

A Study on Removal Characteristics of (Mn^{2+}) from Aqueous Solution by CNT

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Abstract—It is important to remove manganese from water because of its effects on human and the environment. Human activities are one of the biggest contributors for excessive manganese concentration in the environment. The proposed method to remove manganese in aqueous solution by using adsorption as in carbon nanotubes (CNT) at different parameters: The parameters are CNT dosage, pH, agitation speed and contact time. Different pHs are pH 6.0, pH 6.5, pH 7.0, pH 7.5 and pH 8.0, CNT dosages are 5mg, 6.25mg, 7.5mg, 8.75mg or 10mg, contact time are 10 min, 32.5 min, 55 min, 87.5 min and 120 min while the agitation speeds are 100rpm, 150rpm, 200rpm, 250rpm and 300rpm. The parameters chosen for experiments are based on experimental design done by using Central Composite Design, Design Expert 6.0 with 4 parameters, 5 levels and 2 replications. Based on the results, condition set at pH 7.0, agitation speed of 300 rpm, 7.5mg and contact time 55 minutes gives the highest removal with 75.5%. From ANOVA analysis in Design Expert 6.0, the residual concentration will be very much affected by pH and CNT dosage. Initial manganese concentration is 1.2mg/L while the lowest residual concentration achieved is 0.294mg/L, which almost satisfy DOE Malaysia Standard B requirement. Therefore, further experiments must be done to remove manganese from model water to the required standard (0.2 mg/L) with the initial concentration set to 0.294 mg/L.

Keywords—Adsorption, CNT, DOE, Manganese, Parameters.

I. INTRODUCTION

OCURRENCE of manganese in wastewater originate from its non-point source (NPS) pollutant from industrial and agriculture, urban runoff, domestic waste, mining, e-Waste from dry cells and it also occur naturally in groundwater. From mining activity, out of 745 million tons ore mined 70% of that becomes waste [1]. The standard set by Department of Environment (DOE) in Sewage and Industrial Effluents Regulations 1979 Malaysia for manganese is 0.2 mg/L (Standard A) and 1.0 mg/L (Standard B). In Regulation 11 (5) (b), parameters limit of effluents other than Standard A or B for manganese is 10mg/L. Unacceptable amount of manganese entering water will make the water non-potable and non-

palatable. Manganese in water can affect human, aquatic life and some materials. For aquatic life, high level of manganese of more than 10mg/L will be toxic [2]. However, moderate pollution can also kill highly sensitive organisms. Oxidation of metal ions in water can also contribute to less amount of oxygen in water [3] and this may affect the dissolve oxygen in the water. For human beings, some research has been done to relate high concentration of manganese with brain damage and neural problem.

II. MATERIALS, EQUIPMENTS AND METHODS

A. Materials

CNTs were obtained from Department of Biochemical Biotechnology Engineering, International Islamic University Malaysia. CNTs were kept in a Bijou bottle at room temperature as the preservation procedure [4], [5].

B. Equipments

Characterization of CNTs was done to obtain the images of nanotubes produced, thus, determining the diameter, length, properties and purity of nanotubes. The morphology of filamentous carbon grown was observed using Field Emission Scanning Electron Microscopy (FESEM). The concentrations of manganese ions were measured by an atomic absorption spectrometer ((AAAnalyst 400, Perkin-Elmer model Precise, USA).

C. Experimental Procedures

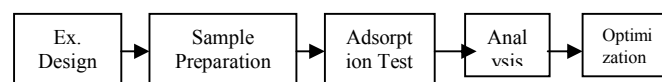


Fig. 1 Experimental procedures.

Aqueous solution with 1.2mg/L concentration of manganese and specific amount of CNTs were prepared and kept at preservative conditions. Manganese concentration was fixed based on the largest value of manganese in ground water recorded by Department of Environment Malaysia. After we have prepared all the solutions, CNTs and equipment, we run the adsorption feasibility tests, which are based on different conditions as in Table 1. Experimental design was used for optimization to determine the optimum value of agitation speed (rpm), contact time (s), pH and manganese dosage (mg/L) for manganese removal from aqueous solution. Using related equations, analysis of results was done.

