of color COD, turbidity and TSS removal was optimized using response surface methodology (RSM). The experimental runs were designed using Design Expert 11.1.2.0, central composite design (CCD) (Stat-Ease, Inc., Minneapolis, U.S.A.) software. The independent factors included the value of pH (X_1), Coagulants dosage (X_2), mixing time (X_3), and mixing speed, (X_4). The maximum (+1), intermediate (0), and minimum (-1) values of each independent variable are illustrated in Table 1.

Response surface methodology (RSM) using central composite design (CCD) was used for optimization of coagulation and flocculation process to see the reflection of coagulant dosage at a different range of pH, mixing rate and mixing time. The range of pH was selected as the average (4-10) which is considered similar to the ranged specified by

Table 1. Coded and un-coded levels of the independent variables used in the current study.

Factor	Symbol	Level		
		Low (-1)	Middle (0)	High (+1)
Value of pH	X_1	4	7	10 (13*)
Iron chloride dosage (g/L)	X_2	1 (0*)	2	3 (4*)
Mixing time (minutes)	X_3	1 (0*)	6	10 (14*)
Mixing speed (rpm)	X_4	30 (0*)	90	150

* A single run was suggested by Design-Expert software among of the 30 experimental runs

Ramli & Aziz, (2015). The coagulant dosage was specified according to research have been performed by Ashtekar, Bhandari, Shirsath, Jolhe & Ghodke (2014). Maxing rate and time were set up as mentioned by Farajnezhad, H. & Gharbani, P. (2012). Factors ranges were specified using various studies to obtain the different results which can more clarify the effects of the factors on the removal efficacies. Table 1 illustrates the factors ranges used during the optimization of coagulation and flocculation process.

In contrast, the dependent variables included removal rate based on the removal of Color)y_1), COD)y_2), Turbidity)y_3) and TSS)y_1). Thirty experimental runs were performed to evaluate the interaction between independent factors and for the optimization of the variables and responses. The significance of the models obtained data and values was specified using the analysis of variance)ANOVA(, where they considered as a significant value when the p-value <0.05.

2.5 Color measurement

Dye wastes are characterized by being high in color, mainly due to the dyes that are present in the pigment printing processes. Samples of dye wastes were filtered using filter paper before measuring the color or dyeing concentration using DR6000. Collected samples subjected to color test before and after treatment processes using spectrometer DR6000 under platinum- Cobalt (Pt. Co) method (number of program 455) with a set wavelength of 120–730 nm.

2.6 Chemical oxygen demand measurements

High range COD by the reactor digestion method was employed to determine COD value using the prepared digestion solution by HACH for cod 20-1500 mg/L range. Samples were prepared by dropping 2 ml of the samples into the digestion solution vials using a clean pipet then the vials were inverted several times gently to mix and put in the preheated DRB200 reactor, which was set at 150 °C for 120 min. After that, the vials were taken out from DRB200 instrument and left for 10 to 15 min to cooling. Finally, COD values were measured using the listed program COD HR at spectrometer DR6000 by cleaning the surface of the vial first and using the pre-preparation sample of distillation water as a blank sample and pressed zero option in the instrument after that COD values of the dyeing waste samples were measured by putting the sample vials in the spectrometer DR6000 separately and pressed measure option.

2.7 Turbidity measurement

The turbidity value of the samples was measured before and after treatment processes where Extech turbidity meter (TB400) employed to measure the turbidity directly. Samples preparation were not required in the turbidity test, the supplied sample bottle of the TB400 was simply filled by sample until the 10 mL line at the TB400 bottle and then the bottle surface was cleaned and dried well to avoid any reading mistakes and then the bottle was placed at the TB400 to measure the turbidity value following Turbidity Meter Model TB400 user guide.

2.8 Total suspended solid measurement

Total Suspended solid value of samples was measured directly using Spectrometer DR6000 with employed program 630. The samples were stirring and immediately poured 10 mL of the blended sample into a sample cell, while a second sample cell was filled with 10 mL of deionized water which considered as blank sample. All the sample cells cleaned and the blank Inserted into the cell holder with Pushing ZERO option in the DR6000 which display shows 0 mg/L TSS then the dye samples was inserted one by one in the cell holder to measure the TSS.

