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Comparison of Synthetic and Natural Organic Polymers as Flocculant for Textile Wastewater Treatment

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Abstract: Performance of synthetic organic polymer (polyacrylamide) and natural organic polymers (pectin) as flocculant in coagulation-flocculation treatment will be assessed. Analysis of functional group of organic polymer was done by Fourier Transform Infrared Spectroscopy - Attenuated Total Reflectance (FTIR-ATR). Response Surface Methodology - Central Composite Design (RSM-CCD) was used to evaluate the interaction effects of pH, coagulant dose and flocculant dose. The experiment was conducted in lab scale of 500mL of sample textile wastewater with six paddle of conventional jar test. Trimmed Spearman-Karber method has been used to estimate median lethal concentration (LC_{50}) values and their confidence intervals. The result shows polyacrylamide added in the treatment was the best at optimum pH 5, coagulant dose at 275 mg/ L and flocculant dose at 35 mg/ L with 88 and 80% removal. In contrast, additions of natural organic flocculant only manage to remove 54.2 and 67 % at the optimum pH 5, coagulant and flocculant dosage at 427.4 and 21.9 mg/ L respectively. However, polyacrylamide treatment claimed to be more toxic based on lethal concentration (LC_{50}) at 17 % compare to natural organic flocculant at 34%.

Key words: Polyacrylamide · Pectin · Coagulation- flocculation treatment · Response Surface Methodology - Central Composite Design · Trimmed Spearman-Karber method · Lethal concentration.

INTRODUCTION

High level of toxicity in textile industrial wastewater has long posed a threat to the environment [1]. Desizing, scouring, dyeing and printing process from textile industries generates high level of COD and dark coloured wastewater. Thus proper treatments are required before the effluent can be discharged [2]. Recently, considerable research on colour removal from textile wastewater effluents has been carried out, where treatment technologies include various physical-chemical processes such as coagulation, adsorption, membrane filtration, advanced oxidation or biological oxidation [3].

Biological treatment processes are frequently used to treat textile effluents. However, longer time needed in order to decolourize textile wastewater compare to other process. Che Noraini *et al*. [4] used bio-sorption process for methylene blue degradation by *Sphingomonas paucimobilis* under aerobic conditions. Results revealed that bacterium could effectively decolourize high concentrations of dye (1,000 mg/L) with a concomitant decrease in COD within 5 days hydraulic retention time (HRT). Comparative studies between enzymatic catalysis, coagulation/flocculation and nanofiltration processes on textile effluent showed 99, 94 and up to 99% colour removal, respectively [5]. However, these processes do not exhibit similar behaviour on chemical oxygen demand (COD) since the obtained results showed a partial removal of COD for coagulation/flocculation and nanofiltration but no effect for enzymatic catalysis.

Coagulation/flocculation is a widely used process for colour removal. It is a favourable process since the removal of dye is not based on partial decomposition of dye compounds thus produced no toxic intermediates or harmful product [6]. Various kind of coagulant-flocculant has been developed including inorganic-organic,

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inorganic-natural polymer, organic-organic and organic-natural throughout the years. Aluminum (alum) sulfate, ferrous sulfate and ferric chloride are extensively used as inorganic polymer from years back. Nowadays, synthetic organic flocculants are introduced to industries and widely used in wastewater treatment plant. For examples, polyacrylamide (PAM) has been used due to its high molecular weight and good performance in coagulation-flocculation treatment in spite of it being non-biodegradable and hazardous to living organisms [7]. Those aluminium based polymer poses a carcinogenic and hazardous effects which produce a secondary pollutant after the treatment. Thus natural organic polymer seems to be a reasonable approach to replace the toxic material in the wastewater treatment. Numbers of natural organic polymers have been studied by previous researchers like moringa oleifera, grape seeds and tannin as plant based meanwhile chitosan from animal based [8]. Therefore, the use of natural organic flocculant extracted from banana pseudo-stem can be considered as an alternative to polyacrylamide. Use of banana pseudostems after harvest season can minimize the amount of waste produced. Natural organic flocculant was chosen due to its potential resemblance to PAM and its relatively mild toxicity effects on the environment since it is occur naturally in most of plant tissues [9]. It can also be considered as synthetic flocculant substitute due to the presence of functional groups such as carboxyl-carboxylate [10]. The role of hydrolysing metal salt namely magnesium chloride is use to induce effective flocculating activity of negatively charged polymers and no further studies involved in combination of hydrolysing metal salt, Magnesium chloride ($MgCl_2$) with natural organic flocculant thus far [11].