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TABLE I
THE PARAMETERS FOR RUNNING THE ADSORPTION EXPERIMENT
AT STATED CONTACT TIME

Parameter (Coded)	Very Low (-2)	Low (-1)	Medium (0)	High (1)	Very High (2)
CNT dosage (mg/L)	5.00	6.25	7.50	8.75	10.00
pH	6.0	6.5	7.0	7.5	8.0
Contact Time (min)	10.0	32.5	55.0	87.5	120.0
Agitation Speed (rpm)	100	150	200	250	300

(Source: Ahmad bin Jusoh *et al.*, 2005) [6]

D. Experimental Design

Many experimental design technique as of the author Box [7] is used for the empirical study of relationships between a measured objective on one hand and a number of operating conditions on the other hand. Design-expert Version 6.0.8 was used to conduct the experimental design for this test. Four parameters were used for the evaluation using Central Composite Design with Full range, which gave 44 experiment runs. For this project, 2 replications with 5 levels were used.

E. Adsorption Experiments

Batch adsorption experiments were carried out by shaking a series of bottles containing various amounts of CNTs and heavy metal ions at different pH's. 250 ml shake flasks to be filled with 50 ml of the stock solution adjusted to pH 6, pH 6.5, pH 7, pH 7.5 or pH 8 at a fixed concentration of 1.2 mg/L. The pHs were adjusted by using 1.0M sodium hydroxide and 1.0M nitric acid. A known amount of carbon nanotubes (5mg, 6.25mg, 7.5mg, 8.75mg or 10mg) was added to one set of conical flask respectively and agitated at five different speeds of 100 rpm, 150 rpm, 200 rpm, 250 rpm and 300 rpm, for the desired time periods (10 min, 32.5 min, 55 min, 87.5 min and 120 min). The filtrates were taken at the stated time intervals for five different pH and five different agitation speeds. The adsorbent were removed from the solution by filtration, using syringe filter (pore size of 0.45µm). The residual concentration of heavy metals was determined by an atomic absorption spectrometer. In addition to adsorption tests, a set of blank tests with fly ash was conducted in order to evaluate the removal by metal hydroxide precipitation at various pH's.

The kinetics of the adsorption of the Mn⁺² ions on CNT were evaluated using a procedure similar to that used in the adsorption experiments [8]. A series of bottles containing 50 g/L CNT slurries and Mn⁺² set the concentration of 1.2mg/L of manganese, 0.06mL from a 1000mg/L manganese standard solution was added into each flask and kept in a thermostatic shaking water bath. After shaking for different time intervals, the samples were collected and analyzed for residual

concentrations as % Manganese Removal = $\frac{C_0 - C_E}{C_0} \times 100 \%$.

Adsorption isotherm are used to relate the amount of adsorbate on adsorbent as in form of Langmuir and Freundlich adsorption isotherms.

III. RESULTS AND DISCUSSION

3 different manganese standards were used with 0.4 mg/L, 0.5 mg/L, 0.6 mg/L and 1.0 mg/L of manganese to determine the characteristics of the solution as seen in Table 2.

