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Development of a Wastewater Treatment System for Chromium Removal Using Chitosan*

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Abstract: This study attempts to evaluate the removal of chromium from aqueous solution using chitosan as an adsorbent. The experiment was conducted by varying chitosan dosage (10-30 mg), pH (5-8), contact time (10-90 min) and agitation speed (50-250 rpm). The initial Cr concentration was fixed to 20 mg L^{-1}. The results indicated that pH is the most significant factor that affects the removal of Cr. The R^2 of 0.9963 showed that the overall model is good as the experimental values are close to predicted values. The optimized conditions obtained at 28.79 mg chitosan dosage, pH 6.40, 20.20 min contact time and agitation speed of 156.20 rpm. This optimum condition obtained to achieve 0.05 mg L^{-1} residual Cr concentration or 99.75% removal that meets Department of Environment Malaysia (DOE) effluent discharge requirement. The design of treatment system that consists of rapid mix, sedimentation and filtration unit is based on the optimum operating conditions. Rapid mix tank was designed with surface area of 9.18 m^2 and volume of 27.8 m^3. Sedimentation basin was designed with surface area of 100 m^2 and volume of 83.33 m^3. Filtration was designed with surface area of 16.67 m^2.

Key words: Chromium, chitosan, wastewater treatment, DOE, toxic

INTRODUCTION

Potable water is the most precious resource. However, it is one that is increasingly under threat from several polluters. Amongst the countless man-made contaminants that infiltrate our water sources are heavy metals. Heavy metals are toxic inorganic contaminants. These metals cannot be degraded or readily detoxified biologically and have tendency to accumulate in living material (Khan *et al*., 2004). Heavy metals discharge in the wastewater can be toxic to aquatic life and make natural water unsuitable for human consumption. Unlike organic contaminants that can be degraded by microorganism, heavy metals must be removed from wastewater before being discharged to the environment (Ilhan *et al*., 2004). The presence of heavy metal ions such as lead, mercury, chromium and other heavy metals in the water is a major concern due to their toxicity to many life forms (Khan *et al*., 2004; Wan Ngah *et al*., 2006). The levels of these contaminants must be strictly controlled to protect the environment from being destroyed (Khan *et al*., 2004). This is because excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great

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**Originally Published in International Journal of Chemical Technology, 2009* problem worldwide. Pollution by chromium is one of worrisome environmental concerns as the metal has found widespread use in many industrial activities such as electroplating, metal finishing, leather tanning, mining, dyeing and fertilizer, photography industries, nuclear power plant and textile industries (Aroua *et al*., 2007; Wan Ngah *et al*., 2006; De Castro Dantas *et al*., 2001). Chromium occurs in aqueous systems as both trivalent, Cr (III) and hexavalent, Cr (VI) forms (Venkateswarlu *et al*., 2007; Selvi *et al*., 2001; Wan Ngah *et al*., 2006). The Cr (VI) is of particular concern because of its toxicity. Hexavalent chromium compounds are carcinogenic and corrosive on tissue and are found to be toxic to bacteria, plant, animals and people even at low concentrations (Demirbas *et al*., 2004). Human toxicity includes lung cancer, as well as kidney, liver and gastric damage (Aroua *et al*., 2007). In 2005, Department of Environment (DOE) Malaysia had monitored 88 wells at 48 sites in Peninsular Malaysia, 19 wells in Sarawak and 15 wells in Sabah (DOE, 2006). Based on their investigation, they found that the chromium levels exceeding the benchmark were recorded in municipal groundwater supply (13 mg L^{-1}), solid waste landfills (3 mg L^{-1}), ex-mining areas (gold mine) (17 mg L^{-1}) and golf-courses (4 mg L^{-1}) (DOE, 2006). However, based on DOE effluent discharge requirements, the tolerance limit for Cr (VI) to discharge into inland surface water and potable water is 0.05 mg L^{-1}. While, for Cr (III), the standard limit is 0.20 mg L^{-1} for standard A and 0.1 mg L^{-1} for standard B.

This study attempts to evaluate the removal of chromium from aqueous solution using chitosan as an adsorbent.

MATERIALS AND METHODS

Materials

Chitosan powder (88% deacytelation) which had been provided by Department of Biotechnology Engineering, Faculty of Engineering at the International Islamic University Malaysia was used for this experiment as adsorbent. Standard solution of chromium (1000 mg L^{-1}) was used to prepare the stock solution. Deionized water was used to dilute the stock solution in order to get the desired concentration. NaOH (1 M) and HCl (1 M) solution was used to adjust the pH.