3. Results and Discussion

3.1 Color, COD, turbidity and TSS results of dye samples before treatment

Color and water quality tests have been performed for the collected samples before treatment process to identify and assess the efficiency of iron chloride in color removal and its effects on water quality. The COD, and TSS values on the raw sample were high compared with the Malaysian sewage and industrial effluent discharge standard shown in Table 2 which estimated by 507 vs. 100 mg/L and 227 vs. 100 mg/L, respectively. While the color value was assessed under APHA 2017, method 2120B due to the incompatibility of color unit with Malaysia standard and as well as described in a previous research performed by Anijiofor, Daud, Idrus & Man (2018). The color concentration of the raw water was very high comparing to the APHA 2017 standard where the value obtained was 650 Pt Co versus the standard value of 300 Pt Co. In the other hand pH value was in the range (Table 2), which was 8.05 ± 0.07 vs. 6.5- 8.5. There were no standard recorded for turbidity of the used standards.

Table 2. Mean±STDEV of color, COD, turbidity, TSS concentration before treatment process compared with Malaysian sewage and industrial effluent discharge standard)number of samples, n=3(.

Parameter	Unit	Mean ± stdev	Standard waste
Color	Pt.Co	650±15	300[a]
COD	mg/L	507±7	100[b]
Turbidity	NTU	72±2	NA
TSS	mg/L	227±10	100[b]

(a) APHA 2017, standard method 2120B, (b) Malaysian sewage and industrial effluent discharge standard

3.2 Color removal efficiency using iron chloride

Thirty experiments were performed during this research as shown the result of each run in Table 3. The screening of color and COD removal by iron chloride was conducted based on the designed performed by using RSM. Four independent variables were tested; central composite design (CCD) was employed with thirty runs (designed by Design expert version 11.1.2.0). According to the study performed by Kumar and Bishnoi, (2017), the iron chloride dosage (X_2) was ranged between 1 and 3 g/L in this study. Table 2 displays the observed and predictable results of color and COD removal which designed by Design Expert software after the analysis of data.

According to the Figure 1 and Table 3, the removal of color was increased by increase the iron chloride dosage. However, the average dosage of iron chloride (2 g/L) was showed a high efficiency of color removal which reached to 95.85% (removed 623.03 Pt. CO) and with increasing the

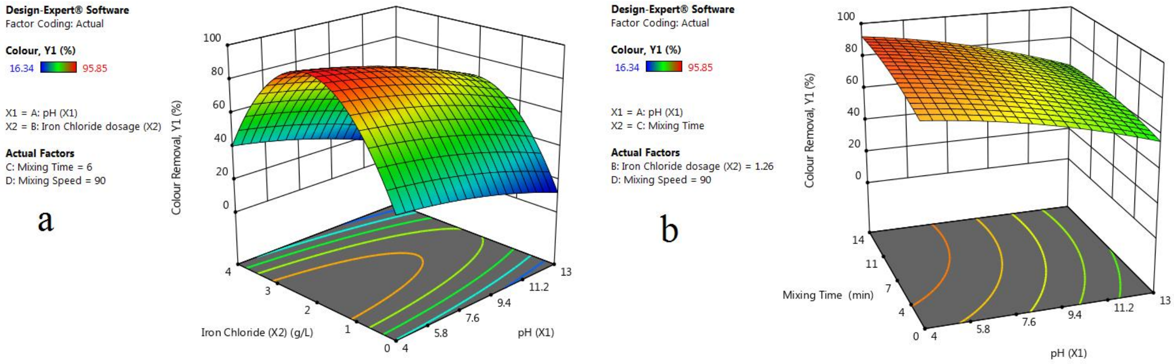

Figure 1. Design-Expert Plot, 3D surface graph showing the effect of iron independent factors on color removal

Table 3. Summary results of all experimental runs of the study (central composite design arrangement and responses)