In this study, Magnesium chloride ($MgCl_2$) was used as inorganic coagulant and two difference types of flocculant namely natural and synthetic organic flocculants. Natural organic flocculant was analysed using Fourier Transform Infrared (FTIR) for functional group identification. In order to examine the efficacy of colour and COD removal from industrial textile wastewater, three variables were selected for coagulation-flocculation process; pH, coagulant and flocculants dose. Optimum condition of the process was designed by using Response Surface Methodology - Central Composite Design (RSM-CCD). The sludge produced after the treatment was analyzed for toxicity assessment according to seed germination test using *Lettuce Sativa* seed.

MATERIALS AND METHOD

Preparation of Natural Organic Flocculant: Raw banana pseudo-stem was obtained after being harvested. Samples preparation started with cleaning the raw material, cutting it into smaller pieces and heating in water bath at 90°C for 15 minutes [12]. Later the samples were dried at 60°C for 48 hours and grind into 500 ìm. Extraction took place in acidic condition at pH 2, 80°C and about 4 hours. It was then collected and ground to powder form. Finally the homogenous powder was stored at room temperature.

Determination of Functional Group: Fourier Transform Infrared Spectroscopy - Attenuated Total Reflectance (FTIR-ATR); brand Perkin-Elmer Spectrum 2000 Spectrophotometer has been used to determine the functional group of natural organic flocculant at mid infrared region (4000-400cm^{-1}).

Jar Tests: Wastewater effluent is collected from one of the textile company in Penang. The samples being preserved by acidification to pH < 2 with H_2SO_4 based on APHA Standard Methods of Examination of Water and Wastewater [14]. Average of the initial COD and colour unit were recorded at 530 mg/L and 610 pt co. An industrial grade Magnesium chloride ($MgCl_2$) and anionic Polyacrylamide (CHEMFLOC 985W) were obtained from Hamburg Ind. Inc (HmBg) and Chemical Systems, respectively.

A standard jar-test apparatus was used for the coagulation and flocculation tests. A defined volume, 250 mL of textile dye wastewater was transferred into 500 mL beaker. The pH level was adjusted with 1M NaOH and 1M H_2SO_4. The samples were rapidly mixed at a paddle speed of 150 rpm after addition of inorganic coagulant. The rapid mixing continued for 3 minutes. Later, the synthetic or natural organic flocculants were added into the samples while the solution was slowly mixed for 15 min at 45 rpm. The samples were left to settle for 30 minutes. Then 10 mL of the supernatant was taken for COD (via HACH method; method number 5220D) and pH measurements by HACH SenIon 3. Concentration of COD was taken using HACH Spechtrophotomer DR 2800. Colour unit was reported according to Method No. 2120C in Platinum-cobalt (PtCo) [14]. Removal efficiency of colour was derived using the following relation:

$$\text{Percentage of Removal} = [(C_i - C_f) / C_i]^* 100 \quad (1)$$

Where,
C_i and C_f refer to the initial and final colour concentration of dyes wastewater, respectively.

Toxicity Assessment: Seed germination test was carried out for the sludge produced after the treatment using lettuce seed (*Lactuca sativa*) as recommended by ISO 1995 [15] and OECD [16]. *Lactuca sativa* was used as the indicator to test the toxicological respond of the sludge produced. Germination index (GI), length of hypocotyl structure and length of the radicle were measured. Five dilutions (1, 3, 10, 30 and 100%) of sludge produced mixed with the nutritive solutions were conducted in triplicate. The control was made by using the nutritive solution. Absolute germination (AG) and Germination index (GI) were calculated as follow:

$$AG = \frac{N_{germ}}{N_{seed}} \quad (2)$$

$$GI = \frac{N_{germ}}{N_{seed}} \times \frac{RL_{germ}}{RL_{cont}} \quad (3)$$

Where:

N_{germ} = The average number of germinated seeds in the sludge produced with addition of nutritive solution
N_{seed} = The total number of seeds
N_{cont} = The average number of germinated control seeds in the nutritive solution
Rl_{germ} = The average root length of germinated seed in the sludge produced with addition of nutritive solution
Rl_{cont} = The average root length of germinated seed in the nutritive solution

Twenty seeds were put on the filter paper Whatman No. 1 in each petri dish with covers in order to prevent contamination. The seed were germinated in the incubator for 120 hours at 22 ± 2°C constant temperature. Lethal concentration, LC_{50} was estimated using Trimmed Spearman-Karber Method [17] at 95 % confidence interval. All experiments were done in triplicate to minimise error.

