

USE OF BAGASSE TO REMOVE 2-CHLOROPHENOL IN AQUEOUS SYSTEM

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Abstract

The adsorption method using waste bagasse has been examined to remove 2-chlorophenol (2-CP) from aqueous solutions at room temperature. The adsorption of 2-chlorophenol by bagasse carbon could be studied in batches by changing the contact time, operating temperature, pH of the solution, initial concentration, adsorbent dose, and particle size. It took three hours to reach equilibrium. The Langmuir model correctly predicted the adsorption equilibrium data for 2-chlorophenol-sorbent systems in the concentration range that was examined. When the pH was lower, getting rid of 2-CP from surfaces was easier. Studies of desorption show that chemisorption is an important part of the adsorption process.

Key words: 2-Chlorophenol, Bagasse, Adsorption, Equilibrium, Desorption

Introduction

Cancer and mutations caused by halogenated aromatics can lead to incurable diseases (Zada *et al.*, 2021). 2-Chlorophenol is a halogenated aromatic molecule that has found utility in several fields, including herbicides, polymers, pharmaceuticals, petroleum, different chemicals, etc. (Huong *et al.*, 2016). The USEPA has designated 2-CP as a priority organic pollutant and established a limit of 0.1 ppb for its presence in potable water supplies (Pera-Titus *et al.*, 2004). Industrial waste, agricultural runoff, and landfill leachate are all pathways via which 2-CP enters the environment (Shen *et al.*, 2021). Given its resistance to degradation, 2-CP tends to accumulate in natural settings. Because of its potency as a mutagen and carcinogen, 2-CP is disastrous for aquatic ecosystems (Barakat *et al.*, 2021). This means that before discharge, 2-CP must be removed from industrial effluent.

Technologies such as chemically induced precipitation, reverse osmosis, oxidation-reduction, and adsorption have all been used to successfully remove 2-CP from

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wastewater (Enoyh and Isiuku, 2021; Liu *et al.*, 2021; Kusmierek *et al.*, 2021). Adsorption has recently replaced all other wastewater treatment methods as the most well-known and widely used option due to its low cost and high efficiency. To offset the high expense of synthetic adsorbents, researchers have been working overtime to find cheaper alternatives. There has been a rise in interest in using adsorbents made from waste biomass to detoxify the environment of contaminants like 2-CP (Kusmierek *et al.*, 2021; Garba *et al.*, 2019).

It is prohibitively expensive for factories in developing nations like Bangladesh to use chemicals, including alum, ferric chloride, polymer flocculants, and activated carbon derived from coal which has been used for decades in conventional wastewater treatment. The bagasse by-product is a low-cost material for waste management in the ongoing search for novel, widely used agricultural wastes (Mandal *et al.*, 2004; Barraclough *et al.*, 2005; Singh *et al.*, 2008). Sugarcane is cultivated on over 425,000 hectares of land in Bangladesh. Every year, we generate almost 800,000 metric tons of discarded bagasse (Mahamud and Gomes, 2012). Using this biomass source would reduce costs associated with cleaning water systems of harmful pollutants (Williams and Nugranad, 2000). More research, however, need to be done to determine whether or not untreated bagasse can efficiently eliminate 2-CP. This research aimed to determine if waste bagasse (specifically, sugarcane industry bagasse) might be used as a substitute adsorbent. To accomplish this, a simple, highly effective adsorption method for removing 2-CP from wastewater was developed and implemented.

Materials and Methods

Chemicals and apparatus: The chemicals and reagents utilized were of the highest quality (BDH). Both of the solutions were prepared by using double-distilled water as starting material. As a stock solution, 0.5 g of 2-CP was dissolved in 500 ml of deionized water. This was a 2-CP stock solution that had 1,000 milligrams per milliliter. A double-beam spectrophotometer, the Shimadzu UV-160, and the 4-aminoantipyrene technique were used to quantify the concentration of 2-CP (APHA 1985). Buffer solutions from the German company E. Merk are used to maintain a constant pH level. A microprocessor-based bench pH meter was used to measure the substrate's pH (HANNA pH 300) (Amin *et al.*, 2012).