Run	X_1	X_2	X_3	X_4	y_1	y_2	y_3	y_4
					Observed	Observed	Observed	Observed
1	7	3	6	90	75.85	69.82	79.26	88.75
2	4	2	1	150	87.77	83.85	69.97	76.23
3	13	3	6	90	54.61	70.81	73.03	93.39
4	7	0	6	90	16.34	20.54	21.64	30.22
5	10	3	1	150	61.69	67.46	99.94	97.80
6	7	2	6	90	94.46	94.89	76.79	80.75
7	7	2	6	0	76.15	65.09	77.03	81.19
8	10	3	1	30	57.23	63.31	62.08	73.74
9	7	4	6	90	47.08	59.82	50.43	71.63
10	7	2	6	90	94.31	95.09	76.74	84.19
11	10	1	1	30	62.15	52.72	58.78	69.87
12	7	2	14	90	95.38	93.43	75.53	84.71
13	10	3	10	30	56.31	60.95	64.42	78.72
14	4	1	1	150	82.62	75.23	98.89	92.95
15	4	1	10	30	81.54	69.45	64.43	72.07
16	4	3	10	150	84.15	64.50	73.56	87.22
17	4	3	1	30	71.77	65.05	99.32	94.71
18	7	2	6	90	93.69	95.69	76.83	80.75
19	10	3	10	150	60.38	62.72	70.85	87.67
20	7	2	0	90	74.62	71.48	85.22	90.97
21	7	2	6	90	94.92	94.75	76.82	83.22
22	7	2	6	150	95.85*	97.42*	72.79	85.15
23	10	1	10	30	68.54	58.85	64.33	75.46
24	4	3	10	30	72.62	86.59	100.00*	99.11
25	4	1	10	150	87.54	78.54	65.35	77.53
26	4	2	6	90	90.15	90.15	99.98	99.56*
27	4	1	1	30	79.92	70.47	61.44	71.63
28	10	1	1	150	65.38	53.16	62.85	75.77
29	7	2	6	90	92.00	81.07	60.75	72.95
30	10	1	10	150	70.69	60.98	74.71	81.62

X_1(pH value), X_2 (Iron chloride dosage, %), X_3 (Mixing time, min), X_4 (Mixing speed, rpm), y_1 (Color removal, %), y_2 (COD removal, %), y_3 (Turbidity, %), y_4 (Total suspended solid, %). * The maximum removal run dosage to 3 g/L the removal percentage of color was decreased due to the excessive dosage of $FeCl_3$ that re-stabilized the dye particles (Wong, Teng, & Norulaini, 2007). Color removal was achieve to 84.15% (546.98 Pt. CO) in the best run of iron chloride is 3 g/L, while the efficiency keep decreasing until reach to 47.08% (306.02 Pt. CO) in the out of range run of iron chloride is 4 g/L. Comparing with the previous study that performed by Kumar & Bishnoi (2017), the low dosage (1 g/L) of iron chloride has been recoded a high removal estimated by 80% while the high dosage of 3 g/L was removed around 70% of color. Moreover, Ramli & Aziz (2015) has been reported similar results where the study used iron ferric chloride and the color removal reach to 97.77% with the average dosage of 3.6 g/L, while in the 4 g/L of dosage, the removal ratio of color was estimated by 95%. A synthetic wastewater with a dye concentration of 100 mg/L has been treated using $FeCl_3$ coagulant with a dosage ratio of 400 mg/L. The dye removal efficiency was estimated by 88% (88 mg/L) (Assadi, Nateghi, Bonyadinejad, & Amin, 2013).

On the other hand, Figure 1a is the summary of the obtained results which indicated to the strong effect of iron chloride dosage (X_2) on the color removal and there was no interaction between pH value (X_1) and iron chloride dosage (X_2) affected on removing color. Figure 1b showed that pH value (X_1) has a direct effect on the color removal, where the removal efficiency was increased with reducing the pH value (pH< 7). Other factors were having no effects on the color removal efficiency or they may have had a slight effect which did not considered during the analysis of variance (ANOVA). The model of ANOVA of color removal response was significant with a P-value of 0.0001 (Table 4). According to Table 4, pH value (X_1) has a linear effect on the color removal with a P-value of 0.0011, and iron chloride dosage (X_2) has a quadratic effect on the color removal with a P-value estimated by 0.0001, while there were no effects of mixing time (X_3) and mixing speed (X_4) factors which recorded insignificant values (P-values >0.05). In addition, no interactions effects between the factors were recorded in color removal (Table 4).

