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Research paper

Phenol adsorption from wastewater using cashew nut shells as adsorbent

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Abstract

The potential of agricultural waste cashew nut shells as an adsorbent for removing phenol from wastewater is presented in this paper. The adsorbent was treated with 3M sulphuric acid in order to improve the properties. The experimental parameters such as adsorbent dosage, concentration and temperature were optimized with response surface methodology (RSM). The isotherm data were tested with different isotherm models and it obeyed Freundlich Isotherm showing the multilayer adsorption. The kinetic data satisfied pseudo-first order kinetic model. The maximum adsorption capacity was calculated to be 35.08 mg/g proving the capability of cashew nut shells for removing phenol from wastewater.

Keywords: *Phenol; Optimization; Cashew Nut Shells; Isotherm; Kinetics.*

1. Introduction

The industries releases wastewater which contains pollutants like phenol, organic compounds, heavy metals and dyes [1]. Phenol one of the toxic and carcinogenic chemical is generally released from petroleum, pharmaceutical, fertilizer, petrochemical industries and is considered to be toxic and carcinogenic. It is also defined as one of the priority pollutants by the environmental regulatory bodies [2]. The existence of phenol in the environment even at very low concentration causes harmful effects on the human beings and the aquatic life. Thus it is required to treat phenol before it is released into the environment [3]. Various treatment methods such as membrane separation, distillation, extraction and adsorption are used for the treatment of phenol from wastewater [4]. Adsorption using activated carbon is considered as efficient method for the treatment of phenol. But because of the expensive nature of materials like fly ash, saw dust and coal, there is a need to produce adsorbents from low cost agricultural materials [5]. Different agricultural waste materials are used as potential adsorbents for wastewater treatment. The present work deals with the adsorption of phenol onto cashew nut shells as an adsorbent and capability of the cashew nut shells for removing the pollutant was also investigated

2. Materials and methods

2.1. Preparation of the adsorbent

The cashew nut shells (African grade) were collected from a local cashew nut industry in Karkala and were used for the adsorbent preparation. The shells were initially washed with water and dried in sunlight for two days. Later the shells were dried inside oven at 100°C for 3 hours. The dried shells were heated inside a muffle furnace at 400°C for 30 minutes. The obtained shells were made into powdered form using mortar-pestle and once again into finer size using mixing equipment. To improve the properties, the powdered sample was mixed with 3M sulphuric acid in 1:1 ratio and kept in an oven at 70°C for 6 hours. It was continuously washed with water to remove the excess chemicals and then heated in an oven at the same temperature for 6 hours [6]. The dried powder was used for the experiments.

2.2. The characterisation of the agricultural materials

The adsorbent was characterized by carrying out the standard procedure [7]. The moisture content, ash content, fixed carbon and volatile matter of the raw sample and the treated sample were determined. The different functional groups existing on the adsorbent surface were found by using Fourier transform infrared spectroscopy (FTIR) instrument, Shimadzu, Japan.

2.3. Batch studies

The experiments were performed in 250 mL conical flask having 200 mL of Phenol (Merck India Limited) and agitated in the shaker to find the equilibrium time. The equilibrium time was obtained as 4 hours. The phenol concentration was determined by U-V spectrophotometer (Shimadzu, Japan) at a wavelength of 270 nm. The influence of operating parameters like dosage, concentration and temperature on the adsorption were optimized using RSM. The concentration values were taken varying from 100 to 300 mg/L which were satisfying the concentration of the pollutants in the industrial wastewater [8]. The experimental dosage and temperature values were selected from the literature of the similar agricultural materials [3], [9]. RSM is an efficient statistical tool used to determine the optimal experimental conditions and the model equations for predicting the response [9]. The effect of these variables are investigated at five different levels and is represented in Table 1. The isotherm studies were carried out for the concentration varying in the range 100, 150, 200, 250 and 300 mg/L. The kinetic experiments were performed at the optimum conditions. The total number of experiments were calculated by taking factorial points, star points and center points and the complete design matrix with percent removal is shown in Table 2.