Phenol concentration measurement: Results from the 4-aminoantipyrene technique (APHA, 1985) were deemed insufficient, prompting researchers to seek alternate approaches. Neither 2-CP nor 4-aminoantipyrene showed any significant color change in

early testing with potassium ferricyanide in an acidic medium. In contrast, 2-CP has a dark reddish hue at a pH of 6.0. This hue becomes more vibrant as the pH increases, to a point where it suddenly fades at a pH of 10.0. This color scheme was developed after researchers found that they could more accurately measure low concentrations of 2-CP by shifting their spectrophotometric measurements to a buffer with a pH of 10.0 (instead of the more often used of pH 8.0). Color fully develops during 25 minutes; the absorption peak has been measured to be at 500 nm using blank reagents. As shown experimentally, the maximal color intensity in a 2-CP solution system with a 5 mg l^{-1} concentration can be achieved using just 0.4 ml of a 2.0% (w/v) 4-aminoantipyrine solution. For a system containing 5 mg l^{-1} 2-CP, the optimal amount of potassium ferricyanide is 0.5 ml of an 8.0% (w/v) solution. The color intensity was also shown to drop gradually after this range. The modified strategy was proven more effective (Amin *et al.*, 2012).

Preparation of adsorbent : This initiative made use of bagasse from a regional sugar mill. The waste bagasse was exposed to the elements for ten days until its moisture content stabilized. The bagasse was chopped and then sieved to remove the fibrous parts. Dust and particles were removed from the gathered items by washing them multiple times in clean water. To ensure that the washed water was completely clear, the washing operation was repeated several times. Materials were washed and dried in a hot-air oven at $60 \text{ }^{\circ}\text{C}$ for 24 hours. After drying, the substance was sieved into five different particle sizes (75, 95, 125, 175, and $400 \text{ }\mu\text{m}$). The materials were used to remove 2-CP from the environment without adding any additional physical or chemical treatment.

Table 1. Sugarcane bagasse characterization (Figueroa *et al.*, 2014).

Proximate analysis (wt%)		Ultimate analysis (wt% free water)		Lignocellulosic analysis (wt% free water)	
Moisture	7.80±0.50	C	44.52±1.59	Cellulose	40.99±0.72
Fixed carbon	10.81±0.33	H	5.90±0.22	Hemicellulose	25.45±0.85
Volatile matter	83.97±0.36	N	0.32±0.08	Acid insoluble lignin	14.47±0.45
Ash	5.22±0.68	S	0.10	Acid soluble lignin	5.26±0.04
		Cl	0.29	Extractives	4.86±1.09
		O*	43.65		
Bagasse particle density			1.49±0.01		

* by difference.

Bagasse characteristics: The sturdy stem of the sugarcane plant sets apart from other types of grass. Table 1 shows the characteristics of sugarcane bagasse.

Adsorption of 2-CP from aqueous solutions: Each batch experiment used a 250-ml sealed bottle containing 100 ml of 2-CP solution and 2.0 g of adsorbent. The pH of all the tests was set at 8.0. The texture of the adsorbent shifts when the pH rises. Next, an electric shaker was used to agitate the bottles at the same rate as they warmed to room temperature. The higher temperatures required the use of beakers in a water bath with a thermostat and an electric stirrer. The contents were centrifuged at predetermined intervals, and spectrophotometry was used to compare the amount of 2-CP in the supernatant to a reagent blank. The bottles containing the various concentrations of 2-CP and the appropriate pH were shaken for 5 hours to ensure that the concentration of the residual 2-CP remained constant. The capacity to absorb was determined by comparing the initial and final 2-CP concentrations.