TABLE II
TABLE OF RESULTS

Run	CNT Dosage (mg/L)	pH	Contact Time (min)	Agitatio n Speed (rpm)	Residual Concentrati on (mg/L)	% Remov al
1	8.75	6.5	87.5	150	0.380	68.33
2	8.75	6.5	87.5	150	0.383	68.08
3	8.75	6.5	32.5	150	0.407	66.08
4	6.25	7.5	32.5	150	0.425	64.58
5	8.75	6.5	87.5	250	0.422	64.83
6	6.25	6.5	32.5	150	0.434	63.83
7	8.75	7.5	32.5	150	0.406	66.17
8	8.75	6.5	32.5	150	0.397	66.92
9	6.25	7.5	32.5	250	0.671	44.08
10	7.50	7.0	55.0	100	0.299	75.08
11	6.25	6.5	87.5	250	0.414	65.50
12	6.25	6.5	87.5	250	0.407	66.08
13	6.25	7.5	32.5	250	0.680	43.33
14	8.75	7.5	32.5	250	0.444	63.00
15	6.25	6.5	87.5	150	0.417	65.25
16	8.75	6.5	87.5	250	0.388	67.67
17	6.25	7.5	87.5	150	0.396	69.25
18	7.50	7.0	55.0	200	0.462	61.50
19	8.75	6.5	32.5	250	0.416	65.33
20	8.75	7.0	55.0	200	0.456	62.00
21	7.50	6.0	55.0	200	0.469	60.92
22	5.00	7.0	55.0	200	0.455	74.50
23	8.75	7.5	32.5	150	0.408	66.00
24	6.25	7.5	87.5	250	0.448	62.67
25	7.50	7.0	55.0	200	0.454	62.17
26	6.25	6.5	32.5	250	0.602	49.83
27	7.50	7.0	10.0	200	0.457	61.92
28	8.75	7.5	87.5	250	0.443	63.08
29	6.25	7.5	32.5	150	0.405	66.25
30	6.25	6.5	32.5	150	0.397	66.92
31	6.25	7.5	87.5	250	0.443	63.08
32	8.75	7.5	87.5	150	0.383	68.08
33	8.75	7.5	87.5	150	0.385	37.92
34	7.50	8.0	55.0	200	0.445	62.92
35	6.25	7.5	32.5	250	0.684	43.00
36	7.50	7.0	55.0	200	0.464	61.33
37	8.75	7.5	87.5	250	0.445	62.92
38	7.50	7.0	120.0	200	0.449	62.58
39	6.25	7.5	87.5	150	0.392	67.33
40	8.75	6.5	32.5	250	0.417	65.25
41	7.50	7.0	55.0	200	0.459	61.75

42	6.25	6.5	87.5	150	0.389	67.58
43	7.50	7.0	55.0	300	0.294	75.50
44	8.75	7.5	32.5	250	0.442	63.17

IV. ADSORPTION ISOTHERM

The equilibrium adsorption is important in the design of adsorption systems because it indicates the capacity of the adsorbent during the adsorption process. To analyze the residual concentration for the experiments, five of the lowest residual concentrations, C_e were chosen and the adsorption capacity, q_e for each are calculated as seen in Table 3.

TABLE III
ADSORPTION ISOTHERM DATA

#	CN T	pH	Time	rpm	C_e	q_e	C_e / q_e	$\text{Log}_{10} q_e$	$\text{Log}_{10} C_e$
43	7.5	7.0	55	300	0.2	0.3171	0.927	0.49	0.531
					94	2	88	7	
11	7.5	7.0	55	100	0.2	0.3379	0.884	0.4712	0.524
					99	9	3		
1	8.7	6.5	87.5	150	0.3	0.3588	1.059	0.4451	0.420
	5				80	1	2		
32	8.7	7.5	87.5	150	0.3	0.3574	1.071	0.4468	0.416
	5				83	6	8		
16	8.7	6.5	87.5	250	0.3	0.3552	1.092	0.4495	0.411
	5				88	2	2		

The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of manganese by CNTs. Based on Figure 2&3, the adsorption capacity (x_m) was determined from the slope the graph. Table 4 summarizes all the coefficients related to the adsorption isotherms plots.

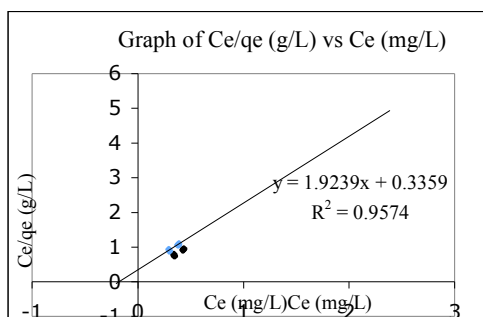


Fig. 2 Adsorption isotherm model for Langmuir kinetic

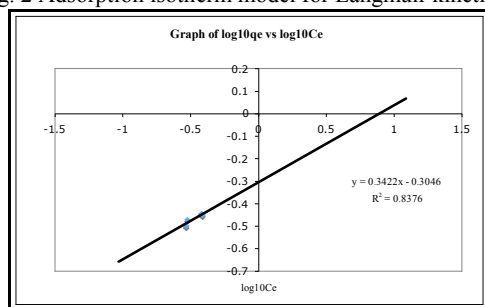


Fig. 3 Adsorption isotherm model for Freundlich kinetic

Based from the comparison of the two models, it is observed that Langmuir isotherm model shows better fitting with the experimental data in which it obtained higher correlation coefficient ($R^2=0.9574$) compared to Freundlich Isotherm ($R^2=0.8376$). The correlation coefficient is very close to 1.0

