

Investigation of activated carbon derived from rice straw biomass for removal of phenol from aqueous solution

Thi Thu Hoai Pham*

Faculty of Food Technology, University of Economics - Technology for Industries, 456 Minh Khai Street, Hai Ba Trung District, Hanoi, Vietnam

Received 27 November 2022; accepted 5 January 2023

Abstract:

The rapidly developing of industry and population leads to various problems, such as an increase in the energy used and discharging of pollutants into the environment. Water pollution is a big issue in Vietnam as well as in the world. Therefore, finding the method for the treatment of water is urgent. This work investigated activated carbon derived from rice straw biomass (ACRS) for the adsorption of phenol. The surface morphology, surface functional group, and surface area of the ACRS were determined by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and Brunauer-Emmett-Teller (BET) analysis, respectively. ACRS had a porous structure along with a larger surface area of 216.3 m²/g, which effectively enhanced the adsorption performance of phenol. The removal performance of phenol increased with increasing the contact time (10-60 min), then reached equilibrium at 90 min. The maximum adsorption capacity of phenol using ACRS was 128.4 mg/g and the adsorption behaviour of the pollutant fit well to the Langmuir and Freundlich isotherms. Experimental results revealed that adsorption by surface area, activated sites, pores, and complexation between functional groups of the adsorbent and phenol were major mechanisms.

Keywords: activated carbon, adsorbent, biomass, phenol, rice straw.

Classification numbers: 2.2, 5.3

1. Introduction

A high level of water pollution worsens the already troubling environmental situation by contaminating drinking water as untreated wastewater flows into surface water bodies at alarming rates. According to the United Nations economic and social commission for Asia and the Pacific 2022, 1.9 billion people throughout the region still lack access to safely managed drinking water and sanitation services. This potentially hazardous wastewater not only affects human health, but other inhabitants as well [1-3]. Phenol is commonly dumped from industrial effluents of various chemical manufacturing plants, for example, plastic, paper bleaching facilities, paint, pharmaceuticals, pesticides, petrochemicals, paint manufacturers. Humans suffer skin, eye, and mucous membrane irritation by phenol exposure. The United States Environmental Protection Agency (EPA) has placed a water purity requirement of less than 1.0 ppb of phenol in surface water [2-6]. Adsorption processes by carbon-based materials have been attractive to researchers for effective removal of organic compounds from water systems [7, 8]. Currently, biochar derived from waste materials are widely applied for the adsorption of organic pollutants like phenol. Indeed, Yusuff and co-workers used eucalyptus bark biochar to remove toxic heavy

metal (Cr⁶⁺) [9]. V.T. Quyen, et al. (2021) and co-workers prepared biochar from coffee husks and applied it to remove heavy metals including Pb (II) and Cd (II) from wastewater [10]. Wu and co-workers also tried to remove methylene blue by using porous biochar derived from eggshells [11]. In another example, G. Wang, et al. (2022) and co-workers utilized porous biochar for chloramphenicol removal [12].

Biochar has various advantages such as low-cost, non-toxicity, and high adsorption performance for many kinds of pollutants. Many studies have investigated the use of biochar produced from agricultural waste materials to remove organic pollutants. As an agricultural country, Vietnam produces huge amounts of rice, over 44 M tons in 2020. Due to the high amount of rice production, a larger rice straw biomass was produced. Therefore, utilizing rice straw waste as a base material to make adsorbent is potentially ideal. Doing so will help decrease waste from agricultural activities as well as bring added value to solve water pollution. Therefore, the present study determines the potential of activated carbon derived from rice straw biomass for the adsorption of phenol. The adsorption behaviours at the solid-liquid interface were investigated by adsorption isotherms and the study of other factors like reaction times, adsorbent dose, and initial concentration of phenol.

*Email: pthhoai@uneti.edu.vn

2. Materials and methods

2.1. Prepare adsorbent

The rice straw waste used in this work was collected from a local corn farm (Nam Dinh city, Vietnam). Rice straw biomass was cut into small pieces, washed with DI water, dried at 80°C for 12 h, then pyrolyzed at a temperature of 450°C for 3 h using a furnace under N₂ gas. After cooling, the product after the pyrolyzed process (ACRS) was taken out and kept for further experiments.

