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Optimization of the Performance of Chitosan for the Nickel Removal from Wastewater

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Abstract: Optimum pH and coagulant dosage for chemical precipitation by coagulation-flocculation process in wastewater treatment plants is conventionally obtained through repeated jar test. In this research, optimization of the performance of chitosan for the removal of nickel from industrial wastewater was carried out using design of experiment and response surface methodology (RSM). The individual linear and quadratic effects of coagulant dosage and pH on the degree of removal of nickel were investigated. The optimum nickel removal from wastewater using Chitosan was 82.31% at optimum variables of pH 10.35 and coagulant dosage of 677 mg/L. The model used in predicting the precipitation process gave a good fit with the experimental variables and hence the suitability of RSM method for the optimization of chitosan performance.

Key words: Chitosan · Nickel · Wastewater · Chemical precipitation · Response surface methodology

INTRODUCTION

There has been a steady increase in quantity of nickel laden wastewater generated worldwide as a result of rapid industrialization. In the year 2000, 158,000 tons of nickel was used in the US, 13 % of which was consumed by the galvanic industry [1]. The annual growth in the demand of stainless steel has been estimated to be at 9.1 million tons per year from 2009 to 2012. This has resulted in a growing demand for raw nickel to a tone of 8.5% annually for the same period [2]. Nickel which has been identified to cause serious problems to human such as allergy, dermatitis, sensitization and lung-nervous system damageshas in fact been placed on a list of thirteen priority metals by the US Environmental Protection Agency [3].

Chemical precipitation is an important process in waste and wastewater treatment used for the removal of heavy metals such as nickel, suspended solids (SS), chemical oxygen demand COD and turbidity [4-9]. Most common coagulants are aluminum based salts and iron-based salts [10,11]. Other coagulant includes chitosan, a biodegradable, non-toxic linear cationic polymer of high molecular weight [12-17].

However, more researches are now being carried out on the application of chitosan due to its numerous advantages. Chitosan is a natural polysaccharide characterized with hydrophilicity, biocompatibility, biodegradability and the capability of adsorbing a number of metal ions because of its amino groups [16]. Chitosan, known as poly[â-(1>4)-2-amino-2-deoxy-D-glucopyranose], is a cellulose like biopolymer of high molecular weight obtained from deacetylation of chitin [18-19]. Chitin, a linear chain polysaccarides, is the second most abundant organic material after cellulose, which is the major structural component of invertebrate exoskeleton, particularly in crustacean, mollusks and insects, as well as the principal fibrillar polymer in the cell wall of certain fungi. Besides the reactive primary and secondary hydroxyl groups, chitosan's versatility as an adsorbent is a function of its highly reactive amino group at the C(2) position. The protonation of the chitosan amino groups (NH_2) in solution makes the chitosan positively charged (exhibit as cationic polyelectrolytes) and there by very attractive for flocculation and different kind of binding application, by allowing the molecule to bind to negatively charged surface via ionic or hydrogen

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bonding. Chitosan offers a broad range of applications favour by unique properties of chitin and chitosan, such as biocompatibility, biodegradation, biological activity, nontoxicity, non-allergenic and ability for fiber and film formation [16,18]. Chitosan is recognized as excellent metal ligands, forming complexes with many metal ions, thus enhance the removal of toxic metal from industrial wastewater. It has been shown to effectively remove metals such as boron, molybdenum, arsenic, gold, cadmium, vanadium, chromium, lead, cobalt, iron, manganese, silver, copper, nickel, mercury and zinc from aqueous solutions [16, 20].

Studies have also shown that, the effectiveness of chitosan as a coagulant is affected by dosage, pH and temperature.There is need to combine these factors appropriately to obtaina high efficiency of treatment. The conventional method to seek the optimal conditions is by trial and error approach using jar tests. This involves changing the levels of one factor and at the same time, keeping the others in constant, running the experiment, observing the results and moving on to the next factor [16]. This is indeed time and energy consuming. It is also usually incapable of revealing the optimal combination of factors due to ignoringthe interaction among them [21-23]. More also, the majority of wastewater treatment processes are multi-variable and optimization through the classical method is inflexible, unreliable and time-consuming [24]. A better alternative is the use of RSM because it includes the influences of individual factors as well as the influences of their interaction. RSM is a technique for designing experiments, building models, evaluating the effects of several factors and achieving the optimum conditions for desirable responses with a limited number of planned experiments [23, 25, 26]. There are some published RSM studies focusing on the usability of RSM for optimization of various types of wastewater treatment processes [22-24]. It is however observed that works concerning the optimization of the nickel removal using chitosan are not readily available. Hence, this work is aimed at investigating the effect of pH and coagulant dosage onnickel removal using chitosan and optimizing these parameters using RSM in order to obtain the optimum degree of removal.

