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Mahogany Fruit Husk-derived Activated Carbon for Removal of Cr (VI) from Aqueous Solution

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Abstract— Lignocellulosic agricultural wastes, such as mahogany fruit husk (MFH), shows great potential as a precursor for the production of activated carbon (AC) because of its abundance in nature and great economic value. In this work, AC was prepared from MFH *via* chemical impregnation with phosphoric acid (H_3PO_4) and thermal treatment. Response surface methodology (RSM) involving central composite design (CCD) was utilized to investigate the interactions among the adsorption parameters pH and adsorbate concentration, and their effect on chromium (VI) removal from aqueous solution. A quadratic regression model was developed for the prediction of Cr (VI) adsorption of MFHAC. Analysis of variance (ANOVA) revealed good agreement between the predicted and experimentally-obtained responses. The surface properties of MFHAC were investigated using scanning electron microscopy (SEM), Fourier transform-infrared (FTIR) spectroscopy, and nitrogen adsorption/ desorption studies. MFHAC proves to be an effective adsorbent for removing Cr (VI) from simulated wastewater.

Index Terms— Adsorption, Activated carbon, Chromium (VI), Heavy metal, Mahogany fruit husk, Response surface modeling; Simulated waste water

1 Introduction

HEAVY metals are considered to be the most toxic pollutants in the environment. The toxic effects they impose to many living organisms, including humans, make them more dangerous than most organic pollutants. Among the known heavy metals, chromium imposes a greater health risk due to its solubility in water, leading to surface and groundwater contamination [1]. Chromium (Cr) occurs in the environment in trivalent (III) and hexavalent (VI) oxidation states. Cr (III) is considered as an essential trace element in humans [2], while Cr (VI) is recognized as a mutagen and carcinogen [3].

The conventional processes utilized in removing Cr (VI) from industrial effluents include membrane filtration, ion exchange, and precipitation [4]. Biomasses from plants, which consist mostly of lignin, cellulose, and hemi-cellulose, have the capability to extract, accumulate, and tolerate high levels of toxic heavy metals from their environment [5]. For this reason, they are considered as a good source of adsorbents that can be applied for heavy metal removal.

Mahogany (*Swietenia macrophylla*) is a member of the *Meliaceae* family. It is a fast-growing tall tree that is abundantly present in many countries, including the Philippines, and is popularly known for its good timber. The mahogany fruit husk (MFH) has a great potential of being converted into AC because of its lignocellulosic character. This work utilized response surface methodology (RSM) involving central composite design (CCD) to investigate the interactions among the adsorption parameters pH and adsorbate concentration of MFHAC and their effect on chromium (VI) removal from aqueous solution.

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2 Methods

2.1 Preparation of activated carbon

The MFH was locally obtained from Batangas City, Philippines. They were rinsed thrice with deionized water to remove soluble impurities and then dried in an oven at 105˚C for 24 h. The dried samples were ground and sieved to a particle size of approximately 800 µm. Carbonization was carried out for 1 h by loading a dried precursor into a stainless steel vertical tube reactor under purified nitrogen flow. The resulting char was chemically activated using 40% (v/v) phosphoric acid (H_3PO_4) as the impregnating agent. The carbonized MFHs were soaked in 40% phosphoric acid (w/v) for 2 h at 80˚C. The thermal treatment of the chemically impregnated char was done using a muffle furnace at 430˚C for 70 mins. The derived AC were cooled to room temperature and washed with hot deionized water and 0.1 M HCl until the filtrate reached a pH of 6 to 7. The MFHAC samples were oven dried for 24 h at 105˚C and stored in air-tight containers.

2.2 Batch adsorption studies

Response surface methodology (RSM) involving central composite design (CCD) to investigate the interactions among the adsorption parameters pH and adsorbate concentration of MFHAC and their effect on chromium (VI) removal from aqueous solution.

2.3 SEM, FTIR, and BET analyses

The surface morphology of the MFHAC prepared under optimized conditions was studied using a JSM-5310 (JEOL Ltd., Japan) scanning electron microscope. The surface functional groups of the derived AC were determined using a Nicolet 6700 (Thermo Nicolet Co., USA) Fourier transform infrared

(FTIR) spectrophotometer. A volumetric adsorption analyzer (Quantachrome, USA) was used to investigate the surface characteristics of the optimized MFHAC. The surface area (S_{BET}), total pore volume (VT), and average pore diameter (D) of the optimized MFHAC were determined through analysis of the N_2 adsorption isotherms at -196˚C. The S_{BET} was measured from the adsorption isotherm using Brunauer–Emmett–Teller (BET) equation. The total pore volume was estimated to be the liquid volume of nitrogen at relative pressure of 0.99.

