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Phenol removal from aqueous medium using chemically modified banana peels as low-cost adsorbent

Ashraf Ali*, Khalid Saeed

Department of Chemistry, University of Malakand, Chakdara, Dir (Lower), Khyber Pakhtunkhwa, Pakistan, Tel. +92 3469449701; email: ashrafaliswati@gmail.com (A. Ali), Tel. +92 3239290054; email: Khalidkhalil2002@yahoo.com (K. Saeed)

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ABSTRACT

The removal of phenol from aqueous medium was investigated using chemically modified banana peels as adsorbent. Banana peels were alkali hydrolyzed at 100˚C for 3 h and then filtered and washed thoroughly with deionized water. The pulp was bleached by treating with $NaClO_3$ and glacial acetic acid. The bleached pulp was treated with Acrylonitrile, Fe^+/H_2O_2, and glacial acetic acid for grafting copolymerization. A comparative analysis of five adsorbents, untreated banana peels, acid hydrolyzed banana peels, bleached banana peels, alkali hydrolyzed banana peels, and grafted banana peels (GBPs) have also been carried out. It was found that GBPs have the highest adsorption capacity for phenol. The adsorption data are fully fitted with Langmuir isotherm model and follow second-order kinetic model. Thermodynamic study shows that the adsorption of phenol is exothermic and spontaneous. This study shows that chemically modified banana peels particularly GBPs can be used as an efficient and low-cost adsorbent for the removal of phenol from wastewater.

Keywords: Banana peel; Adsorption; Low-cost; Phenol; Acrylonitrile; Grafting; Equilibrium; Thermodynamics; Kinetics

1. Introduction

Water pollution is one of the major environmental threats in the world due to rapid industrialization. Various industries such as oil refineries, phenolic resins industries, ceramic plants, and petrochemical plants discharged large amount of phenol and its derivatives into the water. Phenol and its derivatives are toxic to humans, animals, and aquatic life, increase the oxygen demand of receiving water, and change the taste and odor of drinking water. Phenol is mutagenic, causes tissue erosion, paralysis of CNS, damage the liver, kidney, and pancreas in human bodies [1–3]. In portable water, the permissible concentration of phenol is 1 $\mu g\ L^{-1}$ according to the recommendation of World Health Organization. The routes of exposure of phenol are breathing phenol-contaminated air and drinking or skin contact with phenol-contaminated water. The problem of considerable contamination of the aqueous environment with organic pollutants still requires the development of quick and simple methods for the removal of these compounds [4–8]. Phenol wastes are found in pharmaceuticals, paints, synthetic resins, petrochemicals, and coal gas. Phenol removal from wastewater has been carried out by several methods such as solvent extraction, dialysis,

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*Corresponding author.

microbial degradation, ion exchange, reverse osmosis, membrane process, and adsorption by activated carbon [9–15]. Among these technologies, adsorption is found suitable for all classes of organic compounds such as dyes, surfactants, and phenols. The viability of adsorption depends on the cost, stability, and regeneration of the adsorbent. Removal of organic pollutants by adsorption onto activated carbon has been used successfully for a long time, but the high cost of activated carbon prompted search for other low-cost adsorbents [16–20].

The high cost of activated carbon and other conventional adsorbents stimulate the researchers to use low-cost agricultural products and by-products as adsorbents. Nowadays, there is a growing interest in using low-cost materials such as agricultural by-products, fruit peels and clays for the adsorption of heavy metals and organic pollutants such as dyes and phenols. A wide variety of materials such as peat, silica, activated clay, natural minerals, alum sludge, chicken feathers, and banana peels are used as low-cost adsorbents for the removal of toxic heavy metals and organic pollutants from water [21–28]. Cellulosic and lingocellulosic materials are used by several researchers as efficient adsorbents due to their high adsorption capacity for metal ions and organic pollutants [29–31]. The agricultural products and by-products contain cellulose, lignin, pectin, and several other compounds which have potential functional groups such as hydroxyl, carbonyl, amino, carboxylic, and alkoxy which have great affinity for the metal ions, dyes, phenols, and organic acids [32,33]. The adsorption capacities of these adsorbents are reasonable when used as such without any chemical treatment, but not much better. In raw form, the functional groups of these adsorbents (agricultural products and by-products) are not free and several viscous compounds such as lignin and pectin occupy the pores of cellulose fibers [34]. The active groups of these adsorbents are not able to interact with the adsorbates, so their adsorption capacities are lower than chemically treated agricultural adsorbents. Several research groups have used the chemically treated agriculture waste as potential adsorbents and their adsorption capacities are much better than raw adsorbents [35,36].