2.2. Characterization of ACRS adsorbent

The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method (Surface area analyser, JW-BK112, China). Scanning electron microscopy (SEM) images (SU-850, Hitachi, Japan) were recorded to investigate the morphology of the ACRS. The functional groups of adsorbents were identified by FTIR spectroscopy (Nicolet, 12- FTIR spectrometer, US).

2.3. Phenol removal

The bath adsorption experiment was performed by adding 0.5 g of adsorbent in a glass vial containing phenol solution (V=100 ml; C=10 mg/l; pH=6.0). The mixture was stirred at 200 rpm by magnetic stirrer at for different times. The sample was taken out, filtered by a 0.22-μm membrane, and analysed by high-performance liquid chromatography (HPLC) to determine the phenol concentration in the sample.

The adsorption capacities and the removal performance of phenol were calculated based on Eqs. (1) and (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\text{Removal(\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where q_e is the quantity of adsorbed phenol by 1 g ACRS (mg/g), C_0 is the initial phenol concentration (mg/l), C_e is phenol concentration at equilibrium (mg/l), C_t is phenol concentration at time t (mg/l), V is the volume of phenol solution (ml), and m is the amount of dry ACRS (mg).

3. Results and discussion

3.1. Surface morphology of ACRS

Figure 1A shows an image and Fig. 1B displays the surface morphology of the ACRS adsorbent. It can be seen that the ACRS was black in colour like biochar and the surface morphology was jagged and broken with a porous structure. In general, the porous structure provides many active sites and pores to adsorb the pollutant in the solution [12-16].

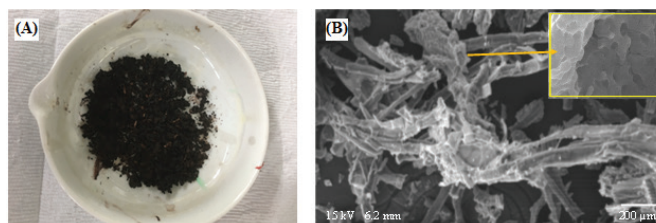


Fig. 1. (A) Image and (B) surface morphology of ACRS.

3.2. The surface area of ACRS

Figure 2 shows the gas adsorption-desorption isotherm on the surface of ACRS, which is classified as type IV along with the micro- and mesoporous structure of the adsorbent. The ACRS had a high surface area of 216.3 m²/g and total pore volume of 0.382 cm³/g. Table 1 compares the physical properties of ACRS and other adsorbents. The surface area and pore volume of the ACRS were higher than other materials, confirming the potential of ACRS for the adsorption of phenol [16-19].

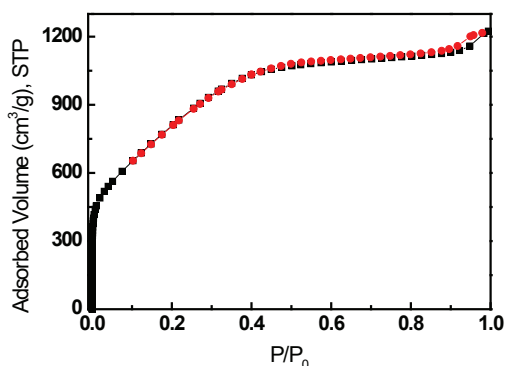


Fig. 2. N₂ adsorption-desorption isotherm analysis of ACRS.

Table 1. Surface area and pore volume of adsorbents.

Materials	S _{BET} (m ² /g)	V pores (cm ³ /g)	References
ACRS	216.3	0.038	This study
Zeolite	24	0.011	[13]
Biochar	17.07	0.035	[14]
Pistachio shells biochar (300°C)	15.12	0.002	[15]
Pistachio shells biochar (600°C)	34.16	0.008	[15]

3.3. Surface functional groups of ACRS

Figure 3 shows the FTIR spectra of the adsorbent in the range of 400 to 4000 cm⁻¹. The peak around ~3620 cm⁻¹ is associated with the bands of the O-H group in aromatic and aliphatic structures [10-12].