This study was conducted at International Islamic University Malaysia, Kulliyyah Engineering, Department of Biotechnology Engineering, Bioenvironmental Engineering Research Unit (BERU), from 2007 to 2009.

Equipment

A 6 place jar test of the model R000100174 from Flocculator SW6 was used in this experiment to run coagulation process. Other equipment used include fine balance (model College B204-S), pH meter (model SevenEasy) and Atomic Absorption Spectrometer (AAS) model A Analyst 400.

Experimental Design

Design of the experiment and statistical analysis in this study was carried out by using statistical software Design Expert (Version 6.0.8). The optimization was done using Central Composite Design (CCD) with a quadratic model. Four independent variables namely dosage of chitosan (x_1), pH (x_2), contact time (x_3) and agitation speed (x_4) were chosen. The low, middle and high levels of each independent variable were designated as −1, 0 and +1, respectively. The actual design of experiments is shown in Table 1. A total 25 different combinations including 2 replications completely randomized order according to a CCD configuration for 4 factors.

Experimental Procedure

Chromium stock solution was prepared from a 1000 mg L^{-1} standard chromium solution. For this study, 20 mg L^{-1} stock solution was prepared according to the chromium concentration of 20 mg L^{-1}

Table 1: Experimental design for process

	Factor 1	Factor 2	Factor 3	Factor 4
Run	A: Chitosan dosage (mg)	B: pH	C: Contact time (min)	D: Agitation speed (rpm)
1	30	8.0	10	50
2	10	8.0	90	250
3	20	8.0	50	150
4	10	5.0	10	50
5	10	5.0	10	50
6	30	8.0	90	50
7	10	6.5	50	150
8	30	5.0	10	250
9	10	5.0	90	50
10	30	6.5	50	150
11	30	5.0	90	250
12	30	5.0	10	250
13	10	8.0	10	250
14	10	5.0	90	50
15	20	6.5	50	150
16	20	5.0	50	150
17	30	8.0	90	50
18	10	8.0	10	250
19	20	6.5	10	150
20	30	5.0	90	250
21	20	6.5	50	250
22	10	8.0	90	250
23	30	8.0	10	50
24	20	6.5	50	50
25	20	6.5	90	150

Experimental runs: 25. Center point: 1. Replications: 2. Option: Small. Completely randomized design

in ex-mining water (DOE, 2006). About 800 mL deionized water was added into 1000 mL volumetric flask. Next 20 mL of standard chromium solution was pipetted into the volumetric flask. Two percent nitric acid (HNO_3) was then added to the solution. Lastly, deionized water was added to make up to the total volume (1000 mL). Adjustment of pH was then carried out using NaOH or HCl. To maximize chromium removal by the chitosan, batch experiments was conducted at ambient temperature by varying all pertinent factors such as dosage, pH, agitation speed and contact time according to the experimental design which are shown in Table 1. For each experiment, chitosan powder was added to the chromium solution and the metal bearing suspension was kept under magnetic stirring at varying speeds in the jar test until the equilibrium conditions were reached. Then the solution was allowed to settle down. The sample of water after flocculation and sedimentation was collected and the concentration of chromium was analyzed. The chromium concentration after the adsorption was measured. The removal efficiency (E) of adsorbent on Cr is defined as:

$$E\ (\%) = \frac{(C_0 - C)}{C_0} \times 100 \tag{1}$$

Where:

C_0 = Initial concentration of chromium solution

C = Final concentration of chromium solution after the experimental run

RESULTS AND DISCUSSION

The results of concentration of residual chromium due to the effects of chitosan dosage, pH, contact time and agitation speed. The highest removal of chromium by chitosan occurred at run 24 with 99.7% removal, while the lowest removal at run 16 with 36% removal. Analysis of Variance (ANOVA)

Table 2: Analysis of variance (ANOVA)