Grafting copolymerization onto cellulose introduces side chains which alter the characteristics of the raw material without destroying its whole structure. Cellulosic materials such as wood, pulp, paper, cotton, rayon and cellophane have been subjected to grafting copolymerization with vinyl or amino monomers by several researchers to produced grafted copolymerized adsorbents for heavy metals, phenols, and dyes removal from aqueous solutions [37–40].

Banana is one of the world's most important crops grown by more than 130 countries. India, China, Uganda, Philippines, Ecuador, Brazil, Indonesia, Columbia, Cameroon, and Ghana were the top 10 bananas producing countries in the world in 2012. In India, the banana production in 2012 was about 24.9 million ton while the total world production of banana during 2012 was about 139.2 million ton [41,42]. Several research groups have used raw and chemically treated banana peels and banana stalks for the removal of dyes, organic pollutants, and toxic heavy metal ions from aqueous solutions and industrial wastewater [43–45]. In our previous work, we have used raw and chemically treated banana peels for the removal of Cr(VI) and Mn(II) ions from aqueous medium, and it was found that chemically treated banana peels have much better adsorption efficiency for both ions than untreated banana peels (UTBPs) [46].

In the present study, the adsorption of phenol from aqueous solution has been carried out using UTBPs, acid hydrolyzed banana peels (AcBPs), bleached banana peels (BBPs), alkali hydrolyzed banana peels (AlBPs), and grafted banana peels (GBPs) as adsorbents. The results showed that the adsorption capacities of chemically treated banana peels are much higher than UTBPs. The enhancement in adsorption capacity of banana peels after chemical treatment may be due to the removal of viscous compounds like lignin and pectin, and the exposure of cellulose functional groups to interact with the adsorbate molecules. The incorporation of arylonitrile ($CH_2{=}CH{-}C{\equiv}N$) monomer to cellulosic skeleton also enhanced its interaction with adsorbate molecules.

2. Materials and methods

2.1. Preparation of adsorbent

Banana peels were collected from the northern part of Pakistan and dried in shade for 80 h. The dried peels were hydrolyzed with 10% NaOH in round bottom flask under reflux at 105˚C for 3 h. The pulp was washed thoroughly with distilled water to remove lignin and pectin and dried in oven at 105˚C for 24 h.

2.2. Modification of banana peel

2.2.1. Acid hydrolysis of banana peel

Raw banana peels (100 g) were taken in a round bottom flask of 1,500 mL capacity and 10% HCl was added to the wet sample (liquor ratio 1:15). The contents were heated under reflux for continuous 3 h. The contents were cooled and washed with distilled water until the sample was neutralized. In pre-hydrolysis (acid hydrolysis), the glycoside linkage in hemicelluloses and lignin de-polymerizes through α and β-aryl ether cleavage to give soluble products [47].

2.2.2. Alkaline hydrolysis of banana peel

Banana peels (100 g) were treated with 10% NaOH solution (1,000 mL) under reflux for 3 h, followed by washing with distilled water till neutrality. During the alkaline hydrolysis, the cellulose long chains are broken down into smaller monomers [48].

2.2.3. Bleaching of banana peel

Bleaching was carried out by treating 60 g pulp with 7.5 g sodium chlorate and glacial acetic acid (2.5 mL). The contents were heated in water bath and finally washed with distilled water till it became neutral.