Table 1: Independent Experimental Parameters and Its Levels.

Independent parameters	Symbol	Coded parameters and level				
		−α	−1	0	+1	+α
Concentration (mg/L)	X_1	31.8	100	200	300	368.17
Dosage (g)	X_2	0.159	0.5	1	1.5	1.841
Temperature (°C)	X_3	23.18	30	40	50	56.82

Table 2: Design Matrix for the Experiments and Obtained Results

Expt No:	Actual variables (without brackets) and coded variables (with brackets) of the experiments			
	Concentration (mg/L)	Dosage (g)	Temperature (°C)	Percent removal
1	100 (-1)	0.5(-1)	30(-1)	10
2	300(+1)	0.5(-1)	30(-1)	25
3	100(-1)	1.5(+1)	30(-1)	57
4	300(+1)	1.5(+1)	30(-1)	55
5	100(-1)	0.5(-1)	50(1)	20
6	300(+1)	0.5(-1)	50(1)	29.33
7	100(-1)	1.5(+1)	50(1)	61
8	300(+1)	1.5(+1)	50(1)	56.67
9	31.8(-1.68)	1(0)	40(0)	13.5
10	368.17(+1.68)	1(0)	40(0)	28.7
11	200(0)	0.159(-1.68)	40(0)	8.78
12	200(0)	1.841(+1.68)	40(0)	61.25
13	200(0)	1(0)	23.18(-1.68)	36.25
14	200(0)	1(0)	56.82(+1.68)	50
15	200(0)	1(0)	40(0)	46
16	200(0)	1(0)	40(0)	46.25
17	200(0)	1(0)	40(0)	46.25
18	200(0)	1(0)	40(0)	46
19	200(0)	1(0)	40(0)	46
20	200(0)	1(0)	40(0)	46

3. Results and discussions

3.1. Characterization of the adsorbent

The moisture content of the treated sample was found to be greater than that of the raw sample, which shows that the treated sample has improved pore volume and surface area. It was found that after the treatment the volatile matter decreases, and hence the fixed carbon content required for adsorption increased as shown in Table 3. Volatile matter in carbon liberates at high temperature in the absence of air. Hemicellulose and other volatile substances degrade during the treatment [10, 11]. Ash content is the residue left behind after the sample is burned. The ash content after treatment has decreased showing the reduced amount of non-combustible matter in the sample.

The FTIR spectrum of the chemically treated sample before adsorption as shown in Figure 1, represents a broad adsorption peak at 3463.92 cm^{-1} corresponding to overlapping of –OH and –NH bonds. A peak obtained at 2923.88 cm^{-1} shows the C-H group. The peak at 3606.64 cm^{-1} represents O-H stretch with functional groups of alcohols and phenols [12]. The peaks at 1180.35 cm^{-1} and 1326.93 cm^{-1} are due to C-H group with alkyl halides functional group and C-O stretch with functional groups alcohols, carboxylic acids respectively [13].

Table 3: The Proximate Analysis of the Sample before and After Treatment.

Sl. No.	Parameter (%)	Raw sample	Chemically treated sample
1.	Moisture Content	10.9	14.3
2.	Volatile Matter	43.76	39.35
3.	Ash Content	15.16	13.23
4.	Fixed Carbon	30.18	33.02