for both values as of table 4. This indicates the applicability of monolayer coverage of manganese ions on the homogeneous surface of the adsorbent. The good correlation coefficient of Langmuir isotherm also indicates that manganese ion was strongly adsorbed to the surface of CNTs. Therefore, it is verified that CNTs have great potential to be a good adsorbent for the removal of manganese in water treatment.

TABLE IV
CONSTANT FOR FREUNDLICH AND LANGMUIR ISOTHERM MODELS FOR THE ADSORPTION OF MANGANESE

Freundlich		Langmuir	
n (mg/g)	R^2	x_m (mg/g)	R^2
2.9223	0.8376	0.5198	0.9574

V. STATISTICAL ANALYSIS

The experiments were designed to have 2 replications ($N = 2$). All the regression, correlation coefficients and standard deviation were analyzed by using Design Expert. Quadratic model was chosen for the analysis using ANOVA. Parameters set for the analysis are:

A = CNT Dosage (mg/L) B = pH, C = Contact Time (min) D = Agitation Speed (rpm)

Quadratic was chosen because from the regression model equation in Design Expert 6.0 has relations of A^2B , A^2D and AB^2 . This shows that the best model should be quadratic. Linear equation will only relate two factors or with the same factor such as A^2 relation. Quadratic model will give an F-value which is closer to 1.0 than in a linear model.

A. ANOVA Analysis

The suitability of the model was further studied by the analysis of variance (ANOVA). To make sure that the design is significant, a few terms must be included and excluded from the design. Values of "Prob > F" which are less than 0.0500 indicate that model terms are significant. For the design used in this experiment, the Table 5 gives the probability of F-values for each linear and quadratic model terms. The Model F-value of 17.36 implies the model is significant. In this case C, D², AC, BD and A²D are significant model terms.

TABLE IV
ANALYSIS OF VARIANCE TABLE (PARTIAL SUM OF SQUARES)

Source	Sum of Squares	DF	Mean Square	F-Value	Prob > F	Status
Model	0.07335	17	0.00431482	17.3649	< 0.0001	significant
	2		3	9		t
	0.00012		0.00012450	0.50105		
A	5	1	1	2	0.4853	-
	0.00021		0.00021329	0.85839		
B	3	1	3	6	0.3627	-
	0.00388		0.00388512	15.6356	0.0005	significant
C	5	1	4	6	0.0005	t
			4.56045E-05	0.18353		
D	4.56E-05	1	05	5	0.6719	-
			7.83953E-05	0.31550		
A ²	7.84E-05	1	05	2	0.5791	-
				0.06631		
B ²	1.65E-05	1	1.6477E-05	2	0.7988	-
				0.23462		
C ²	5.83E-05	1	5.8299E-05	4	0.6322	-

	0.03955			159.182	<	significan
D ²	3	1	0.03955339	4	0.0001	t
	0.00023		0.00023483	0.94509		
AB	5	1	5	3	0.3399	-
	0.00117		0.00117523	4.72973		significan
AC	5	1	6	2	0.0389	t
	0.00058		2.34076			
AD	2	1	0.00058163	5	0.1381	-
	0.00013		0.00013204	0.53140		
BC	2	1	2	3	0.4725	-
	0.00136		0.00136522	5.49435		significan
BD	5	1	9	9	0.0270	t
			0.00032972	1.32698		
CD	0.00033	1	6	2	0.2598	-
	0.00090		0.00090846	3.65610		
A ² B	8	1	3	5	0.0669	-
	0.00331		0.00331494	13.3409		significan
A ² D	5	1	2	7	0.0011	t