3.3 COD removal efficiency using iron chloride

COD tests were shown positive values of all treated samples. COD test results were showed a high efficiency of removal on the average dosage of iron chloride. Table 3 display that four different experimental dosage of iron chloride were used in the thirty experimental runs (1, 2, 3 g/L with a single out of range run of 4 g/L), while the maximum efficiency of COD removal was with iron chloride dosage (X_2) of 2 g/L which achieved to 97.42% (493.92 mg/L). Figure 2a explain the removal of COD with take in consideration the pH value (X_1) and iron chloride dosage (X_2) as affected factors where the obtained results were indicated the pH value (X_1) and iron chloride dosage (X_2) have effects on removing COD where the removal ratio was changed strongly with changing X_1 and (X_2) values. As comparison with Kumar & Bishnoi, (2017), three different dosage of iron chloride have been used which are 2, 2.5, 3 g/L, while the highest removal of COD was recorded from the sample with 2 g/L dosage which estimated by 71.3% (6,844.8 mg/L), where the difference in removal ration could be due to the high concentration of color in Kumar & Bishnoi, (2017) study which was estimated by 9,600 mg/L.

On the other hand, Figure 2b indicated the effect of mixing speed (X_4) on the COD removal, where the removal was improved by mixing speed (X_4) increase. However, Figure 2b showed that mixing time (X_3) has no effect on the COD removal. The model of ANOVA of COD removal response was significant with a P-value of 0.0018 while the

Table 4. ANOVA analysis for optimization response surface quadratic model of color, COD, turbidity and TSS removal

Source model	P-value							
	y_1		y_2		y_3		y_4	
	< 0.0001	Significant	0.0018	Significant	0.0482	Significant	0.0088	Significant
X_1	0.0011		0.0238		0.0620		0.1885	
X_2	0.8411		0.0834		0.0150		0.0006	
X_3	0.1551		0.2012		0.3531		0.8501	
X_4	0.1353		0.4647		0.4947		0.2236	
X_1X_2	0.8157		0.3713		0.3697		0.3978	
X_1X_3	0.8610		0.8061		0.7302		0.8298	
X_1X_4	0.7551		0.8004		0.1656		0.1976	
X_2X_3	0.6354		0.8330		0.5271		0.8687	
X_2X_4	0.6604		0.5473		0.4861		0.6629	
X_3X_4	0.7913		0.5437		0.2628		0.4691	
X_1^2	0.4879		0.6676		0.1538		0.0388	
X_2^2	< 0.0001		< 0.0001		0.0023		0.0005	
X_3^2	0.5765		0.4576		0.5692		0.5979	
X_4^2	0.3190		0.0407		0.8028		0.8689	
Residual								
Lack of Fit			0.1492	Not Significant	0.0995	Not significant	0.0715	Not significant
Pure Error								
Cor Total								

X_1, X_2, X_3 and X_4 are the main effects; X_1^2,X_2^2, X_3^2 and X_4^2 are the square effects; X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4 and X_3X_4 are the interaction effects. X_1(pH value), X_2 (Iron chloride dosage, g/L), X_3 (Mixing time, min), X_4 (Mixing speed, rpm). y_1 (Color removal, %), y_2 (COD removal, %), y_3 (Turbidity, %), y_4 (Total suspended solid, %)

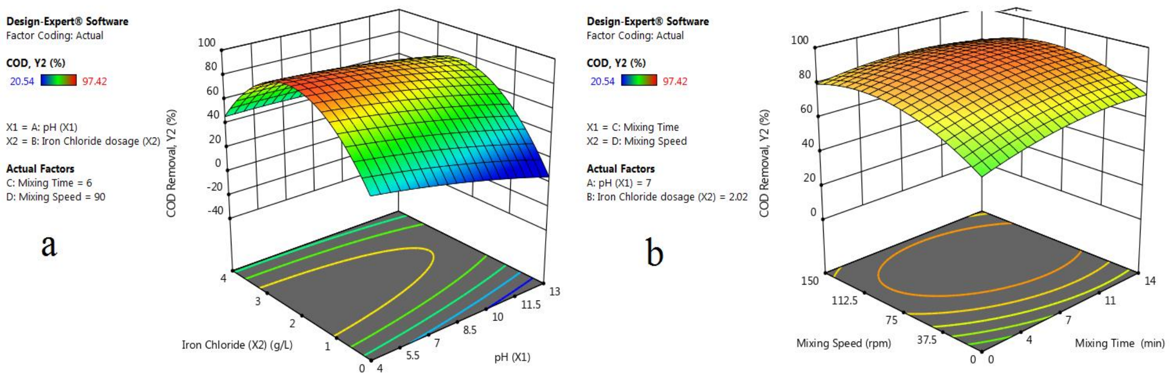

Figure 2. Design-Expert Plot, 3D surface graph showing the effect of iron independent factors on COD removal

lack of fit was not significant with a P-value of 0.1492 which indicate that the model fit is well (Table 4). According to Table 4, pH value (X_1) has a linear effect on the COD removal with a P-value of 0.0238, while iron chloride dosage (X_2) and mixing speed (X_4) factors have a quadratic effect on the COD removal with a P-value of 0.0001 and 0.0407, respectively.