Design of Experiment: The central composite design (CCD) with 2^k factorial design was used to evaluate the effect of pH, coagulant dose and flocculant dose in the optimization of colour removal and COD reduction. Each *k* factors only have two levels, low level (-1) and high level (+1) with a complete factorial design [18]. It is useful for estimating main effects and the interaction of the factors. The experiments were randomly conducted in favour of minimizing the error from extraneous factor [19]. Table 1 shows the condition for coagulation/flocculation treatment for both responses. Each numeric factor is set at five levels, six axial points, eight factorials point and six centre points for pure error evaluation with three blocks. The coded values and factor levels for optimization of coagulation-flocculation treatment are stated in Table 2. Design Expert 6.0.2 software was used to evaluate the interaction effects between independent variables, coefficients, standard deviation and others. The Analysis of Variance (ANOVA) was performed in order to validate the model on p-value with 95% confidence level.

Table 1: Central Composite Design (CCD) for Coagulation-Flocculation Treatment

	Level				
Factor	-α	-1	0	+1	α
pH	1.10	3	6	9	10.90
Coagulant Dose	105.05	200	350	500	594.95
Flocculant Dose	10.50	20	35	50	59.49

Table 2: Input factors for optimization of decolourization of textile wastewater

Run	Blocks	X_1: pH	X_2: Coagulant dose mg/L	X_3: Flocculant dose mg/ L
1	1	1	1	-1
2	1	0	0	0
3	1	-1	1	1
4	1	0	0	0
5	1	1	-1	1
6	1	-1	-1	-1
7	2	0	0	0
8	2	0	0	0
9	2	-1	-1	1
10	2	1	1	1
11	2	1	-1	-1
12	2	-1	1	-1
13	3	0	0	-α
14	3	0	-α	0
15	3	-α	0	0
16	3	0	0	0
17	3	0	α	0
18	3	0	0	α
19	3	0	0	0
20	3	A	0	0

RESULTS AND DISCUSSION

Functional Group of Natural Organic Flocculant from Banana Pseudo-Stem: The functional group of natural organic flocculant from banana pseudo-stem was detected in FTIR spectra as observed in Figure 1. The FTIR spectra showed clear absorption peaks at 655.18, 1031.43, 1089.94, 1120.28, 1196 and 3257 cm^{-1}, due to -OH stretching vibration peaks. The existence of symmetric C-H stretching vibrations of methylene groups at peak 2922 cm^{-1} can be considered as the increment of C-H bond content after amidation reaction [20]. The peaks at 884.09 and 1312 cm^{-1} could be assigned to CH and CH_3 deformation respectively. The spectrum observed also has an ester peak at 1196 cm^{-1}. The FTIR spectra shows there are carboxyl group and amide group at 1424 and 1610 cm^{-1}, which are strongly contributed to the flocculating mechanism [21]. Table 3 summarized the intensities (cm^{-1}) of FTIR extracted pectin from banana pseudo-stem. PAM as a synthetic organic flocculant was also detected to have amide group $-NH_2$; that was high in molecular weight compare to natural organic flocculant [22]. In spite of that, the presence of cationic synthetic polymer with higher molecular weight known to be carcinorgenic poses to the environment [23].

Optimization by Using Central Composite Design (CCD): A 2^3 of Central Composite Design was carried out in 20 runs. Colour removal and COD reduction of textile wastewater treatment using $MgCl_2$-P and $MgCl_2$-PAM is tabulated according to Table 4.

The relationship between two responses (colour removal and COD reduction) and three selected quantitative variables (pH, coagulant dose and flocculant dose) was approximated by the following second order model. Two sets of second order model include $MgCl_2$-P and $MgCl_2$-PAM was given in terms of coded variables as shown in the Eqs. 4, 5, 6 and 7.

Magnesium Chloride with natural organic flocculant ($MgCl_2$-P):

Colour Removal:

$$46.41 - 2.25x_1 - 1.52x_2 + 0.80x_3 - 2.29x_1^2 + 2.77x_2^2 - 4.92x_3^2 + 3.75x_1x_2 + 1.75x_1x_3 + 8.25x_2x_3 \quad (4)$$

Cod Reduction:

$$52.92 - 4.31x_1 + 0.44x_2 - 2.32x_3 - 1.75x_1^2 + 1.49x_2^2 - 8.15x_3^2 + 7.70x_1x_2 + 1.00x_1x_3 + 7.85x_2x_3 \quad (5)$$

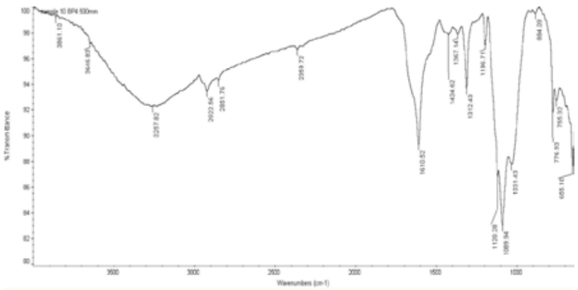


Fig. 1: FTIR spectrum of natural organic flocculant: pectin from banana pseudo-stem.