3 Results and Discussions

Thirteen experiments were performed to obtain a response surface model for the Cr (VI) removal efficiency of activated carbon prepared from mahogany fruit husk at varying solution pH and Cr (VI) concentration. The experimental factors and corresponding response are shown in Table 1. The observed percent removal efficiencies varied between 45.10 and 96.93% for Cr (VI) removal.

TABLE 1
Experimental Factors and Response

Standard No.	Point type	Factors		Cr (VI) Removal* (%)
		A: pH	B: Cr (VI) (ppm)	
1	Fact	3	20	94.83
2	Fact	9	20	89.97
3	Fact	3	80	96.93
4	Fact	9	80	45.10
5	Axial	3	50	94.78
6	Axial	9	50	66.69
7	Axial	6	20	90.14
8	Axial	6	80	88.81
9	Center	6	50	80.60
10	Center	6	50	83.21
11	Center	6	50	85.06
12	Center	6	50	84.36
13	Center	6	50	83.82

**Average of triplicate analysis*

Analysis of variance (ANOVA) was carried out to justify the adequacy of the model. The results of the second-order response surface model fitting in the form of ANOVA are given in table 2 for Cr (VI) removal. The quality of the model developed was evaluated based on correlation coefficient, R-square, and standard deviation. Data also demonstrate that the model was significant at the 5% confidence level. The closer the R-square to unity and the smaller the standard deviation, the more accurate the response could be predicted by the model.

The correlation coefficient for Cr (VI) removal obtained in the present study was 0.8942, indicating that 10.58% of the total dissimilarity are not explained by the empirical model for Cr (VI) removal. The R-squared obtained was higher than 0.80. An R-square value close to 1 demonstrates favorable agreement between the calculated and observed results within the experimental range.

TABLE 2
Analysis of Variance and Adequacy
for the Quadratic Model for Cr (VI) Removal

Source of data	Sum of Squares	Degrees of freedom	Mean Square	F-Value	Prob. > F	Comment
Model	2073.62	3	691.21	25.36	0.0001	significant
A	1197.94	1	1197.94	43.95	< 0.0001	significant
B	324.14	1	324.14	11.89	0.0073	significant
AB	551.55	1	551.55	20.24	0.0015	significant
Residual	245.29	9	*2.93*			
Pure Error	11.73	4	1.3473			
Std. Dev. = 5.22	R^2 = 0.8942					
CV = 6.26	Adjusted R^2 = 0.8590					
AP = 17.869						

ANOVA results for the quadratic response surface model for Cr (VI) removal yielded a model F-value of 25.36 and a probability > F less than 0.05. These values indicated that the model is significant. For the model terms, values of probability > F less than 0.05 indicated that the model terms are significant. In this study, A, B, and AB were significant model terms. Based on the results, the response surface model constructed in this study for predicting Cr (VI) removal efficiency was considered reasonable.

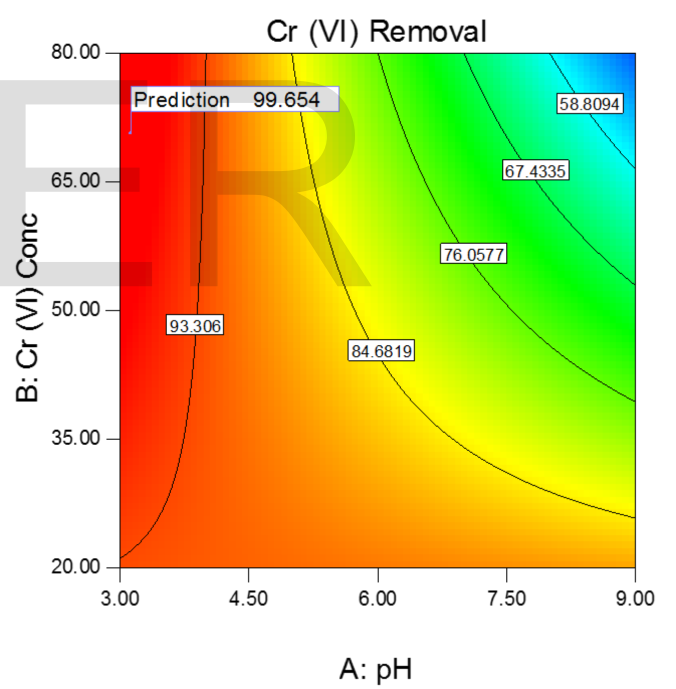

Fig. 1. Contour plot of Cr (VI) removal efficiency of the optimized MFHAC at varying solution pH and Cr (VI) concentration

To assess the effect of solution pH and Cr (VI) concentration on the Cr (VI) removal efficiency of the optimized MFHAC, contour plot was used. In the plot shown in Figure 1, adsorption at around pH 9.00 showed low Cr (VI) removal efficiency while decreasing the solution pH to around 3.15 increased the Cr (VI) removal efficiency optimized MFHAC to its maximum. On the other hand, the effect of Cr (VI) concentration on Cr (VI) removal efficiency showed the highest positive effect at around 73.86 ppm. Efficiency of Cr (VI) removal was observed to decline beyond the optimum concentration.