The decreased of removal ration by increase the iron chloride dosage (X_2) over 2 g/L could be refer to several factors such as the increase of the strength of repulsive forces between dosage particles, or the restabilization of the dye particles by excess iron chloride species **(**Stephenson and Duff 1996**).**

3.4 Turbidity removal efficiency using iron chloride

The efficiency of turbidity removal was estimated from 50.43 to 100 % at the dosage between 2-3 g/L. The removal ratio obtained at iron chloride dosage (X_2) of 4 g/L was 50.43% (30.31 NTU) due to the restabilization of the color particles and excessive dosage of iron chloride which contributed to the turbidity of water. While the turbidity achieve the maximum removal value estimated by 100 % (72) under pH value of 4 with the dosage (X_2) of 3 g/L (Table 3, Figure 3). According to Ramli & Aziz (2015), the removal percentage of turbidity using iron chloride was closed to the results observed in is study, where the maximum value of removal was observed estimated by 97.78% with a dosage of 3.5 g/L. Mohamed *et al.* (2020) reported a high removal of turbidity from dairy soiled water reached 99% (6,484.5 NTU) with a dosage concentration of $FeCl_3$ of 705 mg/L which indicated to the high effects of $FeCl_3$ on turbidity removal even through the small concentration. While there were no effect of the other factors, X_1**,** X_3**,** and X_4 on the turbidity removal**.** Table 4 showed that iron chloride X_2 has a linear and quadratic effects on the removal of turbidity with p value of 0.0150 and 0.0023 respectively, while other factors X_1**,** X_3**,** and X_4 were recorded insignificant effects on the removal ratio (P-value >0.05). The model of ANOVA of turbidity removal response was significant with a P-value of 0.0482 while the lack of fit was not significant with a P-value of 0.0995 (Table 4).

3.5 TSS removal efficiency using iron chloride

According to Table 3, the removal ratio of TSS were estimated as the lowest by 69.87% (158.61 mg/L) with a dosage of 1 g/L and pH value of 10, and the highest removal ratio of TSS reached 99.56% with a dosage of 2 g/L under pH value of 4. Figure 4, indicates to the efficient effect of iron chloride to remove TSS by using the average dosage (2 g/L). The TSS removal ratio was decreased by increasing the iron chloride dosage over 2 g/L which can be due to the disturbance of the sediment particles caused by the excessive dosage. Irfan *et al.* (2017) has been approximately matched the obtained results of the current study, where the maximum removal of TSS was reported using the iron chloride dosage of 2.5 g/L was 95% (10,882.25 mg/L). The removal of TSS had effected by the linear and quadratic effects of iron chloride dosage (X_2) where it affects positively with a P-value of 0.0006 and 0.0005

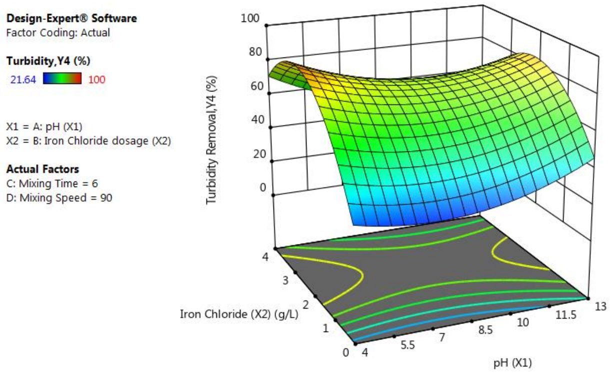

Figure 3. Design-Expert plot, 3D surface graph showing the effect of iron chloride dosage and pH value on turbidity removal