Table 3: Intensity (cm^{-1}) of FTIR extracted pectin from banana pseudo-stem.

Intensity (cm^{-1})	Functional Groups
655.18, 1031.43, 1089.94, 1120.28, 1196 and 3257	Hydroxyl (-OH)
884.09	CH deformation (-CH)
1312	CH3 deformation (CH_3)
1424	Carboxyl group (COOH)
1610	Amide group ($-CONH_2$)
2922	Methylene group ($-CH_2$)

Table 4: Percentage of Colour removal and COD reduction of textile wastewater treatment by using $MgCl_2$-P and $MgCl_2$-PAM

	MgCl2-P		MgCl2-PAM	
Run	Colour removal (%)	COD reduction (%)	Colour removal (%)	COD reduction (%)
1	42	44	61	50
2	45	53.5	55	51
3	55	63	73	66
4	27	22	72	65
5	50	57.6	61	58
6	31	41.1	78	69
7	45	49	50	55
8	51	55.2	54	60
9	31	34	53	57
10	40	46.2	74	68
11	42	39.4	70	63
12	35	41.7	68	70
13	34	40	86	77
14	54	60	90	76
15	50	52	80	70
16	40	42.1	70	65
17	43	30	89	84
18	48	59	88	80
19	64	61.4	82	84
20	51	62	91	86

Magnesium Chloride with Polyacrylamide as synthetic organic flocculant ($MgCl_2$-PAM):

Colour Removal:

$$78.24 - 1.74x_1 - 1.22x_2 - 1.43x_3 - 2.05x_1^2 - 6.55x_2^2 - 2.42x_3^2 - 5.00x_1x_2 + 4.25x_1x_3 - 3.75x_2x_3 \quad (6)$$

Table 5: Analysis of Variance (ANOVA) for colour removal and COD reduction of textile wastewater by using $MgCl_2$-P

Source of variance	Sum of Squares	DF	Mean square	F-value	p-value
Colour Removal					
Block	227.13	2	113.57		
Model	1298.76	9	144.31	8.75	0.0028
X_1	67.33	1	67.33	4.08	0.0780
X_2	31.00	1	31.00	1.88	0.2076
X_3	8.58	1	8.58	0.52	0.4912
X_1^2	69.45	1	69.45	4.21	0.0742
X_2^2	101.27	1	101.27	6.14	0.0382
X_3^2	319.45	1	319.45	19.37	0.0023
X_1X_2	112.50	1	112.50	6.82	0.0312
X_1X_3	24.50	1	24.50	1.49	0.2576
X_2X_3	544.50	1	544.50	33.02	0.0004
Residual	131.91	8	16.49		
Lack of fit	104.91	5	20.98	2.33	0.2587
Pure error	27.00	3	9.00		
Cor total	1657.80	19			
COD Reduction					
Source of variance	Sum of Squares	DF	Mean square	F-value	p-value
Block	153.05	2	76.53		
Model	2254.16	9	250.46	16.34	0.0003
X_1	247.94	1	247.94	16.18	0.0038
X_2	2.62	1	2.62	0.17	0.6900
X_3	71.75	1	71.75	4.68	0.0624
X_1^2	40.62	1	40.62	2.65	0.1422
X_2^2	29.32	1	29.32	1.91	0.2040
X_3^2	876.68	1	876.68	57.21	<0.0001
X_1X_2	474.32	1	474.32	30.95	0.0005
X_1X_3	8.00	1	8.00	0.52	0.4906
X_2X_3	492.98	1	492.98	32.17	0.0005
Residual	122.60	8	15.33		
Lack of fit	85.78	5	17.16	1.40	0.4163
Pure error	36.83	3	12.28		
Cor total	2589.81	19			

Table 6: Analysis of Variance (ANOVA) for colour removal and COD reduction of textile wastewater by using $MgCl_2$-PAM

