MODIFIED ACTIVATED CARBON FOR OPTIMUM DNP REMOVAL

Huzairy Hassan[1], Lai Moon Ting[2]

[1,2] School of Bioprocess Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau Perlis.

Email: [1]huzairyhassan@unimap.edu.my, [2]moonting_lai@yahoo.com

ABSTRACT

This study investigates the capability of chemical pre-treated activated carbon in adsorbing phenolic compound 2, 4-dinitrophenol from aqueous solution. Chemical treatments such as acidic and basic treatment were applied on activated carbon. 0.3 mg of treated activated carbon was placed in Erlenmeyer flasks containing 50 mL of 5 mg/L 2, 4-dinitrophenol and incubated at 25 ± 2 oC with rotation speed of 150 rpm for 6 hours. Absorbance value was measured and calculated as the final concentration of 2, 4-dinitrophenol. The effects of three parameters; pH, temperature and contact time were examined by both treated activated carbons. Acidic treatment of activated carbon has a better adsorption capability. The highest percentage of 92 %, 78 % and 64 % occurred at pH 3, temperature 20 oC and at 2 hours, respectively. For the optimization using Response Surface Methodology, the predicted optimized physicochemical parameters were at pH 4, temperature 40 oC, and 2.5 hours contact time, which resulted in 98% removal of 2, 4-dinitrophenol.

KEYWORDS: Modified activated carbon, adsorption, optimization, 2, 4-dinitrophenol.

1.0   INTRODUCTION

2,4-Dinitrophenol (DNP), $C_6H_4N_2O_5$, or Solfo Black is a cellular metabolic poison, water soluble, which is yellow, crystalline solid that has a sweet and musty odor. It uncouples oxidative phosphorylation by carrying protons across the mitochondrial membrane, leading to a rapid consumption of energy without generation of ATP (Ni *et. al.*, 1989). DNP is considered as a dangerous chemical which may enter the environment through emissions or effluents from manufacturing plants, mines, automobile exhaust gas or even during its use as a pesticide (Mattson *et. al.*, 1969).

Activated carbon (AC) is porous, capable of distributing chemicals on its large hydrophobic internal surface, thus making them accessible to reactants (Yin *et. al.*, 2007). The large number of small holes (for example, AC with Brunauer–Emmett–Teller (BET) N_2 surface area of the order of 2400 m^2/g) in AC can absorb some of the colloidal and soluble organic macromolecules, to a certain extent, purify water, but cannot remove all impurities (Radovic *et. al.*, 2001).

It is essential to understand the various factors that influence the adsorption capacity of AC prior to their modification. This is done so that AC can be tailored to their specific physical and chemical attributes in order to enhance their affinities towards organic species present in aqueous solutions (Yin *et. al.*, 2007). The chemical treatments such as acidic and basic treatment on AC is purposed to modify the AC surface where the chemicals will react with the AC surface functional groups. This reaction will result in increasing uptake of organic-based substances including phenolic compounds by the AC surface.

The aims of this study are to investigate the performance of chemically modified AC towards the DNP in aqueous solution with various physicochemical conditions and to optimize the adsorption of DNP by the AC.

2.0   MATERIALS AND METHODS

2.1   Chemical Treatment of AC

Raw ACs in powder form were pre-treated with 2N HCL and 0.02 g/mL KOH separately at room temperature for 24 hours. Then, the mixtures were washed thoroughly with distilled water and filtered to remove the acidic or basic solutions. The washed AC was dried at 50 ᵒC and stored at room temperature in an airtight container to prevent re-adsorption of moisture.

2.2   Adsorption Experiments

30 mg of both acidic and basic pre-treated AC were placed into 6 Erlenmeyer flask containing 50 mL of 5 mg/L DNP and the pH of each sample was adjusted to pH 3, 5, 7, 9 and 11. The samples were incubated at 25±2 ᵒC and 150 rpm agitation speed, for 6 hours. All the samples were

measured using spectrophotometer at optical density of 458 nm (A_{458}nm). These steps were repeated for studying the effect of temperature having the ranges 20, 40, 60 and 70 ºC and the effect of contact time of 3, 4, 5, and 6 hours.

2.3 Optimization Using Response Surface Methodology (RSM)

The results from adsorption experiments were compared between acidic and basic treated AC and the highest percentage removal between the two was selected for further study of optimization using RSM.

The Central Composite Design with 3 levels was used to determine the optimum values of three physicochemical parameters including pH, temperature and contact time for the highest uptake of DNP from aqueous solutions.