2.2.4. Grafting copolymerization of acrylonitrile monomer

Bleached banana pulp (50 g) was subjected to grafting in the presence of 5 g ferric sulfate in 750 mL distilled water. The reagents were treated at 35°C for 15 min, filtered, washed with distilled water three times, and dried at 105°C for 24 h. The dried cakes were treated with hydrogen peroxide (15 mL) and acrylonitrile (5 mL) at 40°C for 2.5 h, washed, filtered, and dried at 105°C. After grafting copolymerization banana peels were sealed in cotton bags and soxhlet extracted with anhydrous toluene at 100°C. The GBPs were washed with 2-propanol and acetone, respectively, and dried at 105°C under vacuum.

2.3. Calculation of grafting parameters

Grafting yield, graft conversion, monomer to polymer conversion, and homopolymer formation during reaction and grafting efficiency were calculated as follow:

$$\text{Graft yield }(\%) = \frac{(B-A)}{A} \times 100 \tag{1}$$

$$\text{Graft conversion }(\%) = \frac{(B-A)}{D} \times 100 \tag{2}$$

$$\text{Total conversion (Monomer to polymer)}(\%) = \frac{(C-A)}{D} \times 100 \tag{3}$$

$$\text{Homopolymer formation }(\%) = \frac{E}{D} \times 100 \tag{4}$$

$$\text{Grafting efficiency }(\%) = \frac{(B-A)}{(C-A)} \times 100 \tag{5}$$

A = weight of original cellulose (g), B = weight of product (g) after copolymerization and extraction, C = weight of product (g) after copolymerization, D = weight of monomer (g), and E = weight of homopolymer (g).

2.4. Adsorption of phenol

The adsorption studies were carried out using phenol test solution (200 mg/L), with 1 g of each adsorbent UTBPs, AcBPs, BBPs, AlBPs, and GBPs separately, in 500 mL flask at 30°C at pH 8.0 with continuous stirring for 3 h, the contents of each flask were filtered and the phenol concentration in the filtrate was determined by using Nicolet evolution 300, UV–visible spectrophotometer. Color was developed using aminoantipyrine method, and photometric measurement was made against the blank. The amount of phenol adsorbed per gram of adsorbent was calculated by using, (Eq. (6)):

$$q_e = \frac{V(C_o - C_e)}{W} \tag{6}$$

where q_e is the amount of phenol adsorbed (mg/g), V is the solution volume (L), W is the adsorbent dose (g), and C_o and C_e are the initial and equilibrium phenol concentration in solution, respectively. The percent phenol removal was calculated using (Eq. (7)):

$$\text{Adsorption }(\%) = \frac{(C_o - C_e)}{C_o} 100 \tag{7}$$

2.5. Scanning electron microscope characterization

Scanning electron microscopy (SEM) was carried out to observe the changes in surface morphology of adsorbents after adsorption. The SEM images of banana peels were taken by HITACHI (Tokyo Japan) S-4200 field emission scanning electron microscopy (FE-SEM).

2.6. Adsorption isotherm studies

Adsorption isotherm studies were carried out by computing the adsoption equilibrium data by

Freundlich and Langmuir isotherm models. The Freundlich isotherm model explains the interaction between adsorbate molecules and adsorbents with multilayer adsorption on heterogeneous surfaces [49]. It shows that if the concentration of adsorbate increases, its accumulation will also increases on the adsorbent surface. The Langmuir Adsorption isotherm explain that the adsorption onto the adsorbent surface will be monolayer, the adsorption energies will be equivalent and there will be no interaction between adsorbed molecules [50,51]. The regression coefficient values were judged to find the applicability of these models to the adsorption data. Origin pro-8 and Ms. Excel were used for linear regression calculations.

2.7. Kinetics studies

Phenol (100 mg/L) were taken in four conical flasks and 1 g of each adsorbent, UTBPs, AcBPs, BBPs, AlBPs, and GBPs were added separately and shacked continuously. After different time intervals, the flasks were removed from the shaker, filtered, and analyzed. It was noted that adsorption of phenol on modified banana peel was increased with increase in shaking time until the equilibrium established. The optimum adsorption equilibrium time was found to be 3 h. This optimized equilibrium time was used for further adsorption studies.