MATERIALS AND METHODS

Wastewater Sample and Material: The wastewater was collected from electro less plating industry located in Johor Bahru, Malaysia. This is a nickel electroless plating company, which produce a substrate that is use for a memory discs. Aluminum substrate is used as a surface material for nickel to deposit onto it. These aluminum surface needs to undertake nickel electroless plating so as to provide a protective layer between the aluminum surface and the data storage surface and generate amorphous structure with less porosity. Ni-P with > 10% P is non-magnetic and does not interfere with the data storage layer, high hardness and wear resistance and excellent resistance to corrosion. The plating process consists of aluminum substrate, pretreatment and nickel plating. Chitosan was purchased in the form of white fine powder from Agros Company.

Table 1: Wastewater characteristics

Parameter	Total nickel	COD	pH	TSS	Turbidity
values	94.3 mg/L	1320 mg/L	2.6	1780 mg/L	1740 NTU

The wastewater quality is shown in Table 1.

Chemical Precipitation: The chemical precipitation using chitosan for nickel concentration reduction were conducted on a program-controlled jar tester with six stainless steel paddle blade to simulate the chemical treatment plant. The jar tests were conducted in the 1L graduated glass beaker (90mm diameter, 150mm high) fitted with six stirring blade positioned at one-third of the reactor height from the bottom. 1L of the wastewater samples were taken into each of the six beakers and coagulant was added to the samples. The jar test was started with continuous agitation at speed of 250 rpm for 15 minutes. This was then followed by slow mixing at 30 rpm for 30 minutes. The sample was then allowed to settle for 30 minutes. After settling, the top clear phase of supernatant was siphoned with syringe. The supernatant was analyzed to determine the concentration of total nickel. All tests were conducted at an ambient temperature (20-25°C). The above procedure was repeated for 5 times at room temperature (25±1ºC). Similar procedure was repeated at different dosages and pH ranges. The pH adjustment was done by using diluted hydrochloric acid (HCl) and diluted sodium hydroxide (NaOH).

Design of Experiment: In order to achieve optimum nickel removal, RSM experimental design was used to study the response pattern and to determine the best combination of variables which will give the optimum condition for the experiment. In this study, two variables X_1 (coagulant dosage) and X_2 (pH) were used. The effects of the X_1 (coagulant dosage) and X_2 (pH) at two variables levels are shown in Table 2. For statistical analysis, the relationship between the coded and the actual variables can be expressed by eq.(1).

Table 2: Independent variables process and their corresponding levels

Independent variables	Symbols Uncoded	Symbols Coded	Levels -1	Levels 0	Levels +1
pH	X_1	x_1	9.5	10.25	11
Dosage (mg/L)	X_2	x_2	600	685	770

$$x_i = (X_i - X_o) / \Delta X_i \quad (1)$$

Where x_i is independent variable, X_i is independent real value; X_o is independent real value on the center point and ΔX_i is change step value. The removal of nickel is taken as the dependent variable or response. Y_i propose model for the response is described by eq. (2) [27-29]:

$$Y_i = \beta o + \beta_1 x_1 + \beta_2 x_2 + + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 \quad (2)$$

Where Y_i is the predicted response, βo is the offset term, β_1 and β_2 are the linear effect terms, β_{11} and $\beta 12$ are the squared effects and β_{12} is the interaction effects. Student's T-test and P-values were used to determine the significance coefficient of each equation above. Surface behavior was investigated on the response function (Y_i) by using the regression equation. The fitted polynomial equation expressed as surface plots in sequence to visualize the relationship between the response and experimental level of each factor and to figure out the optimum conditions. STATISTICA v8.0 computer software was used in this study.

RESULTS AND DISCUSSION

Modeling and Optimization of Chemical Precipitation Using Chitosan: The results of the experimental design are shown in Table 3.The results in Table 3 were used to run ANOVA and Multiple Regression Analysis in STATISCA software using second order polynomial model Eq. (2). This allows the optimum degree of nickel removal and other variables to be predicted. This is also shown in Table 3. The coefficients of the model equation which are used to predict the optimum degree of nickel removal were determined by multiple regression analysis using STATISCA and are shown as Eq. (3).