The peak appearing at 3300 cm⁻¹ illustrates the N-H stretch in the amine group. The peak at ~2836 cm⁻¹ is attributed to the presence of the aliphatic C-H stretch of CH, CH₂, and CH₃ groups. The O=C=C stretch is observed by a

noticeable peak at 2360 cm^{-1} . The peak at $\sim 1665\text{ cm}^{-1}$ could be assigned to C=O bonds. The peak found below $\sim 910\text{ cm}^{-1}$ is related to the out-of-plane stretching of C-H. These results suggest that ACRS contained various functional groups responsible for adsorbing phenol from solution [19-22].

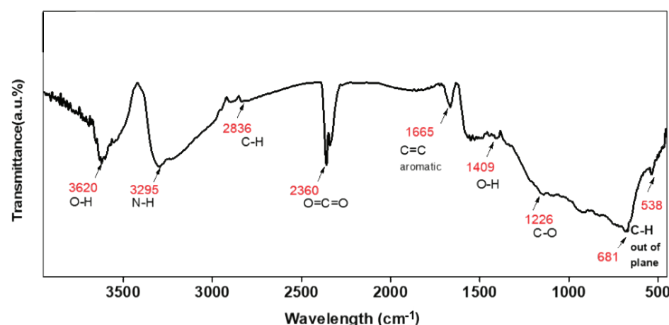


Fig. 3. Surface functional groups of ACRS.

3.4. Effect of contact time on the removal of phenol

Figure 4 displays the effect of time on the adsorption of phenol by ACRS. The removal performance of phenol increased with time, the efficiency was 12.3% at 10 min and it increased up to 93.5% after 90 min. After 90 min of reaction time, the adsorption of phenol by ACRS was negligible due to unavailable active sites, surface area, and pores to adsorb phenol pollutants [18-23]. As shown in Fig. 4, higher initial phenol concentration (50 mg/l) displayed a smaller removal efficiency (83.4%) compared low-level concentration ($C_0=10\text{ mg/l}$ and $R=93.8\%$). At a low concentration of phenol, the adsorption nearly completed in 90 min, while with a high concentration of the pollutant, the adsorption equilibrium was found at 150 min.

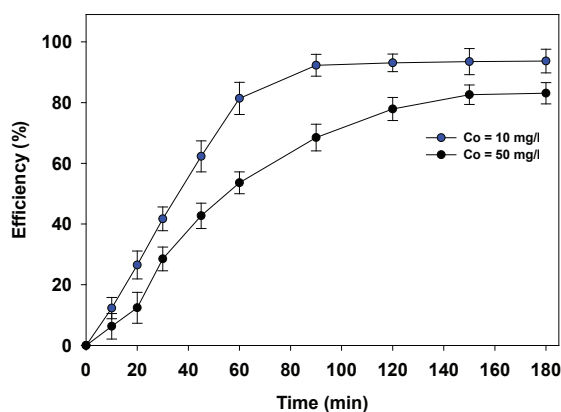


Fig. 4. Effect of reaction time on phenol adsorption by ACRS.

3.5. Effect of ACRS dose on the removal of phenol

The removal performance of phenol rapidly improved from 10.3 to 93.5% as the ACRS amount increased from 0.01 to 0.5 g, respectively (Fig. 5). This was due to the high surface area and active sites available at higher dosages [20-24]. Further increase in adsorbent dosage over 0.5 g did not contribute to any improvement in the removal performance of phenol.

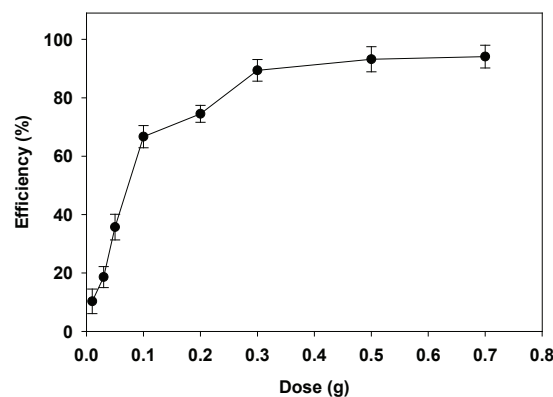


Fig. 5. Effect of ACRS dose on the removal of phenol.

3.6. Adsorption isotherms

Figure 6 displays a linear fit of the Langmuir and Freundlich models and the corresponding adsorption isotherms parameters are listed in Table 2.