The effectiveness of removal (adsorption) was determined using the following equation:

$$\text{Removal (adsorption) efficiency} = ((C_o - C_e)/C_o) \times 100 \quad (1)$$

where C_o and C_e are the 2-CP concentrations in the sample solution before and after the treatment. The uptake of 2-CP by bagasse was also measured in batch tests conducted at 30, 35, 40, and 50°C. Subsequent experiments were conducted at a temperature of 30°C (room temperature), although the concentration is somewhat higher at 50°C. Beer's law predicts that the 2-CP concentration in the research may range from 0 to 10 mg/l.

Results and Discussion

First, nine adsorbents, including coconut shell, motorsuti straw, maize husk leaf, bagasse, mustard straw, rice straw, maize cob, and newspaper, were tested on their ability to remove 2-CP from aqueous solutions. At an initial 2-CP concentration of 5 mg/l, a working temperature of 25°C, an amount of adsorbent of 2.0 g, a contact period of 1 hour, and a solution pH of 6, 2-CP was successfully removed. According to preliminary research, coconut shell, motorsuti straw, maize husk leaf, bagasse, mustard straw, rice straw, maize cob, and newspaper were each 10.3, 11.2, 28.7, 13.9, 9.4, 17.3, 16.8, and 14.3% effective at removing 2-CP. Bagasse was more effective at removing the substance than these eight adsorbents. Therefore, they were disregarded and ignored in the follow-up research.

Effect of adsorbent dosages: How bagasse carbon removed 2-CP as adsorbent amounts varied from 0.5 to 5.0 g is depicted in Fig. 1. It was also ensured that the pH level remained constant at 6.0. The amount of 2-CP eliminated increased as the amount of adsorbent increased, up to a maximum of 2.0 g. After that point, there was slight variation in the total amount of 2-CP that was eliminated. The adsorption rate increases with the amount of adsorbent since there are more adsorption sites and surface area to absorb. Scientists have found that most phenols function similarly (Mustafa *et al.*, 2008).

Effect of contact time: Finding the equilibrium point involved studying how time affects adsorption. This effect of agitation time on bagasse's 2-chlorophenol elimination is shown experimentally in Fig. 2. According to the results, 2-CP takes nearly an hour to establish equilibrium on bagasse. There was little to no noticeable difference in the rate of 2-CP removal between 1-3 h. Adsorption data indicates that adsorbate species are rapidly ingested at the outset of the contract duration. These findings also demonstrate the rapidity of the sorption process, as the major portion of 2-CP was adsorbed to the sorbent in the first 60 minutes. The same sort of outcome was reported by Esmā *et al.* in 1998.

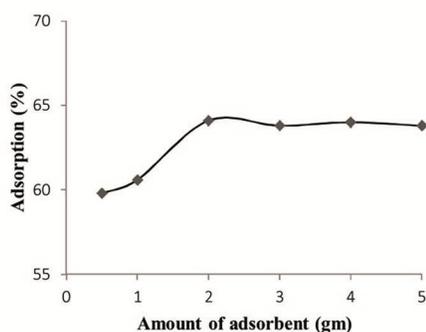


Fig. 1. Effect of bagasse amount on 2-CP adsorption (contact time, 60 min; avg. particle size, 150 μm ; initial 2-CP concentration, 5 mg/l; pH, 6.0; operational temperature, 25 $^{\circ}\text{C}$).

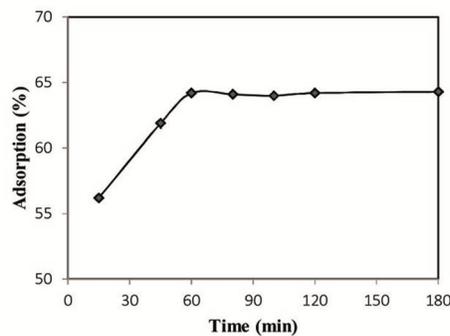


Fig. 2. Effect of contact time on the adsorption of 2-CP (adsorbent dosage, 2.0 g; avg. particle size, 150 μm ; initial 2-CP concentration, 5 mg/l; pH, 6.0; operational temperature, 25 $^{\circ}\text{C}$).