Source of variance	Sum of Squares	DF	Mean square	F-value	p-value
Colour Removal					
Block	2080.92	2	1040.46		
Model	1189.89	9	132.21	12.75	0.0008
X_1	40.60	1	40.60	3.92	0.0832
X_2	20.00	1	20.00	1.93	0.2023
X_3	27.26	1	27.26	2.63	0.1436
X_1^2	55.40	1	55.40	5.34	0.0496
X_2^2	566.25	1	566.25	54.62	<0.0001
X_3^2	77.54	1	77.54	7.48	0.0257
X_1X_2	200.00	1	200.00	19.29	0.0023
X_1X_3	144.50	1	144.50	13.94	0.0058
X_2X_3	112.50	1	112.50	10.85	0.0110
Residual	82.94	8	10.37		
Lack of fit	66.44	5	13.29	2.42	0.2493
Pure error	16.50	3	5.50		
Cor total	3353.75	19			
COD Reduction					
Source of variance	Sum of Squares	DF	Mean square	F-value	p-value
Block	1363.03	2	681.52		
Model	822.21	9	91.36	11.99	0.0009
X_1	12.48	1	12.48	1.64	0.2365
X_2	5.00	1	5.00	0.66	0.4413
X_3	47.12	1	47.12	6.18	0.0377
X_1^2	53.08	1	53.08	6.97	0.0297
X_2^2	496.22	1	496.22	65.12	<0.0001
X_3^2	27.47	1	27.47	3.61	0.0941
X_1X_2	128.00	1	128.00	16.80	0.0034
X_1X_3	18.00	1	18.00	2.36	0.1629
X_2X_3	72.00	1	72.00	9.45	0.0153
Residual	60.96	8	7.62		
Lack of fit	29.96	5	5.99	0.58	0.7230
Pure error	31.00	3	10.33		
Cor total	2246.20	19			

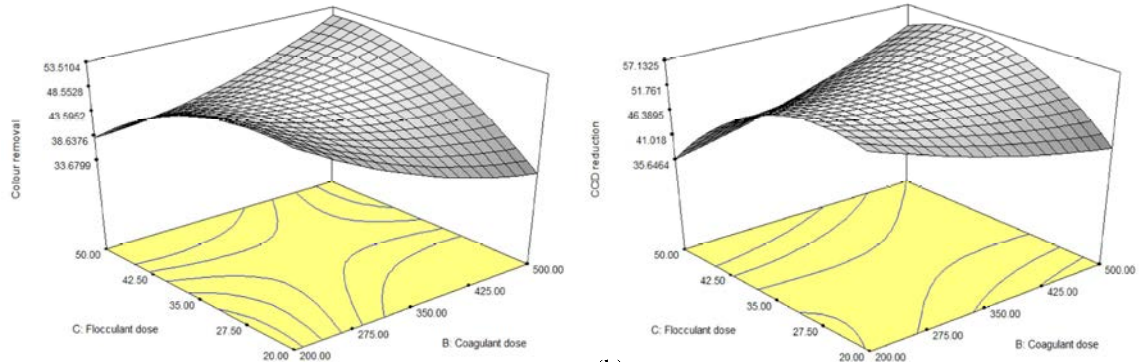
Cod Reduction:

$$72.97 - 0.97x_1 - 0.61x_2 + 1.88x_3 - 2.00x_1^2 - 6.13x_2^2 - 1.44x_3^2 - 4.00x_1x_2 + 1.50x_1x_3 - 3.00x_2x_3 \quad (7)$$

The r^2 values for colour removals of textile effluents by using $MgCl_2$-P and $MgCl_2$-PAM were 0.9078 and 0.9348, respectively. Whereby r^2 values for COD reduction showed 0.9484 and 0.9310, respectively. This indicates that 0.91-0.95 of the total variation is explained by the empirical models, in the mean time a range between 0.05-0.01 is inexplainable. The values of the coefficient of determination are satisfactory since r^2 are reasonably high and close to 1.

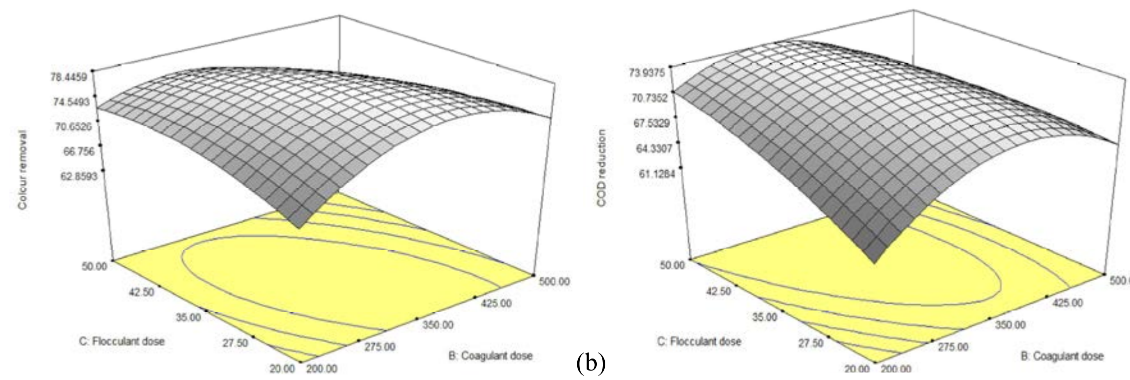
Tables 5 and 6 show the sequential sum of squares, mean square, F-value and significant p-value < 0.05 for the colour removal and COD reduction for each treatment with $MgCl_2$-P and $MgCl_2$-PAM.