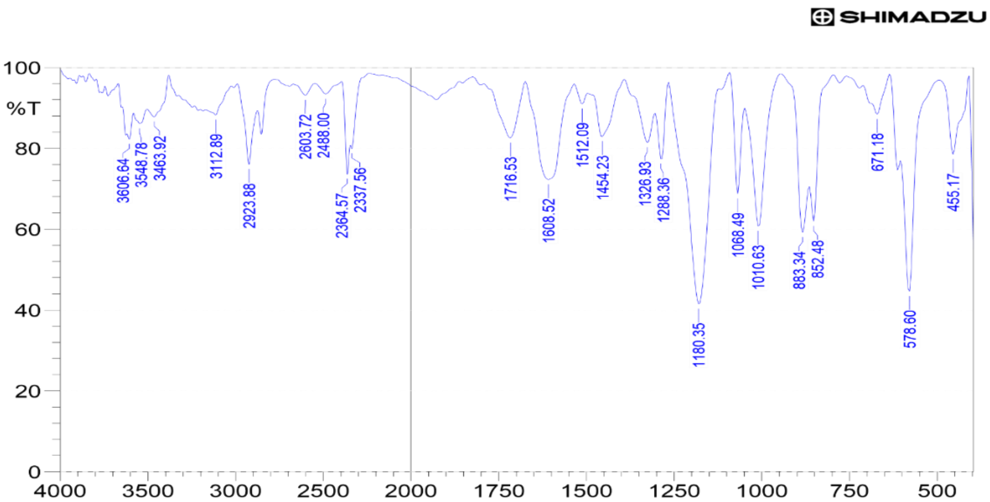

Fig. 1: The FTIR Spectrum of the Chemically Treated Sample.

3.2. Development of model equation and optimization of experimental parameters

Central composite design is a statistical tool which helps in correlating the relation between the operating conditions and the percent removal [9]. The design matrix with response values (percent removal) obtained from experiments is shown in table 2. A quadratic polynomial equation was obtained which is helpful in optimizing the conditions [14, 15]. The values of percent removal obtained from the experiments ranged from 10% to 61.25%. The model equation for percent removal in terms of coded factors can be written as

$$\%\,removal = 44.56 + 17.54\,x_2 - 4.54\,x_1 x_2 - 7.05 x_1^2 \quad (1)$$

The fitness of the model was validated by the value of correlation coefficient (R^2). The R^2 value for the equation was obtained as 0.9499. This describes that 94.99% of the percent removal is due to variation in the experimental conditions [16]. It also explains that 5.01% of the variation is because of residual error and is not described by the model [9]. The R^2 value approaching unity shows that the model is accurate in predicting the response and the experimental values matches with the predicted values [17]. The optimum experimental parameters were found to be 176 mg/L of concentration, 1.49 g of dosage, temperature 39.02°C and percent removal of 61.00%. This also signified that the developed model was efficient in predicting the response from the operating parameters [18].

3.3. Adsorption isotherms

The distribution of solute between the adsorbent and the aqueous solution at the equilibrium condition is studied by adsorption isotherm [19]. The nature and type of adsorption is investigated through adsorption isotherm [20]. The isotherm data is verified with different models like Langmuir, Freundlich, and Temkin models.

The Langmuir isotherm is obtained assuming that adsorption occurs uniformly on the entire surface [21]. The model can be given as

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_m} + \frac{1}{bq_m} \tag{2}$$

q_{eq} and C_{eq} the adsorption capacity (mg/g) and solute concentration (mg/L) at equilibrium respectively, q_m the maximum adsorption capacity (mg/g), b the model constant (L/mg). The constants b and q_m are calculated through the linear plot of C_{eq}/q_{eq} versus C_{eq}.
Freundlich isotherm is based on the assumption that adsorption happens non-uniformly leading to multilayer adsorption. The distribution of adsorption energy is non-uniform on the adsorbent surface [22]. The simplified form of Freundlich isotherm is represented as

$$logq_{eq} = logk_f + \frac{1}{n}\, logC_{eq} \tag{3}$$

$k_f \left(mg^{1-\frac{1}{n}} L^{1/n}\, g^{-1}\right)$ and n are the model constants. The model constants k_f and n are evaluated from the plot of $logq_{eq}$ versus $logC_{eq}$.
The Temkin isotherm explains the interaction between adsorbent and the adsorbate molecules indirectly [19]. The simplified equation is given as

$$q_{eq} = BlnA + BlnC_{eq} \tag{4}$$

A and B are the Temkin model parameters. By plotting q_{eq} versus lnC_{eq}, the model constants are obtained.
The isotherm constants are calculated from various models and are given in Table 4. From the values of regression coefficient, it can be observed that isotherm data is fitting with the Freundlich isotherm suggesting that adsorption is occurring at heterogeneous sites in multilayers on the surface. It also suggests that random distribution of energy takes place having adsorption capacity of 35.087 mg/g.