Source	Sum of squares	df	Mean square	F-value	Prob>F	
Model	580.61	14	41.47	192.53	<0.0001	Significant
A	0.79	1	0.79	3.66	0.0847	
B	71.52	1	71.52	332.03	<0.0001	
C	2.10	1	2.10	9.76	0.0108	
D	8.19	1	8.19	38.02	0.0001	
A^2	0.13	1	0.13	0.61	0.4527	
B^2	80.14	1	80.14	372.07	<0.0001	
C^2	0.20	1	0.20	0.92	0.3604	
D^2	1.89	1	1.89	8.79	0.0142	
AB	2.54	1	2.54	11.79	0.0064	
AC	29.12	1	29.12	135.20	<0.0001	
AD	9.81	1	9.81	45.55	<0.0001	
BC	22.88	1	22.88	106.23	<0.0001	
BD	2.39	1	2.39	11.10	0.0076	
CD	0.10	1	0.10	0.45	0.5193	
Residual	2.15	10	0.22			
Lack of fit	8.242E-003	2	4.121E-003	0.015	0.9848	Not significant
Pure error	2.15	8	0.27			
Cor total	582.76	24				
SD	0.46		R^2	0.9963		
Mean	5.53		Adj R^2	0.9911		
CV	8.40		Pred R^2	0.9836		
PRESS	9.56		Adeq precision	35.469		

test result for 25 runs under CCD experimental design is shown in Table 2. Analysis of Variance is used to investigate and model the relationship between a response variable and one or more independent variables. Values of Prob>F less than 0.0500 indicate model terms are significant. Values greater than 0.1000 indicate the model terms are not significant. The principal variables are A (chitosan dosage), B (pH), C (contact time) and D (agitation speed). B, C and D are significant, while A is not significant. B indicates a very significant model term. B^2 and D^2 are significant but A^2 and C^2 are not significant. B^2 indicates a very significant quadratic model terms. AB, AC, AD, BC and BD show significant model terms but CD show insignificant model terms.

The regression equation obtained after analysis of variance gave the level of adsorption of chromium onto chitosan as a function of chitosan dosage, pH, contact time and agitation speed. All terms, regardless of their significance, are included in the following equation:

$$\begin{aligned} Y = {} & 1.230 - 0.628X_1 - 5.980X_2 - 0.342X_3 + 2.024X_4 - 0.227X_1^2 + 5.610X_2^2 - 0.279X_3^2 + 0.862X_4^2 \\ & + 1.195X_1X_2 + 1.349X_1X_3 - 2.349X_1X_4 - 1.196X_2X_3 + 1.160X_2X_4 - 0.077X_3X_4 \end{aligned} \tag{2}$$

where, Y is the predicted response. Square regression (R^2) was significant at the level of 99.63%. The coefficients were calculated using design expert. Equation 2 shows final equation in terms of actual factors. This equation is used to calculate the predicted value of residual chromium concentration, the coefficient of pH gives the highest value. This indicates that effect of pH contributes more to the successful of lowering the residual chromium concentration.

Effect of Chitosan Dosage

The rate of chromium sorption on chitosan dosage was studied by varying the amount of adsorbents from 10 to 30 mg, while keeping other parameters (pH, agitation speed and contact time) constant. As in Fig. 1, the concentration of residual chromium decreases with the increasing of chitosan dosage. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. Thus, chromium removal can be increased by using high dosage of chitosan.