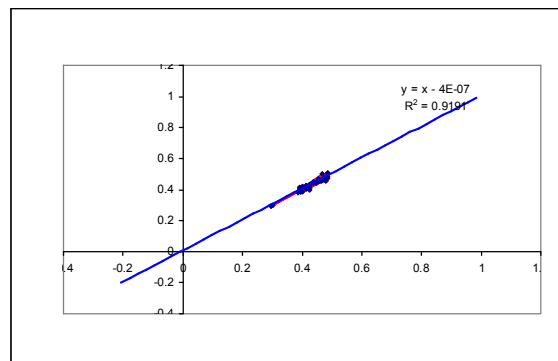


Fig. 4 Graph of actual values vs predicted values for residual concentration

B. Development of regression model equation

From the analysis, final concentrations of the aqueous solution were obtained in Design Expert 6.0. The equations in terms of coded and actual factors are given below:

Residual Concentration (Coded Factors)

$$= +0.45 + 0.013 * A - 0.011 * B - 0.020 * C - 4.855E-003 * D + 0.011 * A^2 + 3.210E-003 * B^2 + 6.037E-003 * C^2 - 0.16 * D^2 + 0.011 * A * B + 0.024 * A * C - 0.017 * A * D + 8.243E-003 * B * C + 0.027 * B * D - 0.013 * C * D + 0.096 * A^2 * B + 0.18 * A^2 * D - 0.13 * A * B^2$$

Residual Concentration (Actual Factors)

$$= + 10.81816 - 0.14234 * \text{CNT Dosage} - 4.82514 * \text{pH} - 2.54407E-003 * \text{Contact Time} + 0.021537 * \text{Agitation Speed} - 0.16436 * \text{CNT Dosage}^2 + 0.39879 * \text{pH}^2 + 1.99578E-006 * \text{Contact Time}^2 - 1.57290E-005 * \text{Agitation Speed}^2 + 0.51237 * \text{CNT Dosage} * \text{pH} + 1.77829E-004 * \text{CNT Dosage} * \text{Contact Time} - 4.46351E-003 * \text{CNT Dosage} * \text{Agitation Speed} + 1.49880E-004 * \text{pH} * \text{Contact Time} + 2.65066E-004 * \text{pH} * \text{Agitation Speed} - 2.35481E-006 * \text{Contact Time} * \text{Agitation Speed} + 0.015362 * \text{CNT Dosage}^2 * \text{pH} + 2.92980E-004 * \text{CNT Dosage}^2 * \text{Agitation Speed} - 0.052744 * \text{CNT Dosage} * \text{pH}^2$$

From the equation, values of R-squared can be used to determine the quality of the results. If the value is closer to 1.0, the result is more accurate and precise when comparing between experimental and predicted value from the design equation of manganese removal. Values of R-squared are given as $R^2 = 0.9191$ and adjusted $R^2 = 0.8661$.

The variation between the actual values as compared to the predicted values from Design Expert 6.0. The actual values are the observed residual concentration from the experiment while the predicted values are simulated from Design Expert 6.0 based on the regression model equation. From the plotted graph in figure 4, the R^2 value is 0.9191, which proves there is a strong relation between the actual and predicted value and the equation developed is valid.

In general, the overall results show strong correlation between both actual and predicted values for manganese removal. It is proven from the plot of graph in figure 5 where the shape of both graphs are similar.

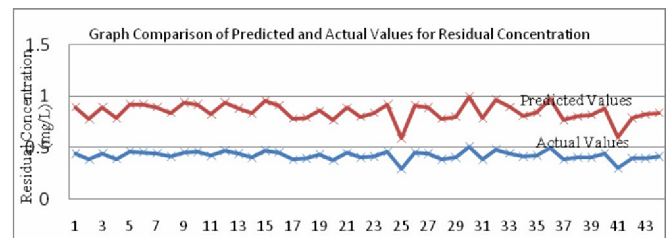


Fig. 5 Plot comparison of predicted and actual values for residual concentration

C. Result validation

To validate the data obtained from the experimental runs, contour plot of Standard Error of Design from Design Expert was used to find the points for validation. Contour plot of CNT dosage vs pH was used where actual factors set are contact time at 17 minutes and agitation speed at 200 rpm. The three dimensional plot from Design Expert is given in figure 6 and contour plot is in figure 7.