Effect of particle size: Taking 2-CP out of an aqueous solution, batch adsorption studies were conducted using a range of five average particle diameters of 60, 100, 150, 200, and 250 μm . The outcomes are depicted in Fig. 3. The percentage of 2-CP eliminated increased from 56% to 72% as particle size decreased. When rice husk is used, similar results are observed (Amin *et al.*, 2006). These occurrences may occur because smaller particles have more surface area and more sites for things to attach to them.

Effect of initial concentration: 2-CP removal efficiency highly depends on the concentration of 2-CP in the starting sample solution. The effectiveness of bagasse in removing 2-CP varies with the starting concentration of the sample, as shown in Fig. 4. According to the data, when 2-CP concentration increased, so did the sorbents' sorption capabilities, but the adsorption yields decreased. The amount of 2-CP that could be adsorbed by bagasse increased from 63 to 68% when the phenol concentration was raised from 1 to 6 mg/l. It's easy to see that the driving force for mass transfer is greater and that there are more adsorption sites. Because of this, the adsorbate can easily access the adsorption site. More adsorbent crowds into the particles, reducing the number of active sites and making it more difficult for the adsorbate to migrate. Because of this, the initial concentration plays a pivotal role in promoting the transformation of 2-CP from the liquid to the solid state by boosting the force responsible for mass transfer. More 2-CP would be taken up if this happened. However, the amount of 2-CP present at the outset reduces adsorbed. Due to its greater specific surface area and microporous nature, bagasse was predicted to have the highest equilibrium uptake and adsorption yield. Rao et al. 2003 also observed similar results.

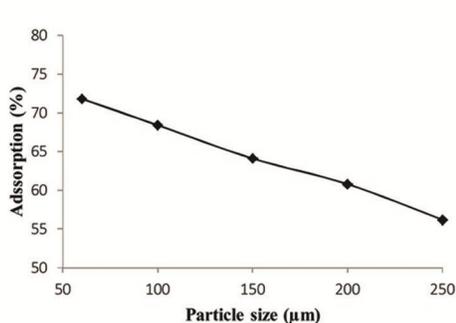


Fig. 3. Effect of particle size on the adsorption of 2-CP (adsorbent dosage, 2.0 min; contact time, 60 min; initial 2-CP concentration, 5 mg/l; pH, 6.0; operational temperature, 25°C).

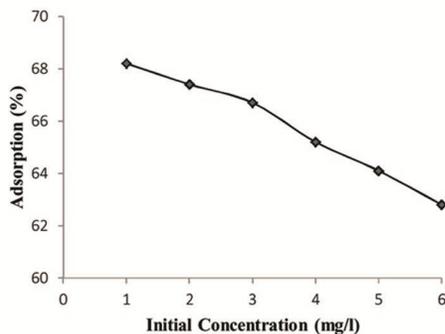


Fig. 4. Effect of initial concentration on 2-CP adsorption (adsorbent dosage, 2.0 min; contact time, 60 min; avg. particle size, 150 µm; pH, 6.0; operational temperature, 25°C).

Effect of pH: The surface charge, ionization level, and separation efficiency of an adsorbent all change when the pH of the solution changes. At varying pH values (from 4 to 12), bagasse uptake of 2-CP was studied. Results are depicted in Fig. 5. There is a positive pH-dependent linear relationship between the amount of 2-CP adsorbed and the pH up to 6. Adsorption of 2-CP decreases sharply when pH increases beyond pH 6 and remains low at higher pH levels. The solution's pH has an impact on the protonation or