Table 4: The Determined Values of Various Isotherms

Freundlich			Langmuir			Temkin		
k_f $\left(mg^{1-\frac{1}{n}} L^{1/n}\, g^{-1}\right)$	n	R^2	q_m (mg/g)	b (L/mg)	R^2	B	A	R^2
0.498	1.428	0.986	35.087	0.0057	0.963	18.96	0.0493	0.9379

3.4. Kinetic studies

Different kinetic models are used for evaluating the rate controlling mechanism. The kinetic study is important in adsorption to investigate the reaction pathways and mechanism for the process [22], [23].

The Pseudo first- order model is obtained assuming that the solute uptake changes with respect to time and is dependent on the difference between the adsorption capacity at equilibrium and the capacity at any time [24]. The Pseudo first-order model is written as

$$log\left(q_{eq} - q_t\right) = logq_{eq} - \frac{k_{fr}}{2.303} t \tag{5}$$

q_{eq} the equilibrium adsorption capacity, q_t the adsorption capacity at any time t (mg/g), k_{fr} the rate constant (min^{-1}). The constants are evaluated by plotting $log\left(q_{eq} - q_t\right)$ v/s t.
Pseudo-second-order model is represented in the form [25 - 27]

$$\frac{t}{q_t} = \frac{1}{k_{st} q_{eq}^2} + \frac{1}{q_{eq}}\, t \tag{6}$$

k_{st} the rate constant (g/mg min). The constants are obtained by plotting t/q_t v/s t . This model is applied for the systems in which chemisorption controls the process.
The intra-particle diffusion is given in the linear form as [28]. The particle diffusion becomes the slowest step in porous adsorbents.

$$q_t = k_{ip} t^{0.5} + c \tag{7}$$

Where k_{ip} is the model constant ($mg^1 min^{-0.5} g^{-1}$), c the intercept that calculates the boundary layer thickness. If the linear plot of q_t vs $t^{0.5}$ is passing through origin, then intra-particle diffusion becomes the rate controlling mechanism.
The kinetic parameters obtained from the above expressions are shown in Table 5. It was found that regression coefficient value was higher for pseudo first order model in comparison with other models. It was also found that the experimental value matches with the calculated value for pseudo first order model.

Table 5: The Calculated Kinetic Parameters through Different Models

Pseudo first order		Pseudo second order		Intraparticle diffusion	
$\left(q_{eq}\right)_{exp}$, mg/g	13.46	$\left(q_{eq}\right)_{exp}$, mg/g	13.46	$k_{ip}(mg/gmin^{0.5})$	0.9315
$\left(q_{eq}\right)_{cal}$,mg/g	12.8	$\left(q_{eq}\right)_{cal}$,mg/g	16.54	c	-4.3977
$k_{fr} \times 10^{-3}\, min^{-1}$	4.125	$k_{st}\ \frac{g}{mg} min$	0.00048	R^2	0.8182
R^2	0.8919	R^2	0.7273		

4. Conclusions

The cashew nut shells were used for adsorbent preparation and studied for the phenol removal from wastewater. The properties of the adsorbent were improved after treating with sulphuric acid and found to have higher fixed carbon content. Using RSM, the optimum conditions were obtained as 176 mg/L of initial concentration, 1.49 g of dosage and temperature 39.02°C. The isotherm data were following Freundlich Isotherm signifying that physical adsorption becomes the slowest step. The kinetic data were obeying pseudo-first order kinetic model. The monolayer adsorption capacity for the cashew nut shells was obtained as 35.08 mg/g showing it is a promising adsorbent.