The adsorption of phenol was fit to the Langmuir model ($R^2=0.98$) and Freundlich model ($R^2=0.91$). The maximum absorption capacity of phenol by ACRS obtained via the Langmuir isotherm was 128.4 mg/g. For the Freundlich model, the value of n is higher than 1.0, which indicates favourable adsorption of phenol onto ACRS [21-23].

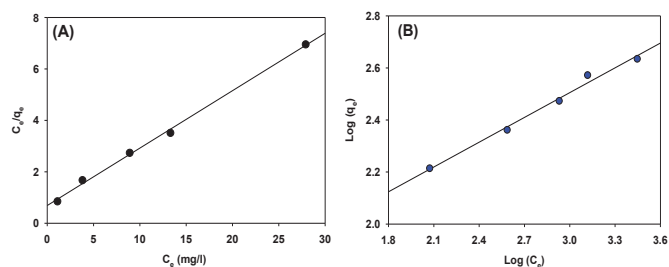


Fig. 6. Adsorption isotherms: (A) Langmuir model and (B) Freundlich model.

Table 2. Adsorption parameters of phenol provided by Langmuir and Freundlich isotherms.

Adsorbent	Langmuir model		Freundlich model			
	q_{max} (mg/g)	b (l/g)	R^2	n	K_F (mg/g)	R^2
ACRS	128.4	0.02	0.98	3.2	42.1	0.91

3.7. Adsorption mechanism

The adsorption mechanisms of phenol by using ACRS could include physisorption and chemisorption as listed in Fig. 7 [9-12]. The main physical adsorption mechanism was controlled by Van der Waals forces and electrical attraction. ACRS is an effective physical adsorbent for phenol removal because of its high surface area, many pores, and active adsorption sites [9, 10, 21-24].

In general, chemisorption occurs by the sharing of electrons between phenol and the surface of the adsorbent, then chemical bonds form between functional groups of phenol and the

adsorbent ACRS. Functional groups like C=O, N-H, and O-H of ACRS could interact with phenol through complexation, resulting in removed phenol from the solution [22-24].

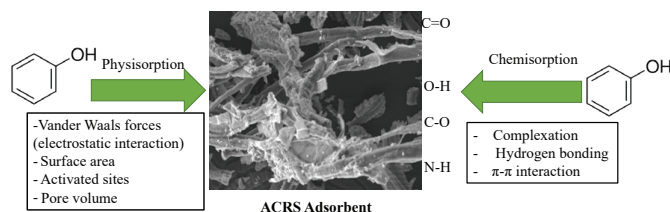


Fig. 7. Adsorption mechanisms of phenol by using ACRS adsorbent.

4. Conclusions

This work identified the potential of ACRS for adsorption of phenol in solution. The removal performance of phenol was over 93% within 90 min of contact time and 0.5 g ACRS. The adsorption data indicated that the adsorption of phenol was well fit by Freundlich and Langmuir isotherms and the maximum adsorption capacity of phenol was 128.4 mg/g. ACRS had a high adsorption performance of phenol due to its high surface area, porous structure, and its various functional groups like C=O, O-H, N-H, and O=C=C. This work provides a method to produce adsorbents from waste material that can be utilized for the removal of organic pollutants like phenol.

COMPETING INTERESTS

The author declares that there is no conflict of interest regarding the publication of this article.

REFERENCES

[1] X. Sun, et al. (2015), "Treatment of phenolic wastewater by combined UF and NF/RO processes", *Desalination*, **355**, pp.68-74.

[2] P. Kazemi, et al. (2014), "Stability and extraction study of phenolic wastewater treatment by supported liquid membrane using tributyl phosphate and sesame oil as liquid membrane", *Chem. Eng. Res. Des.*, **92**(2), pp.375-383.

[3] S. Mohammadi, et al. (2015), "Phenol removal from industrial wastewaters: A short review", *Desalination and Water Treatment*, **53**(8), pp.2215-2234.

[4] G. Veeresh, et al. (2005), "Treatment of phenol and cresols in upflow anaerobic sludge blanket (UASB) process: A review", *Water Research*, **39**(1), pp.154-170.