deprotonation of functional groups in both the adsorbent and the adsorbate. The decrease in CP adsorption as pH increases is presumably due to the charge characteristics of both the adsorbate and the adsorbent (Ghaffari *et al.*, 2014). Since 2-CP has a pKa of 8.44, it is a weak acid. Since the neutral form of 2-CP exists at pH values below 6, nearly no anionic species exist at these lower pH values (Fig. 5). When the pH is higher than its pKa value, more of the anionic CP is present. At a pH of 6, the anionic form of CP predominates, and the neutral form disappears entirely. Adsorbents have positively charged surfaces, but the presence of mostly neutral 2-CP means that electrostatic interactions are negligible. Electrostatic attraction is one of many factors in determining neutral 2-CP adsorption. When a lot of non-positive and anionic 2-CP accumulates on the adsorbent's surface, electrostatic repulsion becomes the dominant force. At pH values greater than its pKa, which is anionic, 2-CP is more common than neutral. At pH >6, the electrostatic repulsion between the adsorbate and the ashes was greater due to the concomitant generation of negative net charges on the ash surfaces. This made it so that 2-CP had much more trouble remaining in the ashes. A similar uptake of 2-CP was seen in the ash produced from rice straw, as reported by Chang *et al.* (2011). According to the results, pH 6 is optimal for absorbing 64%. This led to the conclusion that a pH of 6.0 was the best, and all further studies were conducted in this buffer.

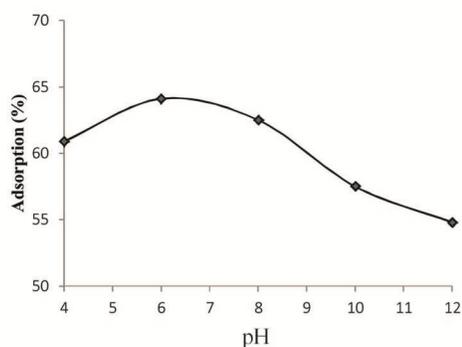


Fig. 5. Effect of solution pH on 2-CP adsorption (adsorbent dosage, 2.0 min; contact time, 60 min; avg. particle size, 150 μm ; initial 2-CP concentration, 5 mg/l; operational temperature, 25°C).

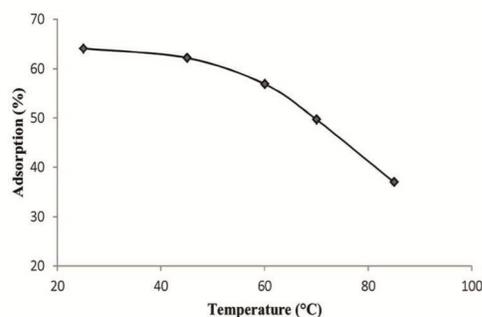


Fig. 6. Effect of temperature on 2-CP adsorption (adsorbent dosage, 2.0 min; contact time, 60 min; avg. particle size, 150 μm ; initial 2-CP concentration, 5 mg/l; pH, 6.0).

Effect of temperature: To separate substances, temperature plays a crucial role. Bagasse was heated to various levels (25, 45, 60, 75, and 85°C) to determine how effectively it eliminated 2-CP. The temperature dependence of adsorption capacity is depicted in Fig.

6. The 2-CP's ability to adhere to bagasse is diminished when the temperature rises from 25 to 85°C. This means that 2-CP is more likely to adhere to a surface at a cooler temperature. Adsorption decreases as temperatures increase. This occurs when the adsorbate's thermal energy increases and the 2-CP's attractive force towards the adsorbent decreases. To put it another way, the molecular attraction between the adsorbent and the 2-CP isn't strong enough to keep the molecules bound. Numerous sources have reached the same conclusion (Ofomaja and Ho, 2007; Jadhav and Vanjara, 2004; Senturk *et al.*, (2009). The efficiency with which adsorbents take in molecules is significantly affected by temperature. Adsorption is an exothermic process, and it stands to reason that as the adsorbate-adsorbent system temperature increases, the sorption capacity decreases. All of the data points in this direction, demonstrating that sorption is an exothermic process (Bazrafshan *et al.*, 2016).