Analysis of Variance (ANOVA) for colour removal of textile effluent using $MgCl_2$-P shows insignificant effect for all the variables except for the quadratic term of coagulant dose (X_2^2), the quadratic term of flocculant dose (X_3^2), the interaction effect of pH and coagulant dose (X_1X_2) and the interaction effect of coagulant dose and flocculant dose (X_2X_3) (Table 5). As for COD reduction, significant effect obtained for the linear term of pH (X_1), the quadratic term of flocculant dose (X_3^2), the interaction effect of pH and coagulant dose (X_1X_2) and the interaction effect of coagulant dose and flocculant dose (X_2X_3). Meanwhile the rest of the interaction shows no significant effect. Lack-of-fit indicates that both responses are not significant relative to the pure error at value > 0.05 (colour removal: 0.2587 and COD reduction: 0.4163). A three-dimensional display of response surface plot is shown in Figure 2. a) Colour Removal; b) COD reduction.



(a) (b)

Fig. 2: A three dimensional display of response surface plot for a) Colour Removal b) COD reduction for interaction between coagulant dose and flocculant dose using $MgCl_2$-P.



(a) (b)

Fig. 3: A three dimensional display of response surface plot for a) Colour Removal b) COD reduction for interaction between coagulant dose and flocculant dose using $MgCl_2$-PAM.

Response surface of flocculant and coagulant dose on colour and COD removal indicate the increase of colour and COD removal in a short time at the beginning and then decreases by increasing coagulant and flocculant dose as shown in Figure 3. It occurs at the constant pH 6. This explains the surface complexation mechanism happened at a low coagulant dosage. Mg(II) salts produce cationic hydrolysis products $Mg(OH)^{2+}$ which leads to the adsorption on the negatively charged dye particles for destabilization purpose [24]. When the cations adsorb the negative particles, a precipitate of the hydrolysing metal salt with the constituent ions may produce at high surface coverage. Thus provide sorption to occur through a continuous series between bulk solution precipitation of the sorbing ion and surface complex formation [25]. The formation of hydroxide surface occurred as consequence with the depletion of negative charge particles. However as hydrolysing metal salts increased, the complex surface and the precipitate also increased until it became saturated. Increase in both pH and coagulant dosage beyond the optimum region resulted in a decrease in the removal efficiency due to over dosing in the reaction solution. Neutralization and stabilization of residual negative charges in natural organic flocculant like carboxyl group of α-?-galacturonic acid was stimulated by Mg^{2+} ion thus provide to the bridge development which causing the dyes particles to hold together [26]. Natural organic flocculant holds hydroxyl group $-OH^-$ and carboxyl group $-COO^-$ for dyes molecule to attach after electrostatic repulsion occurred. As the concentration of flocculant increase, the longer chain yield more binding site to be attach. Figure 4 shows the reaction of cation and anion group take place in the dye mixture.

ANOVA table for colour removal of textile effluent by $MgCl_2$-PAM shows insignificant effect for all the variables except for the quadratic term of pH (X_1^2), the quadratic term of coagulant dose (X_2^2) and the quadratic term of flocculant dose (X_3^2). All interactions; pH and coagulant dose (X_1X_2), pH and flocculant dose (X_1X_3), coagulant and flocculant dose (X_2X_3) revealed a significant effects. At t he same time, the largest effects

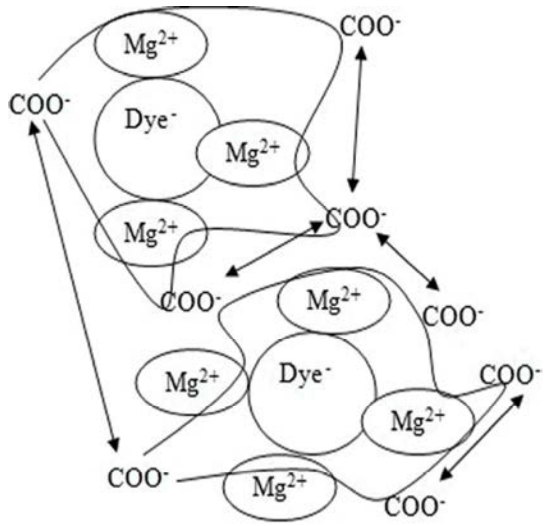


Fig. 4: Bridging between cation and anion group in the mixture of dyes.

resulted in the variables for COD reduction were the quadratic term of coagulant dose (X_2^2), the interaction effect of pH and coagulant dose (X_1X_2), the interaction effect of coagulant dose and flocculant dose (X_2X_3), the quadratic term of pH (X_1^2) and the linear term of flocculant dose (X_3). The rest of the interaction showed no significant effect. Lack-of-fit test shows colour removal (0.2493) and COD reduction (0.7230) are not significant relative to the pure error (F-test at the 95% level) which considered the model fitted for $MgCl_2$-PAM. A three-dimensional display of response surface plot was shown in Figure 3. a) Colour Removal; b) COD reduction. Analysis of Variance (ANOVA) for colour removal and COD reduction of textile wastewater by using $MgCl_2$-PAM is summarized in Table 6.

