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# Nutrient Recovery from Waste Water: Optimization of an Adsorption Process

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Experimental design was used to study the effect of pH, initial solution concentration, contact time and dosage ratio of the adsorption of phosphorus from a synthetic waste water onto calcium carbonate based adsorbents. Interaction between the process variables was found to be important for the adsorption of phosphorus. The significance of these interaction effects have been highlighted by an Experimental Design approach undertaken. There was reasonable agreement between the Experimental Design model and independent experimental data, which indicates that the model equations are suitable for use in predicting the adsorption of phosphorus on calcium carbonate based adsorbents.

## 1. Introduction

Phosphorus is a key element contributing to the accelerated man-made eutrophication of water systems and the harmful effects such as odour, algae growth, fish deaths and decrease in water quality. The removal of phosphorus from point sources may slow the ageing process of the lake and lead to the formation of a mesotrophic water system ((Gibson, 1997)). There are a number of control measures that can be taken to reduce the contamination levels of phosphate in wastewater. These include diverting waste water; removing the phosphorus from sewage, reducing the phosphorus content in detergents and improving agricultural practices.

There are a number of reports in literature that explore the removal of phosphate from contaminated waters. For instance the use of a crystallisation technique for the removal of phosphorus from waste waters has been studied using different materials; for example the use of granular activated magnesia clinker for the removal of phosphorus ((Kaneko and Nakajima, 1988)). The key parameters that affect the removal of phosphorus from contaminated waste water include the temperature, the initial concentration of the effluent, the dosage ratio and the pH of the solution. Thought there are a number of reports found in literature that discuss the removal of phosphorus from contaminated wastewater using adsorption ((Gibson, 1997, Hano et al., 1997, Johansson and Gustafsson, 2000, Joko, 1985, Kaneko and Nakajima, 1988, Karaca et al., 2004)) none of these investigated the combined effect of the process variables on the adsorption capacity of fine dolomite.

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This research focuses on removal of phosphate from synthetic waste water using an adsorption process with fine dolomite as the adsorbent. The overall aim is to optimize the removal adsorption process with respect to process variables such as contact time, dosage ratio, initial phosphorous concentration and solution pH using a Response Surface Methodology (RSM).

## 2. Materials and Methods

Calcium phosphate supplied by Sigma Aldarich Chemicals UK, dissolved in distilled water synthetic solutions of the adsorbate of different concentrations. The adsorbent used in this work was Fine Dolomite ($d_P$ = 50µm) supplied by Killwaughter Chemical Company, UK. The typical chemical composition of the dolomite in the deposit was 44% $MgCO_3$ and 53% $CaCO_3$.

The process variables investigated in this research included initial solution concentration, solution pH, dosage ratio and contact time. The dosage ratio was determined from the volume of solution, V, and mass of adsorbent used, m;

$$DR = \frac{m}{V} \tag{1}$$

The solid phase equilibrium concentration, $q_e$, was determined from mass of the adsorbent, $m$ and volume of solution $V$ the initial and final concentration of the solution, $C_0$ and $C_e$, using the following mass balance;

$$q_e = \frac{(C_o - C_e)}{m} V \tag{2}$$

The volume of absorbate solution used in this experiment was 0.025 litres and all adsorption experiments were performed in water bath at a temperature of 40ºC. The agitation speed was maintained at 150 strokes/ minute for the entire adsorption period.

### 2.1 Experimental Design

Response Surface Methodology (RSM) is a combination of mathematical and statistical techniques used for developing, improving and optimizing processes. It is used to evaluate the relative significance of independent variables even in the presence of complex interactions. The application of statistical experimental design techniques to adsorption process may result in reduced process variability, closer confirmation of the output response to nominal and target requirements, and reduced development time and overall costs ((Can and Yildiz, 2006, Ravikumar et al., 2007)). There are a number of factorial designs available that can be applied to adsorption systems. One of the most successful is the Central Composite Design (CCD). It is obtained by adding two experimental points along each coordinate axis at opposite sides of the origin and at a distance equal to the semi-diagonal of the hyper cube of the factorial design. The new extreme values (low and high) for each factor are included in the design (Kumar et al., 2008). The Central Composite Design (CCD) was selected for use in this research.