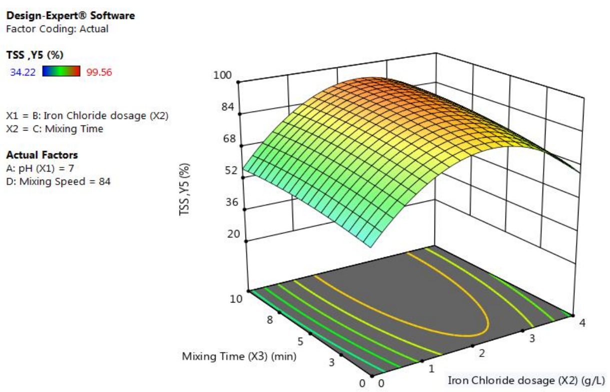

Figure 4. Design-Expert plot, 3D surface graph showing the effect of iron chloride dosage and mixing time on TSS

respectively and/or due to the quadratic effects of pH value (X_1) which affect positively on the TSS removal with a P-value of 0.0388)p <0.05( )Table 4(. Mixing time (X_3) and mixing speed)X_4(factors had no effects on the TSS removal as shown in Table 4)P <0.05(. The model of ANOVA of TSS removal response was significant with a P-value of 0.0088 while the lack of fit was not significant with a P-value of 0.0715)Table 4(.

3.6 Validation of the optimal parameters

The optimal run was provided by the Design-Expert software 11.1.2.0 employing the option of "Point Prediction", where in this option the software suggests an additional run to be tested for the confidence test. The suggested values given by the software for the confidence run for the factors X_1 (pH value), X_2 (Iron chloride dosage, g/L), X_3 (Mixing time, min), X_4 (Mixing speed, rpm) were by 4, 2.27, 3, and 30 respectively (Table 5).

Table 5 were showed that removal ratio of color (y_1), COD (y_2), turbidity (y_3) and TSS (y_4) were compatible to the predicted removal ratio given by Design Expert software which means the analytical of the software was successful with the predicted values of the software with standard error of ±5. According to Table 5 the predicted removal of color (y_1), COD (y_2), turbidity (y_3) and TSS (y_4) were 93.36, 82.52, 96.83, and 99.56%, respectively, versus the tested removal values of 91.89, 85.40, 98.36, and 98.66%. Under this condition, the independent factors exhibited strong interactions by a high percentage of confidence level with a standard error of ±5 for all responses.

4. Conclusions

Color test result of the collected raw water was indicated to the high contaminated of the raw water where comparing to the APHA 2017 standard, the color concentration was higher than the limitation of the standard which estimated as 650 Pt Co versus the standard value of 300 Pt Co as well as COD and TSS tests which indicated to the over range value comparing with the Malaysian Environmental Quality (Sewage and Industrial Effluents) Regulations (EQA, 1979) standard 507 vs 100 mg/L and 227 vs 100 mg/L. It is revealed that the independent factors exhibited high efficiency in the removal of color (y_1), COD (Y_2), turbidity (Y_3), and TSS (Y_4) of printing ink wastewater sample which estimated by 93.36, 82.52, 96.83, and 99.56% respectively at the optimal run which were obtained by combination of a fixed pH value (X_1) of 4, iron chloride dosage (X_2) of 2.72 g/L, mixing time (X_3) f 3 min and mixing speed (X_4) of 30 rpm. According to the obtained results in the current study, the pH (X_1) and iron chloride dosage (X_2) factors were effected strongly on removal efficiency of the all responses (P-value <0.05). Mixing time (X_3) was unaffected factor in the current study where according to the ANOVA analysis there is no effects of the mixing time on the removal efficiency (P-value >0.05). While the mixing speed factor (X_4) had indirect effects (quadratic effect) on the removal of COD only. The obtained results of the current study may indicate that the coagulation process does not significantly affect the removal efficiency of the all responses.

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References

Amal, G. A., Tawfik, M. M., & Hassanein, M. S. (2011). Foliar feeding of potassium and urea for maximizing wheat productivity in sandy soil. *Australian Journal of Basic and Applied Sciences, 5*, 1197-1203.

Al-Sahari, M., Al-Gheethi, A. A. S., & Mohamed, R. M. S. R. (2020). Natural coagulates for wastewater treatment; A review for application and mechanism. In A. Al-Gheethi, R. R. Mohamed, E. Noman, & A. M. Kassim (Eds.), *prospects of fresh market wastes management in developing countries. Water science and technology library* (Volume 92). Cham. Switzerland: Springer. doi:10.1007/978-3-030-4264 1-5_2

American Public Health Association, American Water Works Association, and Water Environment Federation. (2017). *Standard methods for the examination of water and wastewater*. Washington, DC: American Public Health Association.