This may be because at around 73.86 ppm, all the active sites in the activated carbon have been completely filled with Cr (VI) and further agitation only leads to weakening of the interaction between the adsorbent and the adsorbate, leading to a decrease in adsorption efficiency.

3.1 Characterization of Optimized MFHAC

Fig. 2 illustrates the SEM image of the MFHAC prepared under the optimized conditions. The micrograph revealed the development of a highly porous structure on the surface of the MFH, consisting of deep macropores and mesopores. The derived porosity was facilitated upon the employment of phosphoric acid, which was thermally catalyzed

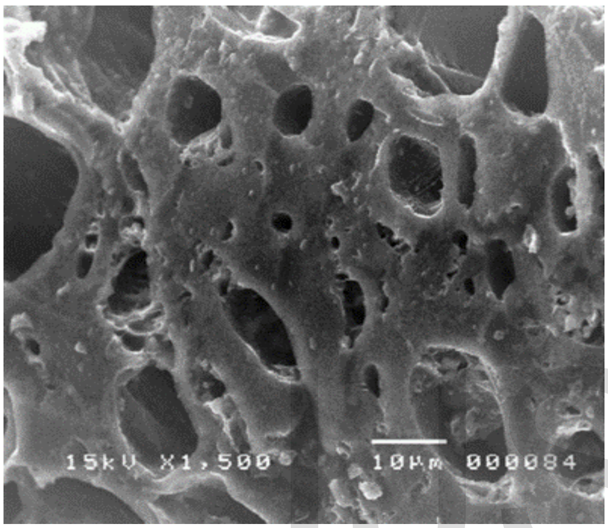

Fig. 2. SEM image of the optimized MFHAC at 1,500x magnification

The FTIR spectrum for the optimized MFHAC is shown in Fig. 3. The presence of various functional groups that were responsible for the interaction with Cr (VI) was observed in the spectrum. The O-H stretching at around 3415 cm^{-1} was characteristic for hydroxyl groups [6]. The narrow bands at around 2918 and 2850 cm^{-1} indicated alkyl C–H stretching [7]. The band at 1078 cm^{-1} of the MFHAC spectrum reveals the occurrence of stretching vibration of C–O groups, such as alcohols, ethers, acids, and esters [8].

The obtained BET surface area (S_{BET}), total pore volume (V_T), and mean pore diameter (D) of the MFHAC derived using the optimized conditions were 1508 m^2/g, 2.832 cm^3/g, and 7.3042 nm, respectively. The large surface area (1508 m^2/g) indicated the presence of more sites for contact between the adsorbent and the adsorbate, which was observed in the high Cr (VI) adsorption onto the MFHAC. Moreover, the attained mean pore diameter (7.3042 nm) was within 2 to 50 nm, which suggested that the type of pores predominantly present in the MFHAC surface were mesopores [1].

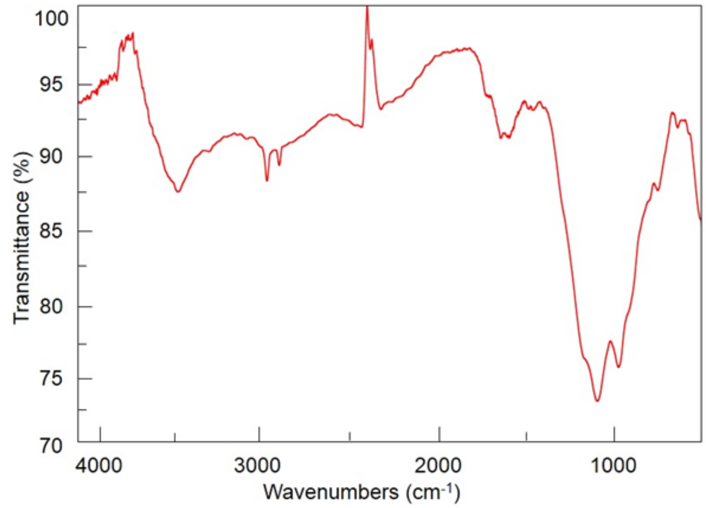

Fig. 3. FTIR spectrum of the optimized MFHAC

4 Conclusions

The effects of solution pH and the adsorbate concentration during adsorption of Cr (VI) using mahogany fruit husk derived activated carbon were investigated in this present work. Adsorption at pH 3.15 increased the Cr (VI) removal efficiency of the MFHAC to its maximum while Cr (VI) concentration showed the highest positive effect on Cr (VI) removal at around 73.86 ppm. The produced AC had a mesoporous structure with a large surface area. MFHAC prepared in this study efficiently removed high amounts of Cr (VI) from aqueous solution, demonstrating its great potential for large scale industrial applications.

5 References

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