[5] G. Calleja, et al. (1993), "Kinetics of adsorption of phenolic compounds from wastewater onto activated carbon", *Carbon*, **31**(5), pp.691-697.

[6] F. Orshansky, et al. (1997), "Characteristics of organics removal by PACT simultaneous adsorption and biodegradation", *Water. Res.*, **31**, pp.391-398.

[7] I. Ali, et al. (2006), "Advances in water treatment by adsorption technology", *Nature protocols*, **1**, pp.2661-2667.

[8] B.C. Pan, et al. (2007), "Improved adsorption of 4-phenol onto a novel hyper-cross-linked polymer", *Environ. Sci. Technol.*, **41**, pp.5057-5062.

[9] A.S. Yusuff, et al. (2022), "ZnCl₂-modified eucalyptus bark biochar as adsorbent: Preparation, characterization and its application in adsorption of Cr(VI) from aqueous solutions", *South. African J. Chem. Eng.*, **42**, pp.138-145.

[10] V.T. Quyen, et al. (2021), "Biosorbent derived from coffee husk for efficient removal of toxic heavy metals from wastewater", *Chemosphere*, **284**, DOI: 10.1016/j.chemosphere.2021.131312.

[11] T. Wu, et al. (2022), "Activation and adsorption mechanisms of methylene blue removal by porous biochar adsorbent derived from eggshell embrance", *Chemical Eng. Research and Design*, **188**, pp.330-341.

[12] G. Wang, et al. (2022), "Structure-performance correlation of high surface area and hierarchical porous biochars as chloramphenicol adsorbents", *Separation and Purification Technology*, **296**, DOI: 10.1016/j.seppur.2022.121374.

[13] L. Tortet, et al. (2017), "Adsorptive elimination of paracetamol from physiological solutions: Interaction with MFI-type zeolite", *Microporous and Mesoporous Mater.*, **252**, pp.188-196.

[14] Z. Zhang, et al. (2023), "Development of iron-based biochar for enhancing nitrate adsorption: Effects of specific surface area, electrostatic force, and functional groups", *Science of the Total Environment*, **856**, DOI: 10.1016/j.scitotenv.2022.159037.

[15] S. Saghir, et al. (2022), "Synthesis of high surface area porous biochar obtained from pistachio shells for the efficient adsorption of organic dyes from polluted water", *Surfaces and Interfaces*, **34**, DOI: 10.1016/j.surfin.2022.102357.

[16] R.M. Zavoid, et al. (2013), "Drug design and relationship of functional groups to pharmacologic activity", *Foye's Principles of Medicinal Chemistry*, **6**, pp 29-60.

[17] M.M. Harussani, S.M. Sapuan (2022), "Development of kenaf biochar in engineering and agricultural applications", *Chemistry Africa*, **5**, pp.1-17.

[18] S.W. Rita, et al. (2013), "A preliminary investigation of wastewater treatment efficiency and economic cost of subsurface flow oyster-shell-bedded constructed wetland systems", *Water*, **5**(3), pp.893-916.

[19] I. Mitra, et al. (2019), "Rice husk: green adsorbent for Pb(II) and Cr(VI) removal from aqueous solution-column study and GA-NN modeling", *SN Applied Science*, **1**, DOI: 10.1007/s42452-019-0513-5.

[20] C. Russo, et al. (2021), "On the application of electron energy-loss spectroscopy for investigating nanostructure of soot from different fuels", *Fuels*, **2**(3), pp.367-375.

[21] S. Yu, et al. (2016), "Experimental and theoretical studies on competitive adsorption of aromatic compounds on reduced graphene oxides", *J. Mater. Chem.*, **4**(15), pp.5654-5662.

[22] A. Singh, et al. (2021), "Low-cost biochar adsorbents prepared from date and delonix regia seeds for heavy metal sorption", *Bioresource Technology*, **339**, DOI: 10.1016/j.biortech.2021.125606.

[23] A. Imran, et al. (2012), "Low-cost adsorbents for the removal of organic pollutants from wastewater review", *Environmental Management*, **113**, pp.170-183.

[24] S.F. Lütkeet, et al. (2019), "Preparation of activated carbon from black wattle bark waste and its application for phenol adsorption", *J. Environ. Chem. Eng.*, **7**(5), DOI: 10.1016/j.jece.2019.103396.