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References

[1] Moraitopoulos, I., Ioannou, Z., & Simitzis, J. (2009), Adsorption of phenol, 3-nitrophenol and dyes from aqueous solutions onto an activated carbon column under semi-batch and continuous operation, Science Engineering and Technology, 58, 218-222.
[2] Santos, L., Estevinho, B.N., Ribeiro, E., & Alves, A. (2008) A preliminary feasibility study for pentachlorophenol column sorption by almond shell residues, Chemical Engineering Journal, 136(2), 188-194.
[3] Milhome, M.A.L., Keukeleire, D.D., Ribeiro, J.P., Nascimento, R.F., Carvalho, T.V., & Queiroz, D.C. (2009) Removal of phenol and conventional pollutants from aqueous effluent by chitosan and chitin, Química Nova, 32(8), 2122-2127. https://doi.org/10.1590/S0100-40422009000800025.

[4] Nagda, G.K., Diwan, A.M., & Ghole, V.S. (2007), Potential of tendu leaf refuse for phenol removal in aqueous systems, Applied Ecology and Environmental Research, 5(2), 1-9. https://doi.org/10.15666/aeer/0502_001009.

[5] Varghese, S., Vinod, V.P., & Anirudhan, T.S. (2004), Kinetic and equilibrium characterization of phenols adsorption onto a novel activated carbon in water treatment, Indian Journal of Chemical Technology, 11, 825-833.

[6] Mishra, S.,& Bhattacharya, J. (2007), Batch studies on phenol removal using leaf activated carbon, Malaysian Journal of Chemistry, 9(1), 1–15.

[7] Rengaraj, S. Arabindoo, B.,& Murugesan, V. (1998), Activated carbon from rubber seed and palm seed coat: preparation and characterization, Journal of Scientific and Industrial Research, 57, 129–3.

[8] Polat, H., Molva, M., & Polat, M. (2006), Capacity and mechanism of phenol adsorption on lignite, International Journal of Mineral Processing, 79(4), 264–2730 https://doi.org/10.1016/j.minpro.2006.03.003.

[9] Salman, J.M. (2014), Optimization of preparation conditions for activated carbon from palm oil fronds using response surface methodology on removal of pesticides from aqueous solution, Arabian Journal of Chemistry, 7(1), 101-108. https://doi.org/10.1016/j.arabjc.2013.05.033.

[10] Ndazi, B.S., Nyahumwa, C.,& Tesha, J. (2008), Chemical and thermal stability of rice husks against alkali treatment, Bioresources, 3(4), 1267-1277.

[11] Afify, A.M.R., El-Beltagi, H.S., Abdel-Salam, S.M., & Omran, A.A. (2012), Effect of Soaking, Cooking, Germination and Fermentation Processing on Proximate Analysis and Mineral Content of Three White Sorghum Varieties (Sorghum bicolor L. Moench), Notulae Botanicae Horti Agrobotanici Cluj-Napoca, 40(2), 92-98. https://doi.org/10.15835/nbha4027930.

[12] Senturk, H.B., Ozdes, D., Gundogdu, A., Duran, C., & Soylak, C.M. (2009), Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study, Journal of Hazardous Materials, 172(1), 353–362. https://doi.org/10.1016/j.jhazmat.2009.07.019.

[13] Malkoc, E., Nuhoglu, Y., & Abali, Y. (2006), Cr (VI) adsorption by waste acorn of Quercusithaburensis in fixed beds: Prediction of breakthrough curves, Chemical Engineering Journal, 119(1), 61-68. https://doi.org/10.1016/j.cej.2006.01.019.

[14] Dutta, S., Bhattacharyya, A., Ganguly, A., Gupta, S., & Basu, S. (2011), Application of response surface methodology for preparation of low-cost adsorbent from citrus fruit peel and for removal of methyl.ne blue, Desalination, 275(1-3), 26-36. https://doi.org/10.1016/j.desal.2011.02.057.

[15] Zaviska, F., Drogui, P., Blais, J.F., Mercier, G., & Lafrance, P. (2011), Experimental design methodology applied to electrochemical oxidation of the herbicide atrazine using Ti/IrO_2 and Ti/SnO_2 circular anode electrodes, Journal of hazardous materials, 185(2),1499-1507. https://doi.org/10.1016/j.jhazmat.2010.10.075.