Adsorption isotherm: An adsorption experiment is set up in the lab by dispersing 150 ml of the solution into five flasks, each containing a known amount of bagasse. Initial 2-CP concentrations in the solutions were 5 mg/l (pH 6), and the amounts of adsorbent ranged from 0.5 to 2.0 gm. Afterward, the bottles were sealed and stirred in a rotary shaker for an hour at 25°C.

Many different models have been proposed to account for experimental results. Two of the most prevalent isotherm models are the Langmuir isotherm (Langmuir, 1918) and the Freundlich isotherm (Freundlich, 1906). Both models described the correlation between 2-chlorophenol uptake by the bagasse and equilibrium concentration. In its linear form, the Freundlich isotherm model is expressed as follows (Rengaraj *et al.*, 2002; Banat *et al.*, 2000; Aksu and Yener, 2001; Khalid *et al.*, 2000):

$$\ln q_e = \ln K + 1/n \ln C_e$$

where K and $1/n$ are the Freundlich constants for the sorbent's adsorption capacity and intensity, respectively, and q_e is the amount of adsorbate at equilibrium (mg/mg) and C_e is the concentration of adsorbate at equilibrium (mg/l). Linear regression of q_e data versus C_e can be used to determine K and $1/n$ by analyzing the intercept and slope of the plot (Rengaraj *et al.*, 2002; Banat *et al.*, 2000; Aksu and Yener, 2001; Khalid *et al.*, 2000). The following is a linear representation of the Langmuir isotherm model (Rengaraj *et al.*, 2002; Banat *et al.*, 2000; Aksu and Yener, 2001; Khalid *et al.* 2000):

$$1/q_e = 1/Q^o + 1/bQ^o 1/C_e$$

where maximal adsorption capacity (Q^o) and adsorption energy (b) are given in milligrams per milligram of solid (mg/mg). The intercept and slope of a line plot of

experimental data for $1/q_e$ against $1/C_e$ (Rengaraj *et al.*, 2002; Banat *et al.*, 2000; Aksu and Yener, 2001; Khalid *et al.*, 2000) can be used to figure out these constants.

Table 2. Isotherm model parameters.

Adsorbents	Freundlich			Langmuir			Reference
	K	$1/n$	R^2	Q^o	b	R^2	
Barley straw	0.032	0.389	0.99	0.067	1.017	0.98	Maleki <i>et al.</i> , 2010
Bagasse	0.11	0.62	0.98	0.41	0.46	0.99	Present study

Table 2, Fig. 7, and Fig. 8 demonstrate the values of the isotherm constants and the correlation coefficients. In comparing the Freundlich equation with the Langmuir isotherm equation, the latter is more accurate in capturing the equilibrium data. The sorption equilibrium data is almost perfectly described by the Langmuir and Freundlich equations, with R^2 values of 0.99 and 0.98, respectively. Increases in the Freundlich constant k indicate that phenol can be readily absorbed from an aqueous solution (Rengaraj *et al.*, 2002, Aksu and Yener, 2001). Compared to the phenol-barley straw

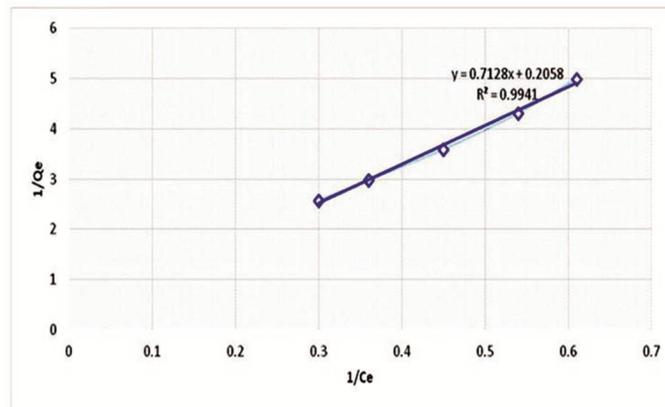


Fig. 7. Langmuir isotherm curve for removing 2-CP by the adsorption onto the bagasse.