Table 3: Experimental Design and predicted responses

Experiment No.	pH	Coagulant Dosage (mg/l)	Predicted responses Nickel Removal (%)
1	9.50	600.0	74.1
2	9.50	770.0	73.9
3	11.00	600.0	74.68
4	11.00	770.0	70.18
5	10.25	685.0	87.2
6	9.20	685.0	69.82
7	11.31	685.0	78.94
8	10.25	564.8	73.68
9	10.25	805.2	71.24
10	10.25	685.0	82.5

$$Y = 84.82+2.51\ X_1 - 2.04\ X_2 - 10.62\ X_1^2 - 12.45\ X_2^2 - 2.15\ X_1X_2 \quad (3)$$

With the variables; nickel removal (Y) and the responses for the tested variables in coded units: pH (x_1) and coagulant dosage (x_2).

A plot of predicted versus observed variable shown in Figure 1 yielded straight line with the coefficients of determination (R^2) as 0.8431, for nickel removal (Y_1).

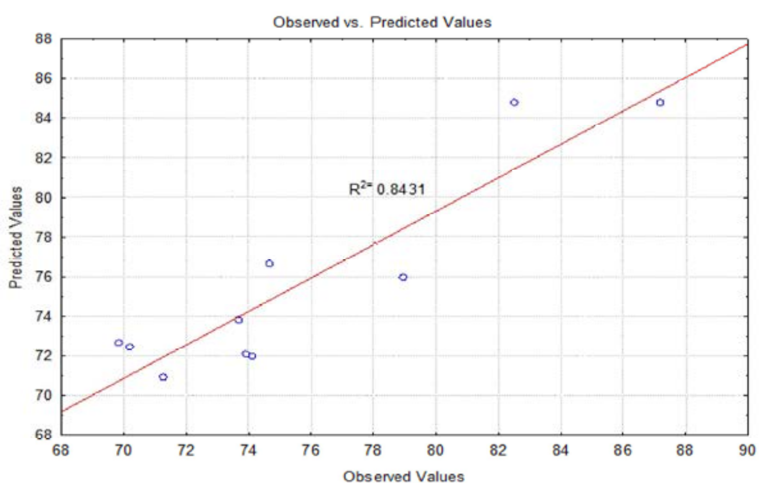

Fig. 1: A plot of predicted versus observed values of percentage nickel removal

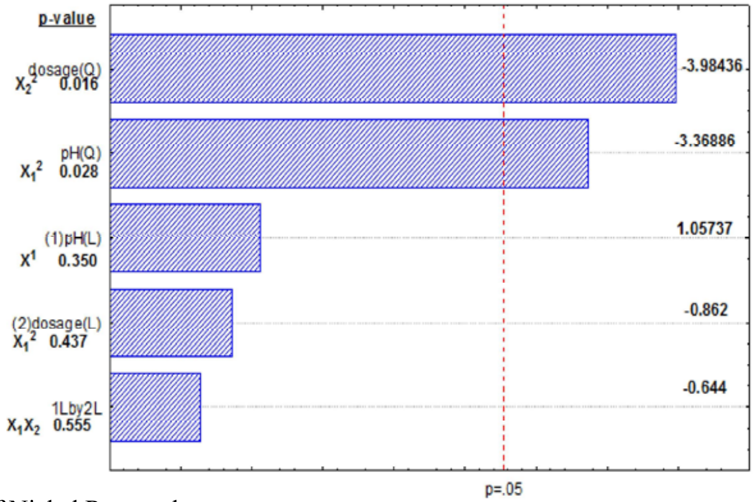

Fig. 2: Paretto Chart of Nickel Removal

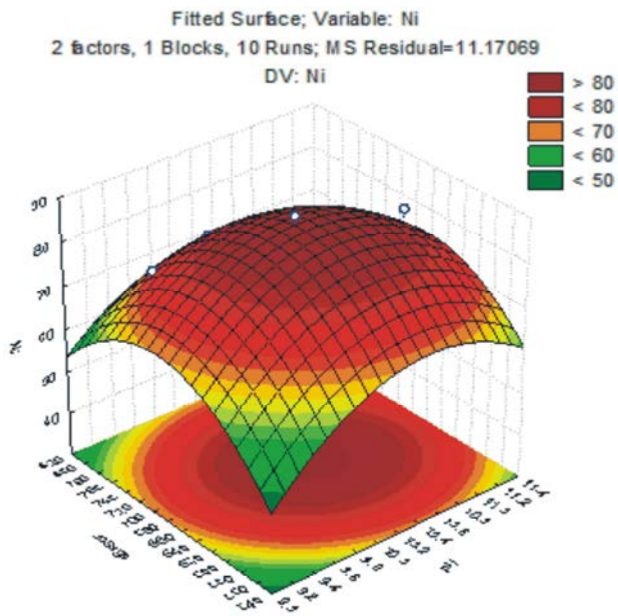

Fig. 3: 3D response surface plots of nickel removal versus coagulant dosage and pH.

