INTRODUCTION

Suspended particles are one of the natural pollutants in surface water. Since turbidity in water is usually caused by the presence of these impurities. However, Kaolin clay particles often produce a turbid suspension when they disperse in water. One of the most powerful methods of removing colloidal particles in water and wastewater is the coagulation/flocculation process. Coagulants/flocculants are the key important of coagulation/flocculation process. Various flocculants including inorganic flocculants, organic flocculants, composite flocculants and hybrid flocculants have recently been developed. The synthesis and the application of inorganic-organic flocculants are increasing rapidly now. Research focuses on the synthesis of hybrid flocculants, which are a combination of both inorganic and organic materials. The hybrid flocculants are used as reagents in the flocculation process of water and wastewater (Dawood and Li, 2012; Lee et al., 2011). Based on their advanced preparing procedure the work contains the most effective flocculation species and it is more effective than the traditional mixing of inorganic salts and organic flocculants. In order to achieve better flocculation efficiency, synthetic hybrid flocculants are often used in water flocculation (Lee et al., 2010).

It is highly necessary to optimize the flocculation process for effective turbidity removal. Many experiments need to be carried out in the flocculation process to study the effects of different parameters on turbidity removal. This traditional technique of accomplishing these experiments is not considered to be economical and practical because these experiments have to be carried out with all possible parameter combinations. For this case, the Design of Experiment (DOE) is employed to study the effect of variables and their responses with a minimum number of experiments (Bhatia et al., 2007). Taguchi method of Orthogonal Array (OA) experimental design is a collection of statistical techniques that can be used for improving, developing and optimizing processes. The Taguchi method is utilized to discover the impact of individual factors and to find out the relationship between the variables and the operational conditions. This method also determines the performance at the optimum levels by few numbers of experiments.

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Artificial Neural Networks (ANNs) are used in many fields of science and engineering because of their simplicity towards simulation, prediction and modeling (Elmolla et al., 2010). ANNs are applied in biological wastewater treatment (Moral et al., 2008; Gontarski et al., 2000; Zeng et al., 2003; Baruch et al., 2005; Griew et al., 2005; Ren et al., 2005; Hong et al., 2007; Machón et al., 2007; Mjallì et al., 2007; Pai et al., 2007), electrochemical wastewater treatment (Daneshvar et al., 2006; Murugan et al., 2009; Bhatti et al., 2011) and physicochemical wastewater treatment (Aber et al., 2007; Aleboyeh et al., 2008; Yetilmėsoy and Demirel, 2008; Kardam et al., 2010; Raj et al., 2010; Aghav et al., 2011; Turan et al., 2011).

In the present study, a new AlCl$_3$-P(AM-co-DADAAC) inorganic-organic hybrid copolymer was synthesized by free radical solution polymerization. The characterization of the new hybrid copolymer was examined by Fourier Transform Infrared spectroscopy (FT-IR) and Transmission Electron Microscopy (TEM). Taguchi method is used to analyze the effect of three variables (initial turbidity, pH and dosage of the hybrid inorganic-organic copolymer). Taguchi method was used to show the optimum flocculation efficiency for kaolin suspension by using the new flocculant of AlCl$_3$-P(AM-co-DADAAC) hybrid copolymer in the flocculation process. A model based on Artificial Neural Network (ANN) was constructed to predict turbidity concentration from kaolin suspension.

**MATERIALS AND METHODS**

**Materials:** Acrylamide (AM) was purchased from AMRESCO (USA). Diallyldimethylammonium Chloride (DADAAC) of (65% solid Content) was provided by TelSun Chemical and Scientific Limited (China). Ammonium Persulfate (APS) and Sodium bisulfite were purchased from Shanghai Reagent Corp (China). N, N'-Methylenebisacrylamide (MBA) was supplied by Sigma (USA). All other chemicals were used as received. All solutions were prepared by using deionized water.

**Preparation of hybrid copolymer:** The AlCl$_3$-P(AM-co-DADAAC) hybrid copolymer was prepared by free radical solution polymerization using ammonium persulfate and sodium bisulfite as redox initiator. Briefly, 5 g of acrylamide and 5 mL of DADAAC monomers were dissolved in 95 mL of deionized water and the product solution was moved to 500 mL three-necked flask equipped with a mechanical stirrer, reflux condenser, rubber septum cap and a thermostatic water bath. Afterward, 10 mg of the cross-linker (MBA) was added to the solution and the system was heated to 30°C, throughout stirred and purged with nitrogen gas for 30 min to get rid of the dissolved oxygen from the solution. Then, the temperature of the system was raised to 45°C, a redox initiator was added to the solution to initiate the polymerization, 6.4 mg of ammonium persulfate and 1 mg of sodium bisulfite were added to the stirred solution under atmospheric nitrogen. The polymerization took place for 2 h; an equivalent mole ratio of aluminum chloride was then added to the medium. The solution was mixed under atmospheric nitrogen for 4 h until it became homogenous (Lee et al., 2010; Yang et al., 2004). The AlCl$_3$-P(AM-co-DADAAC) was filtered, precipitated with acetone, vacuum dried and milled.