system, the 2-CP-bagasse system (this study) had a greater k value for adsorption (Maleki *et al.*, 2010). The n value, which represents the sorption intensity, decreases. However, as demonstrated in Table 3, both the sorbents and the pollutants have n values that are sufficiently high to separate. When $1/n$ is not exactly 0, the sorbent's surface is not

perfectly smooth and uniform (Khalid *et al.*, 2000). The agro-waste bagasse's maximal sorption capacity under a uniform covering was calculated using the Langmuir isotherm model. As shown in Table 2, the 2-CP-bagasse system has a maximum sorption capacity of 0.41 mg/g, which is more than that of barley straw (0.067 mg/g) and carbonized beet pulp (0.064 mg/g), but less than that of activated rice husk (75.15 mg/g) and burned water hyacinth (30.49 mg/g) (Uddin *et al.*, 2008).

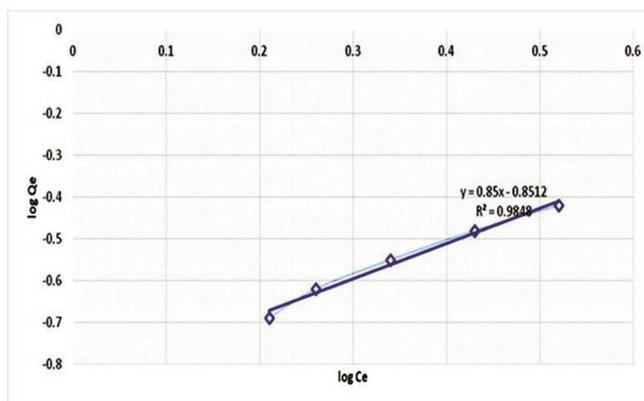


Fig. 8. Freundlich isotherm curve for removing 2-CP the adsorption onto the bagasse.

Desorption studies

Recovering the adsorbed material and regenerating the adsorbent are crucial steps in wastewater treatment. Hydrochloric acid, nitric acid, and sodium hydroxide solutions were used as eluents on trial to dissolve the 2-CP from the bagasse's surface. This desorption procedure was carried out using a batch procedure. 1.0 g of spent adsorbent after adsorption at pH 6 was shaken with 1M NaOH, 1M HCl, and 1M HNO₃ in a volume of 100 ml. It takes roughly 60 minutes to replenish the adsorbent. Single-step desorptive evaporation removed approximately 88.17%, 85.02%, and 77.30% of the adsorbed 2-CP from samples with an initial concentration of 5 mg l⁻¹. In the current study, alkaline solutions were shown to be more effective for desorption. The observed influence of pH is consistent with these considerations. The effectiveness of phenol desorption generally increases with increased desorption duration. So, the 2-CP was removed from the bagasse's surface with a sodium hydroxide solution.

The desorption (after biosorption) efficiency of 2-CP is calculated using the equation,

$$\text{Per cent desorption of 2-CP} = \frac{\text{Amount desorbed after desorption}}{\text{Amount sorbed before desorption}} \times 100$$

Conclusion

The current investigation demonstrated that waste bagasse an excellent approach to eliminating 2-CP from wastewater by absorbing it. Bagasse's adsorbent potential also represents a new frontier in discovering novel applications for biomaterial. The pH range of aqueous solutions that can be treated with bagasse is from 4.0 to 12.0. The Langmuir and Freundlich adsorption isotherms fit the experimental adsorption equilibrium data very well. Reviving adsorbed 2-CP with 1M NaOH allowed it to be used again. Because they are simple, easy to use, and easy to handle, the batch treatment systems proposed by our research group will be appropriate and suitable for removing organic compounds containing 2-CP from industrial wastewater. Bagasse, after desorbed, is clean enough to be utilized as fuel and contains no noxious substances.

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