3. Results and discussion

3.1. Effect of initiator (Fe^{2+}) concentration on grafting copolymerization

The effect of initiator (Fe^{2+}) concentration on grafting copolymerization is shown in (Fig. 1). The grafting yield was increased with increasing initiator ($FeSO_4$) concentration from 0.5 g to 3.5 (g/10 g) of the bleached pulp. The increase in grafting yield occurred due the production of more active grafting sites on cellulosic back bone. Increasing the initiator concentration beyond 4 g decreased the grafting yield because most of the active sites were occupied by the initiator and monomers combine to form bulk polymers i.e. homopolymers [52,53].

3.2. Effect of temperature on grafting copolymerization

The effect of temperature on grafting copolymerization is shown in (Fig. 2). Results show that increasing the temperature up to 90°C increases the diffusion of monomers through cellulose chains, swelling of cellulose, and the rate of initiation and propagation of the grafting reaction. The grafting copolymerization decreases above 90°C due to the oxidation of free radicals, and mutual termination of growing macro-radicals favors more homopolymer formation [54,55].

3.3. Effect of acrylonitrile concentration on grafting copolymerization

From (Fig. 3), it is obvious that increasing the acrylonitrile concentration up to 3 g increase the grafting yield due to the increasing the number of monomer molecules which react with the available active sites of cellulose to form grafting copolymers. Further increasing monomer concentration above 3 g, increases the viscosity of reaction mixture and retards the penetration of monomer to the active sites of cellulosic backbone due to formation of bulk polymer and grafting yield decreases [56,57].

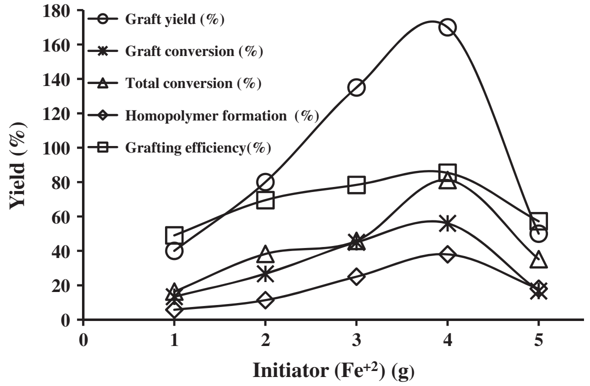

Fig. 1. Effect of initiator concentration on grafting copolymerization.

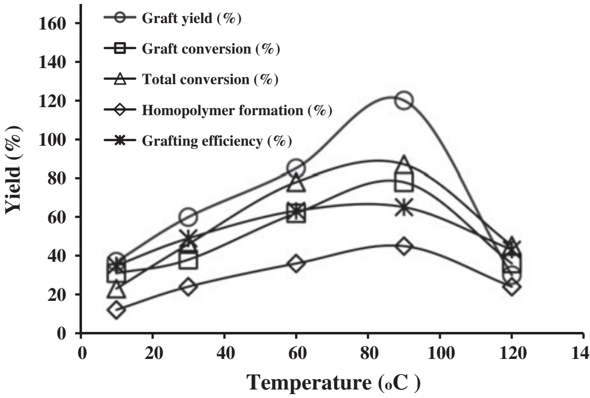

Fig. 2. Effect of temperature on grafting copolymerization.

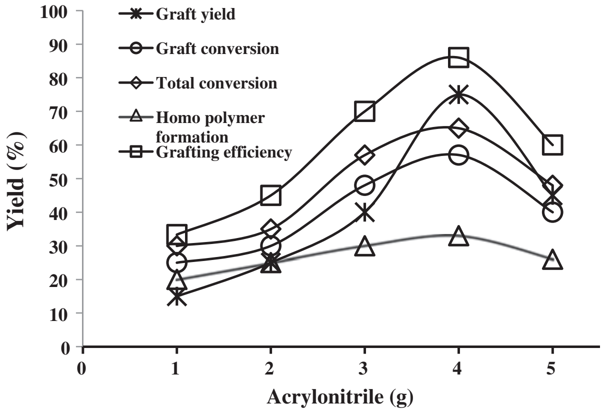

Fig. 3. Effect of monomer ratio on grafting copolymerization.