All the four factors were varied at three levels (low (-1), medium (0) and high (+1)); the different levels for each of the variables are given in Table 1. A face-centred central composite design with a total of 30 experiments with different combinations of experimental conditions was used to investigate the effect of pH, initial solution concentration, dosage ratio and contact time on the adsorption of phosphorus on dolomite.

*Table 1: Range of values of the independent variables used in the design of experiments*

| Level | Independent Variable | | | |
|---|---|---|---|---|
| | pH | Concentration | Dosage ratio | Contact time |
| | - | ppm | g/L | hrs |
| low | 2 | 200 | 1 | 72 |
| Medium | 6 | 1100 | 5 | 168 |
| High | 11 | 2000 | 9 | 264 |

The experimental data set was used to determine an empirical model relating the response variable, $Z$ to the process variable $X_i$ according to;

$$Z_i = \beta_0 + \sum_i \beta_i X_i + \sum_{ij} \beta_{ij} X_i X_j \quad \text{with} \quad i, j = 1,2,3,4 \tag{3}$$

where $\beta_o$, $\beta_i$ and $\beta_{ij}$ are the regression coefficient for the intercept, linear terms and interaction terms respectively. In this research only one response variable was chosen, which was the amount of phosphorus adsorbed ($q_e$) onto fine dolomite obtained from equation 2. The $q_e$ values from the 30 adsorption experiments that were done were used to determine the regression coefficients in equation (3) using Design-Expert software.

## 3. Results and Discussion

Results from ANOVA analysis from data is shown in Table 2.
After regression analysis using the Design-Expert software, to obtain the regression coefficients, the following model equation was obtained;

$$\begin{aligned}\sqrt{q_e} &= -0.0542 + 1.000X_1 + 0.0110X_2 - 0.0214X_3 + 1.109X_4 \\ &+ 3.121*10^{-4}X_1X_2 + 3.504*10^{-3}X_1X_3 - 0.230X_1X_4 \\ &- 1.562*10^{-5}X_2X_3 - 6.647*10^{-4}X_2X_4 + 1.103*10^{-5}X_3X_4\end{aligned} \tag{4}$$

where: $X_1$ is the pH of the solution; $X_2$ is the initial concentration of the solution; $X_3$ is the contact time (H); and $X_4$ is the dosage ratio (g/L).

The terms with a *p*-value less than 0.05 are considered to be the most significant. This selection is based on the fact that p-value of less than 0.05 implies that there is more that 95% chance the observed change in the response variable is due change in the given model term (Myers and Montgomery, 2002). It is noted from Table 2 that the significant model terms for the adsorption of phosphorus are initial pH of solution ($p = 0.0068$), initial concentration of solution ($p = 0.0006$), the dosage ratio ($p = 0.0005$), the interaction term between initial pH and initial concentration ($p = 0.0236$), the interaction term between dosage ratio and initial pH ($p = 0.0236$), interaction term between dosage ratio and pH ($p = 0.007$).

The empirical model obtained predicts that increasing the initial concentration of phosphate solutions would increase the amount of phosphate adsorbed which is in agreement with literature. The model predicts that increasing the initial pH of the solution result in an increase in the adsorption capacity of dolomite. This concurs with observations from literature (Karaca et al., 2004).

Figure 1 a shows the comparison of the predicted and actual $q_e$ values. The $r^2$ value of the linear fit is above 0.99 which is reasonable. Figure 1b shows the surface response curve obtained from the model which is obtained by plotting equation 4 for fixed values of contact time and dosage ratio. It can be noticed the effect of initial pH on $q_e$ is more pronounced at high initial concentration than at lower concentrations. Similarly influence of concentration on $q_e$ is more significant at high pH than at low initial pH.

*Table 2: ANOVA for Response Surface 2FI Model*

| Source | Sum of Squares | df | Mean Square | F-Value | p-value Prob > F |
|---|---|---|---|---|---|
| Model | 2338990 | 10 | 233899 | 8.74 | < 0.0001 |
| A-pH | 249838 | 1 | 249838 | 9.33 | 0.0068 |
| B-Co | 456959 | 1 | 456959 | 17.07 | 0.0006 |
| C-T | 1127 | 1 | 1127 | 0.04 | 0.8397 |
| D-DR | 489162 | 1 | 489162 | 18.27 | 0.0005 |
| AB | 163633 | 1 | 163633 | 6.11 | 0.0236 |
| AC | 4377 | 1 | 4377 | 0.16 | 0.6907 |
| AD | 274766 | 1 | 274766 | 10.26 | 0.0049 |
| BC | 1030 | 1 | 1030 | 0.04 | 0.8467 |
| BD | 247386 | 1 | 247386 | 9.24 | 0.007 |
| CD | 7547 | 1 | 7547 | 0.28 | 0.6019 |
| Residual | 481834 | 18 | 26769 | | |
| Lack of Fit | 453189 | 13 | 34861 | 0.608 | 0.287 |
| Pure Error | 28645 | 5 | 5729 | | |
| Cor Total | 2820824 | 28 | | | |