3.0 RESULTS

3.1 Effect of pH

Figure 1 shows the percentage removal of DNP at different pH ranging from 3 to 11. The uptake of DNP by modified AC decreases sharply by increasing the pH from pH 3 to 8. Then, the percentage removal increases slightly for further increase in pH. The decreasing and increasing profile implies for both HCl- and KOH-treated AC.
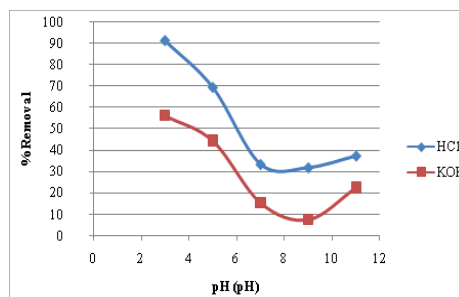

Figure 1 Percentage removal of DNP at different pH

3.2 Effect of Temperature

Figure 2 shows the percentage removal of DNP from aqueous solution at various temperatures ranging from 20 to 70 ºC. The DNP uptake decreases with the increasing temperature up to 50 ºC and starts to increase with further increase in temperature.
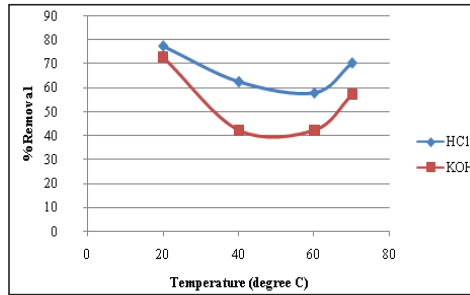
Figure 2 Percentage removal of DNP at different temperatures

3.3 Effect of Contact Time

Figure 3 shows the percentage removal of DNP from aqueous solution at different contact times from 2 to 5 hours. The DNP uptake slightly decreases for longer contact time and the KOH-treated AC seems to reach equilibrium at hour fourth contact time.
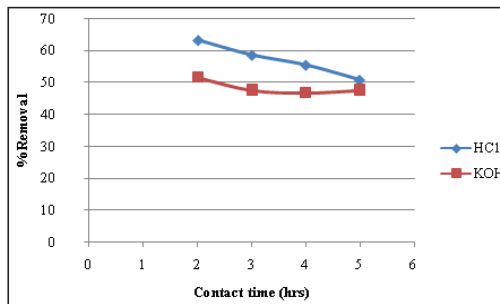

Figure 3 Percentage removal of DNP at different contact times

For the three studies of physicochemical effects on the chemically treated AC adsorption, HCl-treated AC indicates better performance compared to KOH- treated AC by having higher percentage removal values. Therefore, AC with the HCl pre-treatment was used in the optimization study using RSM.

3.4 Optimization Using RSM

Table 1 shows the Analysis of Variance of removal by HCl-treated AC, which indicates that the optimization model is significant having *p-value* of 0.17%. Figure 4 shows the percentage removal of DNP with respect to contact time and temperature.

Table 1 ANOVA of DNP removal by HCl-treated AC

| Response 1	% Removal					
ANOVA for Response Surface Reduced 2FI Model						
Sources	Sum of Squares	df	Mean Square	F value	p-value Prob > F	
Model	2220.13	3	740.04	8.02	0.0017	Significant
B - Temperature	1640.19	1	1640.19	17.77	0.0007	
C – Contact time	15.62	1	15.62	0.17	0.6862	
BC	564.31	1	564.31	6.11	0.025	
Residual	1477.02	16	92.31			
Lack of fit	1429.31	11	129.94	13.62	0.0049	Significant
Pure Error	47.71	5	9.54			
Cor Total	3697.15	19				
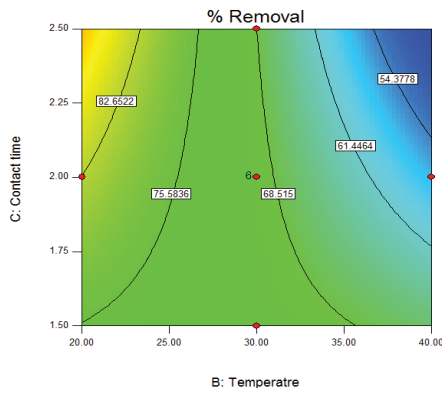
Figure 4 Analysis of RSM on contact time versus temperature

There are three conditions predicted by RSM in obtaning the optimum value of DNP removal as shown in Table 2. The most preferable optimum conditions for about 90% DNP removal are at pH 4, temperature 20 ºC and the contact time is 2.5 hours.