The model shows adequate relationship between the observed and predicted results with coefficient (R^2) for all the responses closer to 1. Therefore, the can be used to predict the nickel removal.

Analysis of Response Surfaces and Pareto Chart: The effects of the independent variables on the dependent variable are elaborated by visualization using response surface plots and pareto charts generated by the STATISTICA software. Figure 2 (Pareto charts) shows the significance of each variable in Equation 3 for nickel removal form the probability (P) values. It shows that quadratic term of dosage (X^2_2) has the most significant effect on nickel removal with P value of 0.016 followed by the quadratic term of pH (X^2_1) with P value of 0.028, since P values less than 0.05 indicates that a variable is statistically significant [22]. Figure 2 also show that the linear terms of dosage (X_2) and pH (X_1) and the interaction between dosage and pH (X_1X_2) with p values of 0.350, 0.437 and 0.555 respectively have the least significant effect on nickel removal. These agree with the result of the optimization of the coagulation-flocculation process for wastewater treatment using polymeric ferric sulfate (PFS)-poly-diallyldimethylammonium chloride (PDADMAC) composite coagulant with 89.5% PFS and 10.5% PDADMAC (Zeng *et al*., 2012) [15].

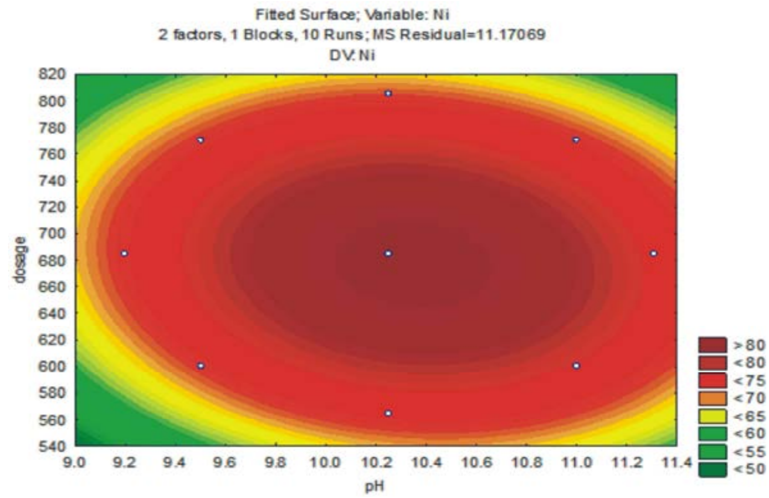

Fig. 4: 2D response surface plots of nickel removal versus coagulant dosage and pH.

The combined effect of pH and coagulant dosage on nickel removal is shown in Figures 3. The response surface curve were plotted to explain the interaction of the variables and to determine the optimum level of each variable for maximum response. The combined effects of pH and coagulant dosage on nickel removal are shown in Figures 3 and 4. The response surface curve were plotted to explain the interaction of the variables and to determine the optimum level of each variable for maximum response. As can be seen from Figures 3 and 4, the maximum percent removal for nickel of 87.2% was at pH of 10.25 and chitosan dosage of 685.0 mg/l. In general, the response surface plots indicate that the maximum nickel removal efficiency is located inside the design boundary.

Optimization of Nickel Removal Using Chitosan: The model gave critical Values of pH and dosage as 10.35 and 677.1 mg/l respectively with an equivalent predicted value of 84.95% nickel removal. Confirmatory experiments were run with these optimum values of pH and dosage. The actual percentage nickel removal at this critical value was found to be 82.31%, which is equivalent to percentage error of 3.11%. This error is considered small as the observed value is within the 5% of significance level. This result shows that the RSM approach was appropriate in optimizing the conditions of the coagulation process.

CONCLUSION

In this research, RSM was used study the optimization of nickel removal from wastewater using chitosan. The result shows that quadratic term of dosage (X^2_2) has the most significant effect on nickel removal with P value of 0.016 followed by the quadratic term of pH (X^2_1) with P value of 0.028. The modeling and optimization of chemical precipitation of nickel from wastewater using chitosan shows that the optimum nickel removal from wastewater using Chitosan was 82.31% at optimum variables of pH 10.35 and coagulant dosage of 677 mg/L. The coefficients of determination (R^2) of0.8431 show that the model used in predicting the precipitation process has a good fit with the experimental variables and hence the suitability of RSM method for the optimization of chitosan performance.

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