The examination of three-dimensional display plots shows a point of maximum response in Figure 3. The mound shape shows the coagulant and flocculant dose should be around the intermediate phase to get the highest removal. A higher coagulant dose may lead to a lower rate of COD and colour removal. Meanwhile increasing of flocculant dose may rapidly enhance the percentage removal. The effective bridging flocculation depends on how far the adsorbed polymers extend from the particle surface to bind other particles, provided that there is sufficient unoccupied surface available. In any case of excessive polymer added into the suspension, the particles can easily restabilized due to surface saturation or steric stabilization. Thus the removal rate of colour and COD drop down after $MgCl_2$ dosage 350 mg/ L. Previous study reported that molecular weight of PAM was higher compare to natural organic flocculant [27]. Zahrim *et al*. [28] stated that higher molecular weight provide an increasing chain length in order to give a better flocculation. As a result, more binding site can be attached onto the surface.

Validation of the Models: Confirmation experiments were carried out for three different conditions chosen randomly from the optimized results to validate the developed model. The results of the selected pH, coagulant dosage and flocculant dosage are given in two different treatments ($MgCl_2$-P and $MgCl_2$-PAM) as summarized in Table 7. The validation test indicates good agreements between the actual and predicted values of colour removal and COD reduction.

Toxicity Assessment for Sludge Production: The growth of the root and the root length shows the best results at 34 % LC_{50} sludge from $MgCl_2$-P. Rosa *et al*. [29] suggest that the sludge from textile wastewater treatment have a potential to be compost in agricultural site once it is stabilized. The existences of toxic compound in 100% sludge from the treatment demonstrate a strong effect for both treatments. However sludge from coagulation-flocculation treatment using $MgCl_2$-PAM shows higher toxicity effect for AG and GI compare to $MgCl_2$-P sludge even at lower percentage of sludge solution mixed to control solution (1, 3, 10 and 30 %). As the increasing amount of sludge solution mixed to control solution the mortality rate of *L. Sativa* start to increase up to 70 % as shown in Table 8. $MgCl_2$-P resulted as the lowest mortality at 35% out of 20 germinated seeds in all ratios. Percentage mortality rate of $MgCl_2$-PAM is higher at all ratio of sludge mixed to control solution (1, 3, 10, 30 and 100 %) compare to $MgCl_2$-P as shown in Figure 5. These demonstrate the toxicity effect from the sludge influenced the germination of *L. Sativa* due to the formation of toxic nitrogen [30, 31]. The sensitivity of root growth is higher compare to seed germination where GI for $MgCl_2$-PAM resulted in lower value. Residual of acrylamide in the sludge appeared to be significantly toxic due to lower result in LC_{50}. Absolute germination, AG and germination index, GI were calculated by using the germination and root growth measurement and summarized in Table 9.

Table 7: Validation Test for Colour Removal and COD Reduction by using $MgCl_2$-P and $MgCl_2$-PAM

				Colour Removal		COD Reduction	
Types	pH	Coagulant Dose	Flocculant Dose	Actual	Predicted	Actual	Predicted
$MgCl_2$-P	5.0	427.4	21.9	54.2	56.5	67.0	62.7
	3.6	414.4	32.5	50.0	52.0	57.9	60.0
	3.1	387.7	33.4	52.7	50.1	59.9	57.0
$MgCl_2$-PAM	4.5	275	35	88.0	86.3	80.0	79.8
	4.0	350	36	80.0	81.3	74.0	75.6
	6.4	390	25	75.0	78.2	70.0	73.0

Table 8: Set of experimental assay data mortality percentage of $MgCl_2$-P and $MgCl_2$-PAM sludge.

Types of Toxicant/ Ratio	1%	3%	10%	30%	100%
$MgCl_2$-PAM	40	50	55	65	70
$MgCl_2$-P	35	40	45	60	70

Table 9: Percentage of absolute germination, AG and germination index, GI and the estimated median lethal dose (LD_{50}) for $MgCl_2$-P and $MgCl_2$-PAM sludge.