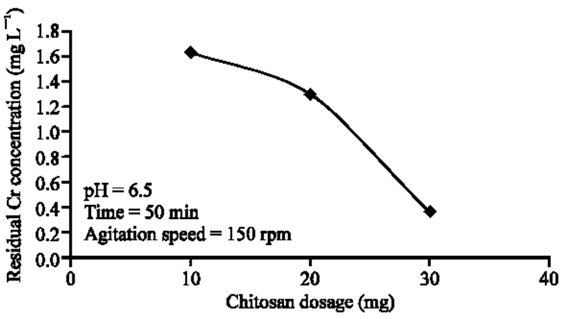

Fig. 1: Effect of chitosan dosage on chromium removal

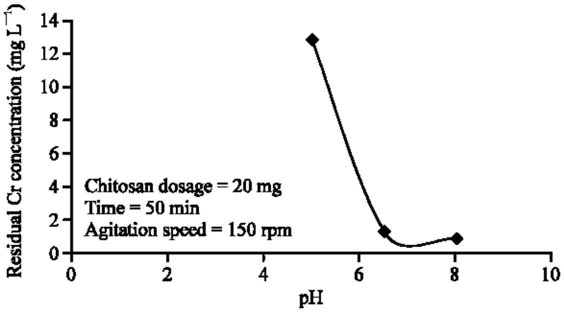

Fig. 2: Effect of pH on chromium removal

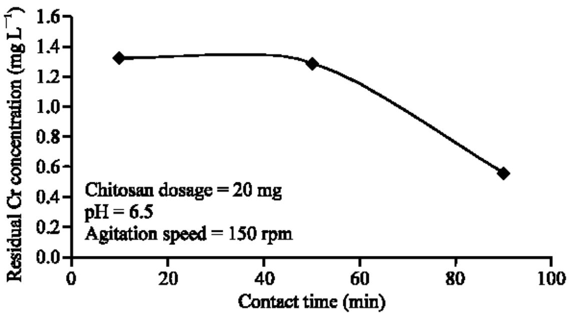

Fig. 3: Effect of contact time on chromium removal

Effect of pH

The sorption onto chitosan is basically electrostatic attraction type. As Fig. 2 shows, increasing pH while fixing other factors enhance chromium removal. However, the removal is not effective at pH greater than 7. The low sorption efficiency at pH less than 6 is probably due to a weak interaction between the ammonium groups of chitosan and chromium ions. Furthermore, chitosan is soluble in pH less than 6. The optimum pH for removal of chromium is at pH 6.5.

Effect of Contact Time

As shown in Fig. 3, the concentration of chromium residual decreases with the increase of contact time. When time less than 50 min, concentration of residual chromium decreases gradually and decreases instantaneously when time is greater than 50 min. Therefore, the removal of chromium is effective when chromium interact with chitosan for longer time.

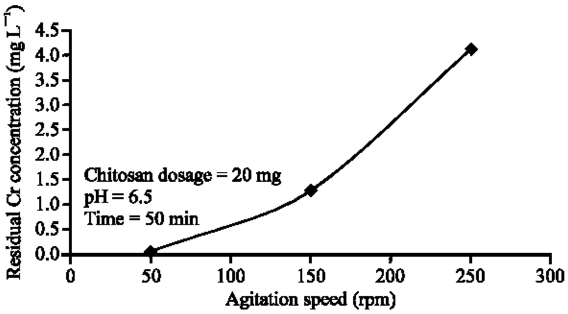

Fig. 4: Effect of agitation speed on chromium removal

Table 3: Numerical solution for optimization

Chitosan dosage (mg)	pH	Contact time (min)	Agitation speed (rpm)	Concentration of residual chromium (mg L^{-1})	Desirability
28.65	6.95	75.82	68.96	0.05	1
28.79	6.39	20.16	156.23	0.0500055	1
18.37	7.64	27.18	131.95	0.0500068	0.999999
22.78	7.71	84.30	186.08	0.0500075	0.999999
27.44	6.60	33.23	152.69	0.0500087	0.999999
19.31	6.81	85.08	174.05	0.0500096	0.999999
25.88	6.78	15.66	186.96	0.0500137	0.999999
27.10	6.68	46.16	137.39	0.0500149	0.999999
28.50	6.66	39.84	185.78	0.0500159	0.999999
28.09	7.08	76.19	202.06	0.0500316	0.999998

Effect of Agitation Speed

The effect of agitation speed on removal efficiency of chromium was studied by varying the speed of agitation to 50, 150 and 250 rpm, while keeping the optimum dose of adsorbents and optimum pH as constant. From Fig. 4, it is observed that the concentration of residual chromium increases as the agitation speed increases. These results can be associated to the fact that the increase of the agitation speed improves the diffusion of chromium towards the surface of the chitosan.

Under optimization in the design expert, a set of numerical solutions will be recommended by the software according to the range and desirability of each factor and response. As shown in Table 3, a set of 10 solutions was suggested by the software according to the concentration of residual chromium which was set to achieve the target value of 0.05 mg L^{-1}. To check the validity of the model, one of these solutions can be selected and then an experiment is carried out by modifying the values of the factors according to the numerical solution that we have selected. The selection is based on the desirability. The selection of the solution is preferable when desirability = 1.

The preferable solution is solution number 1 and number 2 since desirability is equal to 1. However, the solution number 2 is most preferable. This is because the contact time in solution number 2 is shorter than contact time in solution number 1. Furthermore, solution number 2 has higher agitation speed compare to solution number 1. This is consistent with the theory of mixing where good mixing is achieved at higher speed and shorter time. Therefore, solution number 2 with 29 mg chitosan dosage, pH 6.39, 20.16 min contact time and 156 rpm agitation speed has been selected to validate the model. The optimization result that had been generated using design expert is shown in Table 4. For the validation of the model, the value of residual chromium concentration that has been selected was higher (0.210 mg L^{-1}) than the predicted. This is because the analysis of residual chromium concentration depends on the calibration made in the AAS machine.