**Characterization of the hybrid copolymer:** Infrared spectra of the prepared hybrid copolymer were recorded using Fourier transform infrared spectroscopy (Nicolet 6700, Thermo Scientific, USA). The Transmission Electron Microscopy (TEM) of the prepared hybrid copolymer was investigated by the following method: a small amount of the AlCl$_3$-P(AM-co-DADAAC) hybrid copolymer was dispersed into ethanol followed by ultrasonic treatment for 10 min. One drop of the hybrid copolymer solution was then put onto a copper grid and dried at room temperature. The final sample for the test was visualized using transmission electron microscopy (TECNAI G2 20, USA).

**Kaolin flocculation:**

**Preparation of Kaolin suspension:** Kaolin suspension was prepared by mixing 2 g of kaolin with 1000 mL of distilled water using a magnetic stirrer at room temperature. The suspension was then slowly stirred and its pH was adjusted to 7.5. Finally, the suspension was left to stand overnight. Afterwards, the upper supernatant was decanted carefully for further dilution. Turbid water was prepared with desired turbidity by diluting the kaolin suspension with the distilled water to the required turbidity.

**Floculation tests:** The flocculation experiments were conducted by flocculate the turbid water (80 NTU, 160 NTU and 240 NTU) using programmable jar-test apparatus (TA6, Wuhan, China). The desired turbid water was added to the jar after its pH was adjusted to the required value by 0.1 M NaOH or 0.1 M HCl solution. The turbid water was mixed at a rapid speed of 200 rpm for 3 min and followed by a slow speed of 100 rpm for 6 min. Thereafter, the Jar-test apparatus was powered off and the jars were allowed to be undistributed settle for 30 min and then the samples of the supernatant were withdrawn. The pH of the water was measured using HANNA portable pH meter and the turbidity of the water was measured with HACH DR/890 portable colorimeter.

**Taguchi method and design of experiments:** Taguchi approach was applied to study the effect of three
variables on the flocculation of kaolin suspension. These variables were turbid water concentration, initial pH and dosage of AlCl₃-P(AM-co-DADAAC) hybrid copolymer.

In general, the optimized process in Taguchi method consists of four main steps, planning, conducting, analysis and validation. These main steps can be summarized as follows:

- Identifying the factors to be optimized, identifying the control factors and their levels and selecting an appropriate orthogonal array for the design of experiments
- Performing the experiments according to orthogonal array arrangement
- Analyzing data by calculating the S/N ratio, analyzing the experimental results by ANOVA test and finding the optimal level for each of process parameters
- Validating experiments by conducting confirmation experiments

To observe the influence of flocculation parameters (variables) on the response (final turbidity), the three parameters of the flocculation process had three levels each as shown in Table 1. The advantages of Taguchi method are: saving the efforts in conducting experiments, saving experiment’s time, reducing the cost and exploring significant factors quickly. In order to reduce the time and the cost of experiments, nine flocculation experiments were conducted according to Taguchi optimization method with an L9 orthogonal array (Table 2).

In Taguchi approach, there are three standard types of Signal to Noise ratio (S/N). These are: smaller the better, normal the better and larger the better. Signal to noise ratio depending on the desired performance response (Phadke, 1995; Taguchi et al., 1989). The Signal to Noise ratio (S/N) of our experiments is of type: smaller the better because the factors are used to reduce the turbidity by making the system response as small as possible. The Signal to Noise ratio (S/N) is derived from the quadratic loss function as follows:

$$S / N = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} (y_i)^2 \right)$$  \hspace{1cm} (1)

**Artificial Neural Network (ANN):** Artificial Neural Network (ANN) has received considerable attention in recent years mostly due to its wide range of applications (Aghav et al., 2011; Çelekli and Geyik, 2011). The common type of ANNs that is frequently used for process modeling is layered feed forward neural networks, also named as multi-layer perception with back propagation learning algorithm. MATLAB mathematical software was used to predict the turbidity using ANN model. All of Taguchi’s experiments were used for model training while three additional experiments were used for model validation. The ANN model was designed as it contains a three-layered back propagation neural network with a tangent sigmoid transfer function (tansig) at the hidden layer and a linear transfer function (purelin) at the output layer. Since the function was sigmoid that was used in the hidden layer, then all the inputs data must be normalized ($X_{\text{norm}}$) in the 0.2-0.8 range as follows (Daneshvar et al., 2006):

$$X_{\text{norm}} = 0.2 + 0.6 \frac{(X_i - \min(X_i))}{\max(X_i) - \min(X_i)}$$  \hspace{1cm} (2)