	% Sludge solution mixed to control solution										
	1%		3%		10%		30%		100%		
Types of Toxicant	AG	GI	AG	GI	AG	GI	AG	GI	AG	GI	LD_{50} %
$MgCl_2$PAM	60	50	50	35	75	60	38	24	25	8	17
$MgCl_2$P	65	70	60	50	31	9	44	19	31	10	34

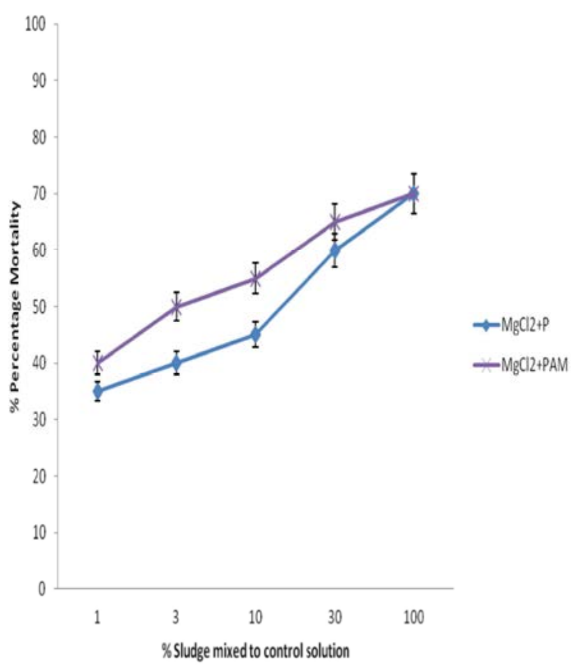


Fig. 5: Percentage mortality of Lactuca sativa seed based on five difference ratio of sludge produced mixed with the nutritive solutions at 1%, 3%, 10%, 30% and 100%.

CONCLUSION

This study attempts to compare performance of synthetic organic polymer PAM and natural organic polymer as flocculant to treat textile wastewater effluent using statistical Response Surface Design-Central Composite Design. From the results, interaction between pH and coagulant dose; coagulant dose and flocculant dose clearly shows that it influences the colour and COD removal. From the optimization of $MgCl_2$-P, the maximum value of colour and COD removal is achieved at pH 5, coagulant and flocculant dosage at 427.4 and 21.9 mg/ L respectively. Meanwhile in treatment using $MgCl_2$-PAM maximum colour and COD removal are achieved at optimum pH value of 4.5, coagulant dosage at 275 and 35 mg/ L for the flocculant dose. ANOVA result shows the value of r^2 up to 94% and significance value of lack-of-fit for both treatments, thus demonstrate the second order model in a good agreement. Even though the percentage of colour removal and COD for treatment with synthetic organic flocculant is better than using natural organic flocculant, the value of LC_{50} in sludge after the process indicates PAM is relatively more hazardous to the environment. This finding calls for further research in order to find a substance/ chemicals with effective performance as PAM but which is also environmentally friendly.

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Persian Abstract

چکیده

عملکرد پلیمر آلی سنتزی (پلی اکریل آمید) و پلیمرهای آلی طبیعی (پکتین) به عنوان منعقد کننده در انعقاد-لخته سازی مورد بررسی قرار خواهد گرفت. آنالیز گروههای عاملی به روش (FTIR-ATR) انجام شد. روش پاسخ سطح(RSM-CCD) برای بررسی اثر متقابل pH، دوز منعقد کننده و لخته ساز مورد استفاده قرار گرفت. این آزمایش در مقیاس آزمایشگاهی با ۵۰۰ ml نمونه از فاضلاب نساجی با شش پره همزن به روش معمولی انجام شد. روش Trimmed Spearman-Karber به منظور برآورد مقادیر غلظت موثر با ۵۰ درصد کشنده بودن (LC50) و فواصل اطمینان آنها استفاده شد. پلی اکریل آمید اضافه شده در شرایط بهینه pH ۵، دوز منعقد کننده ۲۷۵ mg/l و دوز لخته ساز ۳۵ mg/l به ترتیب با ۸۸ و ۸۸٪ حذف، بهترین نتیجه را نشان می دهد. در مقابل افزودن لخته کننده آلی طبیعی تنها موفق به حذف ۵۴/۲ و ۶۷٪ در حالت بهینه pH ۵، دوز منعقد کننده و لخته ساز به ترتیب ۴۲۷/۴ و ۲۱/۹ mg/l بوده است. با این حال ادعا می شود که درمان با پلی اکریل آمید بر اساس غلظت کشنده (LC50) در ۱۷٪ نسبت به لخته ساز آلی طبیعی در ۳۴٪ سمی تر است.