[16] Hank, D., Saidani, N., Namane, A., & Hellal, A. (2010), Batch phenol biodegradation study and application of factorial experimental design, Journal of Engineering Science & Technology Review, 3(1).

[17] Sin, J.C., Lam, S.M., & Mohamed, A.R. (2011), Optimizing photocatalytic degradation of phenol by TiO_2/GAC using response surface methodology, Korean Journal of Chemical Engineering, 28(1), 84-92. https://doi.org/10.1007/s11814-010-0318-0

[18] Hameed, B.H., Tan, I.A.W., & Ahmad, A.L., (2009), Preparation of oil palm empty fruit bunch-based activated carbon for removal of 2, 4, 6-trichlorophenol: Optimization using response surface methodology, Journal of Hazardous Materials, 164(2), 1316-1324. https://doi.org/10.1016/j.jhazmat.2008.09.042.

[19] Smitha, T., Santhi, T., Prasad, A.L., & Manonmani, S. (2017), Cucumis sativus used as adsorbent for the removal of dyes from aqueous solution, Arabian Journal of Chemistry, 10, S244-S251. https://doi.org/10.1016/j.arabjc.2012.07.030.

[20] Nieto, L.M., Alami, S.B.D., Hodaifa, G., Faur, C., Rodríguez, S., Giménez, J.A., & Ochando, J. (2010), Adsorption of iron on crude olive stones, Industrial crops and products, 32(3), 467-471. https://doi.org/10.1016/j.indcrop.2010.06.017.

[21] Omri, A., & Benzina, M. (2012), Removal of manganese (II) ions from aqueous solutions by adsorption on activated carbon derived a new precursor: Ziziphus spina-christi seeds, Alexandria Engineering Journal, 51(4), 343-350. https://doi.org/10.1016/j.aej.2012.06.003.

[22] Ahmaruzzaman, M., (2011), Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals, Advances in colloid and interface science, 166(1-2), 36-59. https://doi.org/10.1016/j.cis.2011.04.005.

[23] Koswojo, R., Utomo, R.P., Ju, Y.H., Ayucitra, A., Soetaredjo, F.E., Sunarso, J., & Ismadji, J.S. (2010), Acid Green 25 removal from wastewater by organo-bentonite from Pacitan, Applied clay science, 48(1-2), 81-86. https://doi.org/10.1016/j.clay.2009.11.023.

[24] Kurniawan, A., & Ismadji, S. (2011), Potential utilization of Jatropha curcas L. press-cake residue as new precursor for activated carbon preparation: application in methylene blue removal from aqueous solution, Journal of the Taiwan Institute of Chemical Engineers, 42(5), 826-836. https://doi.org/10.1016/j.jtice.2011.03.001.

[25] Salem, N.M., & Awwad, A.M. (2014), Biosorption of Ni (II) from electroplating wastewater by modified (Eriobotrya japonica) loquat bark, Journal of Saudi Chemical Society, 18(5), 379-386. https://doi.org/10.1016/j.jscs.2011.07.008.

[26] Demirak, A., Dalman, Ö, Tilkan, E., Yıldız, D., Yavuz, E., & Gökçe, C. (2011), Biosorption of 2, 4 dichlorophenol (2, 4-DCP) onto Posidonia oceanica (L.) seagrass in a batch system: Equilibrium and kinetic modelling, Microchemical Journal, 99(1), 97-102. https://doi.org/10.1016/j.microc.2011.04.002.

[27] Girish, C.R., Singh, P., & Goyal, A.K., (2017), Removal of Phenol from Wastewater Using tea waste and optimization of conditions using response surface methodology, International Journal of Applied Engineering Research, 12(13), 3857-3863.

[28] Zhao, G., Li, Y., Liu, X., & Liu, X. (2010), Preparation of capsules containing 1-nonanol for rapidly removing high concentration phenol from aqueous solution, Journal of hazardous materials, 175(1-3), 715-725. https://doi.org/10.1016/j.jhazmat.2009.10.068.