Anijiofor, S. C., Daud, N. N. N., Idrus, S., & Man, H. C. (2018). Recycling of fishpond wastewater by adsorption of pollutants using aged refuse as an alternative low-cost adsorbent. *Sustainable Environment Research, 28*(6), 315-321.

Ashtekar, V. S., Bhandari, V. M., Shirsath, S. R., Jolhe, P. S., & Ghodke, S. (2014). Dye wastewater treatment: Removal of reactive dyes using inorganic and organic coagulants. *I Control Pollution, 30*(1).

Table 5. The best operating for removal color, COD, turbidity and TSS using iron chloride

Responses	X_1	X_2	X_3	X_4	Experimental result		
					Tested	Predicted	Error %
y_1	4	2.72	3	30	91.89	93.36	1.57
y_2	4	2.72	3	30	85.40	82.52	3.49
y_3	4	2.72	3	30	98.36	96.83	1.56
y_4	4	2.72	3	30	98.66	99.56	0.91

y_1 (Color removal %), y_2 (COD removal, %), y_3 (Turbidity removal, %), y_4 (TSS removal), X_1(pH value), X_2 Iron chloride dosage, g/L), X_3 (Mixing time, min), X_4 (Mixing speed, rpm

Assadi, A., Nateghi, R., Bonyadinejad, G. R., & Amin, M. M. (2013). Application of coagulation process reactive blue 19 dye removal from textile industry wastewater. *International Journal of Environmental Health Engineering*, *2*(1), 5.

Aziz, H. A., Alias, S., Assari, F., & Adlan, M. N. (2007). The use of alum, ferric chloride and ferrous sulphate as coagulants in removing suspended solids, colour and COD from semi-aerobic landfill leachate at controlled pH. *Waste Management and Research*, *25*(6), 556-565.

Bhayani, R. B. (2014). *Color Removal of dyes wastewater by coagulation and microfiltration processes* (Doctoral dissertation, Cleveland State University, Cleveland, OH).

Bhuiyan, M. R., Rahman, M. M., Shaid, A., Bashar, M. M., & Khan, M. A. (2016). Scope of reusing and recycling the textile wastewater after treatment with gamma radiation. *Journal of Cleaner Production*, *112*, 3063-3071.

Crini, G., & Lichtfouse, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, *17*(1), 145-155.

Environmental Quality Act. (1974). Environmental quality act under the environmental quality (sewage and industrial effluents) regulations (EQA), 1979, regulations 8 (1), 8 (2) and 8 (3). Retrieved from https://www.span.gov.my/document/upload/p9tEiK2zpNaAu3QkfEx7qER6Dpu1g0JB.pdf

Farajnezhad, H., & Gharbani, P. (2012). Coagulation treatment of wastewater in petroleum industry using poly aluminum chloride and ferric chloride. *International Journal of Research and Reviews in Applied Sciences*, *13*(1), 306-310.

Gupta, V. K., Moradi, O., Tyagi, I., Agarwal, S., Sadegh, H., Shahryari-Ghoshekandi, R & Garshasbi, A. (2016). Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification: a review. *Critical Reviews in Environmental Science and Technology*, 46(2), 93-118.

Hassaan, M. A., El Nemr, A., & Madkour, F. F. (2017). Testing the advanced oxidation processes on the degradation of Direct Blue 86 dye in wastewater. *The Egyptian Journal of Aquatic Research*, *43*(1), 11-19.

Holkar, C. R., Pandit, A. B., & Pinjari, D. V. (2014). Kinetics of biological decolorisation of anthraquinone based Reactive Blue 19 using an isolated strain of Enterobacter sp. F NCIM 5545. *Bioresource Technology*, *173*, 342-351.

Irfan, M., Butt, T., Imtiaz, N., Abbas, N., Khan, R. A., & Shafique, A. (2017). The removal of COD, TSS and colour of black liquor by coagulation–flocculation process at optimized pH, settling and dosing rate. *Arabian Journal of Chemistry*, *10*, S2307-S2318.

Khehra, M. S., Saini, H. S., Sharma, D. K., Chadha, B. S., & Chimni, S. S. (2006). Biodegradation of azo dye CI Acid Red 88 by an anoxic–aerobic sequential bioreactor. *Dyes and Pigments*, *70* (1), 1-7.

Kumar, S. S., & Bishnoi, N. R. (2017). Coagulation of landfill leachate by $FeCl_3$: Process optimization using Box–Behnken design (RSM). *Applied Water Science*, *7*(4), 1943-1953.

Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., & Wang, X. C. (2014). A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of Total Environment*, *473*, 619-641.

Madhav, S., Ahamad, A., Singh, P., & Mishra, P. K. (2018). A review of textile industry: Wet processing, environmental impacts, and effluent treatment methods. *Environmental Quality Management*, *27*(3), 31-41.

Moghaddam, S. S., Moghaddam, M. A., & Arami, M. (2010). Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology. *Journal of Hazardous Materials*, *175* (1-3), 651-657.

Mohamed, A. Y. A., Siggins, A., Healy, M. G., Ó hUallacháin, D., Fenton, O., & Tuohy, P. (2020). Appraisal and ranking of poly-aluminium chloride, ferric chloride and alum for the treatment of dairy soiled water. *Journal of Environmental Manage ment*, *267*,110567.

Noman, E., Al-Gheethi, A. A., Talip, B., Mohamed, R., & Kassim, A. H. (2019). Mycoremediation of Remazol Brilliant Blue R in greywater by a novel local strain of Aspergillus iizukae 605EAN: optimisation and mechanism study. *International Journal of Environmental Analytical Chemistry*, 1-19.

Noman, E., Al-Gheethi, A., Talip, B. A., Mohamed, R. & Kassim, A.H., (2020). Decolourization of dye wastewater by a malaysian isolate of *Aspergillus iizukae* 605EAN Strain: A biokinetic, mechanism and microstructure study. *International Journal of Environmental Analytical Chemistry*, 1-24.

Papić, S., Koprivanac, N., Božić, A. L., & Meteš, A. (2004). Removal of some reactive dyes from synthetic wastewater by combined Al (III) coagulation/carbon adsorption process. *Dyes and Pigments*, 62(3), 291-298.

Paz, A., Carballo, J., Pérez, M. J., & Domínguez, J. M. (2017). Biological treatment of model dyes and textile wastewaters. *Chemosphere*, *181*, 168-177.

Ramli, S. F., & Abdul Aziz, H. (2015). Use of ferric chloride and chitosan as coagulant to remove turbidity and color from landfill leachate. *Applied Mechanics and Materials*, *773*, 1163-1167).

Ranganathan, K., Karunagaran, K., & Sharma, D. C. (2007). Recycling of wastewaters of textile dyeing industries using advanced treatment technology and cost analysis-case studies. *Resources, Conservation and Recycling*, *50*(3), 306-318.

Šekuljica, N. Ž., Prlainović, N. Ž., Stefanović, A. B., Žuža, M. G., Čičkarić, D. Z., Mijin, D. Ž., & Knežević-Jugović, Z. D. (2015). Decolorization of anthraquinonic dyes from textile effluent using horseradish peroxidase: Optimization and kinetic study. *The Scientific World Journal*, *2015*.

Sivarajasekar, N., & Baskar, R. (2015). Agriculture waste biomass valorisation for cationic dyes sequestration: A concise review. *Journal of Chemical and Pharma ceutical Research*, *7*(9), 737-48.

Solís, M., Solís, A., Pérez, H. I., Manjarrez, N., & Flores, M. (2012). Microbial decolouration of azo dyes: A review. *Process Biochemistry*, *47*(12), 1723-1748.

Stephenson, R. J., & Duff, S. J. (1996). Coagulation and precipitation of a mechanical pulping effluent—I. Removal of carbon, colour and turbidity. *Water Research*, *30*(4), 781-792.

Verma, A. K., Dash, R. R., & Bhunia, P. (2012). A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management*, 93 (1), 154-168.

Verma, P., & Madamwar, D. (2005). Decolorization of azo dyes using Basidiomycete strain PV 002. *World Journal of Microbiology and Biotechnology*, *21*(4), 481-485.

Wong, P. W., Teng, T. T., & Norulaini, N. A. R. N. (2007). Efficiency of the coagulation-flocculation method for the treatment of dye mixtures containing disperse and reactive dye. *Water Quality Research Journal*, *42*(1), 54-62.

Zayneb, C., Lamia, K., Olfa, E., Naïma, J., Grubb, C. D., Bassem, K. & Amine, E. (2015). Morphological, physiological and biochemical impact of ink industry effluent on germination of maize (Zea mays), Barley (Hordeum vulgare) and Sorghum (*Sorghum bicolor*). *Bulletin of Environmental Contamination and Toxicology*, *95*(5), 687-693.