Table 2 Solution predicted by RSM Analysis

No.	pH	Temperature (ºC)	Contact time (hours)	% Removal	Desirability	
1	4	20	2.50	89.7207	0.806	Selected
2	4	20	2.49	89.5647	0.804	
3	4	20	1.72	78.5439	0.596	

4.0 DISCUSSION

At low pH value, a better percentage removal of DNP was obtained. Acid introduces additional protons in the solution, which competed for the carbonyl sites and lead to higher DNP adsorption (Yahya *et. al.*, 2007). The graph in Figure 1 shows the same trend between AC-HCl and AC-KOH.

Higher temperature is attributed to increase penetration of reactive dyes inside micro-pores or the creation of new active sites (Yahya *et. al.*, 2007). However, the experimental results do not follow this principle as the adsorption capacity decreases with temperature increase. This could be suggested that the temperature increase will alter the strength of bonding among the DNP molecules in aqueous solutions. This molecules dispersion process may lead to reverse attraction of DNP molecules to the AC surface.

The adsorption capacity is decreasing as the time increases because at initial stage of adsorption, the concentration gradient between the adsorbate in solution and adsorbate in the adsorbent increase as there must be an increased number of vacant sites available at the beginning (Kumar *et. al.*, 2010).

Poor mass transfer of adsorbate molecules to the AC surface is one of the critical problems which reduce the performance of adsorption. Other than that, the fast attainment of equilibrium adsorption state also prevents the achievement of the optimum removal of DNP molecules in bulk solution.

The optimization analysis using RSM shows that the significant parameters are temperature and contact time. At lower limit, the optimum temperature and contact time are at 20 ºC and 1.5 hours with 46.9 % removal. For upper limit, the optimum temperature and contact time are at 40 ºC and 2.5 hours with 100 % removal. From Table 2, the average percentage of experimental result is 97.7% compared to the predicted percentage of 89.7 %.

5.0 CONCLUSION

In conclusion, the RSM analysis shows that the optimum percentage removal of DNP can be achieved at pH 4, temperature 20ºC and contact time of 2.5 hours by using HCl-treated AC with up to 100 % removal. The

average percentage differences between predicted and experimental value is 8.13 %.

6.0 REFERENCES

C. Y. Yin, Mohd Kheireddine Aroua and Wan Mohd Ashri Wan Daud. 2007. Review of Modifications of Activated Carbon for Enhancing Contaminant Uptakes from Aqueous Solutions. Faculty of Chemical Engineering, Universiti Teknologi MARA, and Department of Chemical Engineering,Faclty of Engineering, University of Malaya, Kuala Lumpur, Malaysia.

F. Ni, L. Thomas, and T. M. Cotton. 1989. Surface-enhance Resonance Raman Spectroscopy as an Ancillary High-performance Liquid Chromatopraghy Detector for Nitrophenol Compound. Anal. Chem. Volume 8. pp. 888-894.

J. D. Box. 1983. Investigation of the Folin-Ciocalteau Phenol Reagent for the Determination of Polyphenolic Substances in natural. Freshwater Biological Association. Ferry House, England.

J. S. Mattson, Jr. Mark, H. B. Malbin, M. D. Weber Jr. and W. J. Crittenden. 1969. Surface Chemistry of Active Carbon: Specific Adsorption of Phenols. J. Colloid Interf. Volume 31.

L. R. Radovic, C. Moreno-Castilla and J. Rivera-Utrilla. 2001. Carbon Material as Adsorbents in Aqueous Solutions. In: Radovic, L.R, (Ed.). Chemistry and Physics of Carbon. Volume 27.

P. S. Kumar, C. Vincent, K. Kirthika and K. S. Kumar. 2010. Kinetics and Equilibrium Studies of Pb^{2+} in Removal from Aqueous Solutions by Use of Nano-silversol-coated Activated Carbon. Department of Chemical Engineering, SSN College of Engineering.

Yahya S. Al-Degs, Musa I. El-Barghouthi, Amjad H. El-Sheikh and G. M. Walker. 2007. Effect of solution pH, Ionic Strength, and Temperature on Adsorption Behavior of Reactive Dyes on Activated Carbon. Chemistry Department, The Hashemite University, Zarqa, Jordan and School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast, Northern Ireland UK.