The primary goal of training is to minimize the error function by searching for a set of connection weights and biases that cause the ANN to produce outputs that are equal or close to the target values. Mean Square Error (MSE) is used as the error function. MSE measures the performance accuracy of the network according to the following equation (Çelekli and Geyik, 2011; Khataee et al., 2010):

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (Y_{\text{predict}} - Y_{\text{exp}})^2$$  \hspace{1cm} (3)

where,
\[ N \] = The number of data points
\[ Y_{\text{predict}} \] = The predicted value of turbidity using the ANN model
\[ Y_{\text{exp}} \] = The experimental value of turbidity
RESULTS AND DISCUSSION

Characterization of the hybrid copolymer: The characterization of the prepared hybrid copolymer was carried out using FT-IR and TEM tests. The infrared spectra of the hybrid copolymer were shown in Fig. 1. The peak observed at 3028 cm$^{-1}$ was due to the stretching vibration of the C-H group. A band at 1592 cm$^{-1}$ resulted from -NH- stretching vibration. The band at 1652 cm$^{-1}$ was assigned to C-O stretching vibration (Lu et al., 2004). The peak observed at 572 cm$^{-1}$ resulted from C-Cl axial bond (Pretsch et al., 2009). It can therefore be believed that AlCl$_3$-P(AM-co-DADAAC) has been synthesized and the final product contained both inorganic and organic groups in its structure.

Figure 2 shows the TEM image of the hybrid copolymer particles on copper grid. It was noticed clearly that the inorganic particles appeared with a size of 2-10 nm in diameter and they were linked with the organic chains. Hence, it can be said that the AlCl$_3$-P(AM-co-DADAAC) hybrid copolymer was a combination of inorganic and organic materials.

Analysis of S/N ratio: The L9 orthogonal array contained nine rows corresponding to the number of experiments, with three columns at three levels. The final turbidity presented in Table 3 was the responses after the flocculation treatment. The S/N values for the experiments were calculated according to Eq. (1) and these values are listed in the same table.

Based on the analysis of S/N ratio, the optimum obtained turbidity was at 80 NTU of initial turbidity (level 1), pH 11 (level 3) and 0.6 mg/L dosage of the AlCl$_3$-P(AM-co-DADAAC) hybrid copolymer (level 3).

Analysis of Variance (ANOVA): The ANOVA is carried out to inquire the statistical significance of the process parameters impacting the response. This was attained by comparing the mean square with the estimate of the experimental error at specific confidence levels. F-test was used to check which factor has a significant effect on the response. F-test represents the ratio of the mean square error to the residual error. p-value was used to show the significant level. ANOVA results are shown in Table 4 and Fig. 3. All of ANOVA results were carried out at a significant level of 0.05. From the ANOVA results, it is clearly noted that the dosage of the hybrid copolymer is a significant parameter in the turbidity reduction.

Artificial Neural Network (ANN) modeling: Six Backpropagation (BP) algorithms were compared to select the best suitable BP algorithms and six neurons were used in the hidden layer for all BP algorithms. Levenberg-Marquardt backpropagation (LMA) with a minimum MSE was found as the best algorithms between these six Back propagation algorithms (Table 5). Thus, LMA was considered the training algorithm in the present study. The optimum number of neurons was determined by being based on the minimum value of MSE of training and the prediction
Table 3: L9 (3^4) orthogonal array in coded values, experimental results and S/N ratio

<table>
<thead>
<tr>
<th>Runs</th>
<th>Initial Turbidity (NTU)</th>
<th>pH</th>
<th>Hybrid copolymer dosage (mg/L)</th>
<th>Final Turbidity (NTU)</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>56.8</td>
<td>-35.087</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>61.3</td>
<td>-35.749</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>1.5</td>
<td>-3.522</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>110.7</td>
<td>-40.883</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3.8</td>
<td>-11.596</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>71.1</td>
<td>-37.037</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>5.2</td>
<td>-14.320</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>53.8</td>
<td>-34.616</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>70.2</td>
<td>-36.927</td>
</tr>
</tbody>
</table>