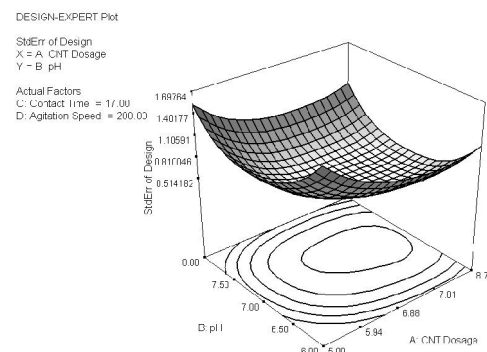


Fig. 6 Three dimensional response surface plot of manganese removal (pH vs CNT Dosage)

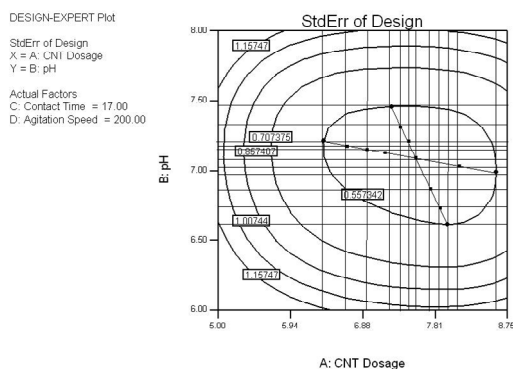


Fig. 7 Contour plot of Standard Error of Design (pH vs CNT Dosage)

VI. CONCLUSION

In this study, tests were performed to evaluate the use of CNT as an adsorbent for Mn^{+2} ions. From the results obtained in this experiment, it can be concluded that pH and CNT dosage give the most distinct relationship in the removal of manganese. This is based on the contour plot of the relationship between the factors and residual concentration. The only plot which shows a valid relation is between pH and CNT dosage. The highest removal of manganese, with 75.5% removal is for Run 43 with 7.5 mg/L of CNT dosage, agitated at 300 rpm for 55 minutes and the solution is set to pH 7.0. Agitation time is the only single factor to give significant value, it also has the lowest $P > F$ ratio among all the significant factors. It explains why in validation experiment runs, at a shorter time adsorbance was not at its optimum. The regression line analysis given in Design Expert can also be used to determine the validity of the results.

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From the result with the highest percentage removal, 75.5% is for run 43 at 300 rpm, 55 minutes, pH 7 and 7.5mg CNT dosage. Therefore, the point for reference in validation will be at Run 43. Agitation speed of 300 rpm will be the initial optimizing value and to have a more precise value based on the contour plot, agitation level chosen is at 200 rpm which is 2 level lower than 300 rpm. This is chosen because 300 rpm is the highest level of agitation speed, it requires higher power and not suitable for optimizing the parameters. Data from validation experiment is given in Table 6 to check whether the parameters set at the most optimum condition will give the highest removal.

TABLE IV
 VALIDATION VALUE FOR MANGANESE REMOVAL

CNT (mg/L)	pH	Residual Concentration (mg/L)	Percentage Removal (%)
6.65	7.2	0.491	59.08
7.30	7.2	0.466	61.17
7.40	7.1	0.480	60.00
7.80	7.0	0.473	60.58
8.26	7.0	0.484	59.67
7.65	7.3	0.481	59.92
7.70	7.7	0.470	60.83
7.90	6.9	0.411	65.75
8.00	6.7	0.461	61.58

From the data, percentage removal values obtained from validation experiments are not the lowest among all the experiments done previously. This may be due to the pre-set value for agitation time at 17 minutes as compared to 55 minutes which gives the lowest residual concentration in Run 43. Manganese must have not been fully adsorbed to the CNTs during this very short agitation time even other factors were set to their optimum. Furthermore, agitation time is the only single model term which is significant. Other terms are linearly or quadratically related to other single terms.