Table 4: Optimization solution

Chitosan dosage (mg)	pH	Contact time (min)	Agitation speed (rpm)	Residual Cr concentration (mg L^{-1})
28.79	6.39	20.16	156.23	0.050

Table 5: Comparison of various adsorbents and its percentage uptake of Cr (III)

	Condition					
Adsorbent	pH	Initial contact time (min)	Agitation speed (rpm)	Dosage (mg L^{-1})	Removal (%)	References
Chitosan gel beads	6.00		-	20	96.00	Tirgar *et al.* (2006)
Chitosan coated with oil palm shell charcoal	5.00	180-300	100.00	-	-	Nomanbhay and Palanisamy (2005)
Chitosan flakes	5.00	30		50	-	Cervera *et al.* (2003)
Cross-linked and non cross-linked chitosan	5.00	30	400.00	100	-	Schmuhl *et al.* (2001)
Chitosan coated montmorillonite	4.00	-	-	-	-	Fan *et al.* (2006)
Chitosan impregnated with a microemulsion	3.50	-	-	-	-	De Castro Dantas *et al.* (2001)
Chitosan	6.39	20.16	156.23	20	99.75	This study

Not mentioned

$$\text{Percentage removal: } E = \frac{(20-0.05)}{20} \times 100\% = 99.75\% \quad (3)$$

The value of optimized residual chromium concentration achieves the DOE standard limit for chromium which is 0.05 mg L^{-1}.

The literature showed that chromium can be removed by different techniques. Several researchers investigated the removal of chromium using chitosan coated with oil palm shell charcoal. From their research, they found that, the practical problems of chitosan solubility at low pH aqueous systems, gel forming behavior and mass transfer limitations can be solved by coating chitosan on oil palm shell charcoal. Tirgar *et al.* (2006) carried out a study on the removal of airborne hexavalent chromium mist using chitosan gel beads, the highest Cr (VI) removal obtained at pH 6, low Cr (VI) concentration (<50 µg m^{-3}) and high sorbent concentration (20 mg mL^{-1}). The higher ions removal efficiencies were achieved at lower levels of air velocities, pollution concentrations and higher levels of solution pH values, temperatures and sorbent concentrations. Several reports evaluated the use of chitosan flakes for the removal of heavy metal ions. The results showed that a 0.4 g portion of activated alumina can retain 0.6 mg Cr (III) from 20 mL sample adjusted at pH 4 and stirred for 30 min.

Table 5 shows that there are many studies on the removal of Cr (III and IV) using various types of adsorbent. However, the percentage removal for each adsorbent is different due to the variation in the operating parameters (pH, agitation speed, dosage, temperature and many more). Thus, this comparative study was conducted to further understand the mechanism of adsorption and compare the types of adsorbents that were previously used to remove Cr (VI). In comparison with the adsorption kinetics of the various adsorbents, it was concluded that most of the removal process occurred very fast within the first 20 min. Thus, from Table 5 comparisons, it can be concluded that the adsorption capability of the adsorbent is highly dependent on many factors such as surface functional groups, the specific surface area and the solution components. In order to achieve optimal removal of Cr (VI) ions, the pH of the solution must be maintained in normal conditions for the complete removal of Cr (VI) as it has been found in this research by having the optimum condition obtained to achieve 0.05 mg L^{-1} residual Cr concentration or 99.75% removal that meets Department of Environment (DOE) Malaysia effluent discharge requirement.

CONCLUSION

The performance of chitosan for the removal of chromium from water is 99.75% good since percentage of removal is high. It can be concluded that chitosan is a good candidate for biosorption of chromium. Thus, the use of chitosan as an adsorber for heavy metal removal (Cr) from aqueous solution is highly an efficient alternative. Besides that, the operating condition for the removal of chromium using chitosan was successfully optimized. The optimum condition is 28.79 mg of chitosan dosage, 6.39 pH, 20.16 min contact time and 156.23 rpm agitation speed. This optimum operating condition was achieved at initial chromium concentration of 20 mg L^{-1} which then reduced to 0.05 mg L^{-1}. The minimum residual chromium concentration was found to be 0.059 mg L^{-1} and the percentage of removal was 99.7%. Therefore, this residual chromium concentration meets the permissible limit of chromium effluent discharge that has been regulated by Department of Environment (DOE) which is 0.05 mg L^{-1}.

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