Table 4: Analysis of Variance (ANOVA) for S/N ratios

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq. S.S.</th>
<th>Adj. S.S.</th>
<th>Adj. M.S.</th>
<th>F-test</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>41.72</td>
<td>41.72</td>
<td>20.859</td>
<td>3.81</td>
<td>0.208</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>28.15</td>
<td>28.15</td>
<td>14.075</td>
<td>2.57</td>
<td>0.280</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1455.40</td>
<td>1455.40</td>
<td>727.698</td>
<td>132.74</td>
<td>0.007</td>
</tr>
<tr>
<td>Residual error</td>
<td>2</td>
<td>10.96</td>
<td>10.96</td>
<td>5.482</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>1536.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5: Comparison of 6 back propagation algorithms with 6 neurons in the hidden layer

<table>
<thead>
<tr>
<th>Back Propagation (BP) algorithm</th>
<th>Function</th>
<th>MSE</th>
<th>Epoch</th>
<th>R^2</th>
<th>BLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levenberg-Marquardt backpropagation</td>
<td>Trainlm</td>
<td>0.0820</td>
<td>1260</td>
<td>0.99997</td>
<td>Y = T + 0.0029</td>
</tr>
<tr>
<td>Powell-Beale conjugate gradient backpropagation</td>
<td>Traincg</td>
<td>0.2714</td>
<td>79</td>
<td>0.99989</td>
<td>Y = T + 0.15</td>
</tr>
<tr>
<td>Polak-Ribi'ere conjugate gradient backpropagation</td>
<td>Traincg</td>
<td>0.2060</td>
<td>217</td>
<td>0.99992</td>
<td>Y = T + 0.15</td>
</tr>
<tr>
<td>BFGS quasi-Newton backpropagation</td>
<td>Trainbfg</td>
<td>0.2939</td>
<td>307</td>
<td>0.99988</td>
<td>Y = T + 0.011</td>
</tr>
<tr>
<td>Flecher-Reeves conjugate gradient backpropagation</td>
<td>Traincgf</td>
<td>0.3400</td>
<td>189</td>
<td>0.99986</td>
<td>Y = T + 0.013</td>
</tr>
<tr>
<td>Batch gradient descent</td>
<td>Traingd</td>
<td>0.5612</td>
<td>5000</td>
<td>0.99998</td>
<td>Y = T + 0.019</td>
</tr>
</tbody>
</table>

MSE: Mean square error; R^2: Correlation coefficient; T: Target; BLE: Best linear equation

Fig. 3: Effect of flocculation process parameters on turbidity

sets (Yetilmezsoy and Demirel, 2008). The optimization was done by using LMA as training algorithm and varying neuron number in the range 4-14. Figure 4 shows the relationship between the number of neurons and MSE in LMA algorithm. As shown in Fig. 4, the MSE decreased significantly from 0.29389 to 0.000000310 when the number of neurons changed from 4 to 14. Then, it was observed that when the number of neuron increased to more than 12, there was no significant change in the MSE. Therefore, the neuron of 12 was selected to represent the best suitable BP algorithms (minimum error) as shown in Fig. 5.

Conformation tests: The purpose of the conformation tests is to verify the response based on Taguchi’s design method. In this study, the conformation experiments were utilized at the levels of the optimal process parameters for turbidity in the flocculation process. The results of the conformation experiment were found to be in good agreement with the optimum value.
Mechanism of hybrid copolymer employment: When the dosage of the AlCl₃-P(AM-co-DADAAC) hybrid copolymer increased in the flocculation process, the turbidity removal increased with more flocsettling. It could be assigned to the bonding between the cationic copolymer and the negative edge of the kaolin-aluminum chloride particles or aggregates through electrostatic attraction (Zhu et al., 2009). Whereas, when a small dosage of the hybrid copolymer is used, small flocs are formed but no apparent aluminum hydroxide is formed. As hybrid copolymer dosage is increased to 0.6 mg/L, the negative charge of particles or floc surface will be neutralized further and repulsive interaction between the particles will be reduced, leading to the shortening of bridge length between particles. Hybrid copolymer has the ability to form large size flocs due to both charge neutralization and bridging.
CONCLUSION

In this study, AlCl₃-P(AM-co-DADAAC) hybrid copolymer has been successfully prepared and its characterization has been done using FT-IR and TEM. The hybrid copolymer was employed in the flocculation of kaolin suspension. The flocculation process of kaolin suspension was modeling using Taguchi approach to determine the significance of the variables in the flocculation process. ANOVA showed that the AlCl₃-P(AM-co-DADAAC) hybrid copolymer dosage is a significant variable in flocculation process of kaolin suspension. ANN model of LMA with 12 neurons in the hidden layer and one output layer performed better than the other proposed models due to its lowest MSE value. The implementation of the proposed ANN model for the turbidity prediction and by depending on the network results that were compared with those obtained through experiments, it was found that the predicted turbidity using ANN model is in a very good agreement with the experimental data ($R^2 = 1$). As well as, the ANN model was able to make an accurate prediction of turbidity by using small sized training and validation data.

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