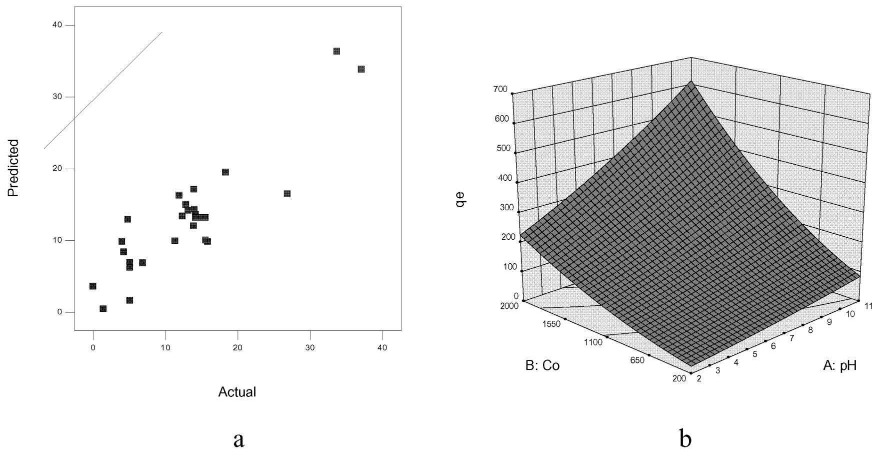


*Figure 1: a) Plot showing the predicted $q_e$ values of Phosphorus versus the experimental values. b) Response surface plot.*

### 3.1 Model Verification

A separate set of experiments were undertaken to verify the model. The concentration of the absorbent was varied between 70 and 900 ppm, whilst holding the other variables constant (dosage ratio of 4g/ L, solution pH of 3.66 and contact time of 96 hours). The $q_e$ values of phosphorus obtained from experiment were then compared with those predicted by equation 4 with results presented in Figure 2. It is apparent from Figure 2 there is reasonable agreement between the experimental data and the data predicted by equation 4. It is also noted from the analysis that the model prediction is between the range of the design space (i.e., to the right of the dotted line) as opposed to outside the range of the design space as expected.

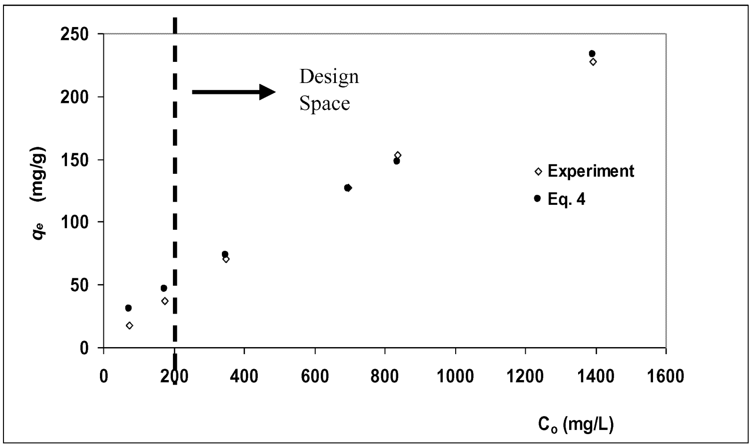


*Figure 2: Verification of model equation 4; $q_e$ as a function of initial concentrations*

## 4. Conclusion

Response Surface Methodology provides a novel approach for the optimization of adsorption processes. The model predictions are in agreement with literature for instance it predicts an increase in the adsorption capacity of dolomite as the initial pH of the solution is increased and an increase in adsorption with increasing initial concentration. Moreover, the model obtained from design of experiment methodology can be used to predict the experimental conditions required to maximise solid phase concentrations within adsorption systems.

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