3.4. *Effect of time on grafting*

The graft yield increases up to 3 h, where the equilibrium established as shown in (Fig. 4). Initially, the monomers interact with the cellulosic skeleton to form copolymers and the active site of cellulosic skeleton fully saturate in 3 h. Further increase in reaction time has no effect on grafting yield as the available active sites have saturated and the equilibrium has established in 3 h [58,59].

3.5. *Scanning electron microscopic (SEM) studies*

The SEM images of GBPs before and after adsorption are shown in Fig. 5. The SEM micrographs of GBPs in Fig. 5(A) show the open pores and fibers before adsorption, because during chemical treatment, the lignin, pectin, and other viscous compounds are removed. After the adsorption, the pores and caves are occupied by phenol molecules and the surface become smooth so the surface morphology of GBPs has changed after the adsorption of phenol as shown in Fig. 5(B). The same changes in surface morphology after adsorption are also observed for (UTBPs), acid (AcBPs), (BBPs), and (AlBPs). The similar change in morphology after adsorption onto banana peels are also reported by other researchers [44].

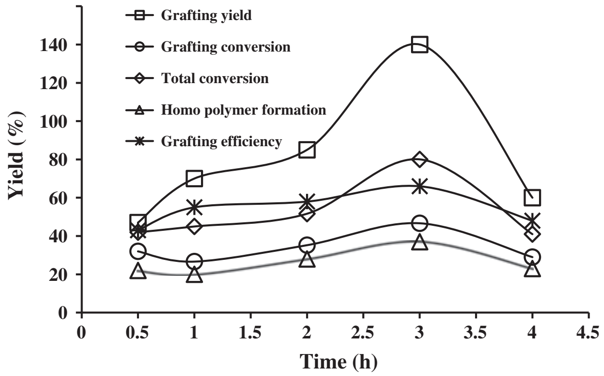

Fig. 4. Effect of time on grafting copolymerization.

3.6. *Effect of concentration on phenol removal*

Effect of concentration on phenol removal was investigated during batch experiments and the results are presented in (Table 1). Phenol solutions of different concentrations (50–90 mg/L) were separately agitated at 250 rpm with 1 g/L of each adsorbent (UTBPs), (AcBPs), (BBPs), (GBPs), and (AlBPs) at 30°C for 3 h. The results show that increasing the solution concentration up to 70 mg/L increases its adsorption until the equilibrium establish. Further increasing the phenol concentration up to 90 mg/L has brought no significant change as the available sites on adsorbents have saturated with adsorbate molecules. At lower concentration, the ratio of number of moles of phenol to the surface area of adsorbents is large and adsorption take place without any interruption till the equilibrium [60,61].

3.7. *Effect of adsorbent dose on phenol removal*

The effect of adsorbent dose on phenol removal is shown in Table 2. Different amount (1–5 g L^{-1}) of each adsorbent (UTBPs), (AcBPs), (BBPs), (GBPs), and (AlBPs) were taken at constant pH 8, solution concentration 70 mg/L and equilibrated for 3 h at 300 rpm. Results show that the adsorption increases from 27% at lower adsorbent dose (1 g L^{-1}) to 96% at higher adsorbent dose (4 g/L). Increasing the adsorbents dose from 1 g/L increases the adsorption of phenol because the number of active sites increases for phenol molecules. Further increasing the adsorbent amount above (4 g/L) has no effect on adsorption of phenol, because the available phenol molecules in solution have already been picked up by adsorbents [62].

3.8. *Effect of contact time on phenol removal*

Fixed amount (1 g/L) of each adsorbent (UTBPs), (AcBPs), (BBPs), (GBPs), and (AlBPs) were taken separately at 25°C, pH 8, and solution concentration 70 mg/L were agitated at 300 rpm from 1 to 6 h. Results in Table 3 show that phenol adsorption has increased with increasing the shaking time from 1 to

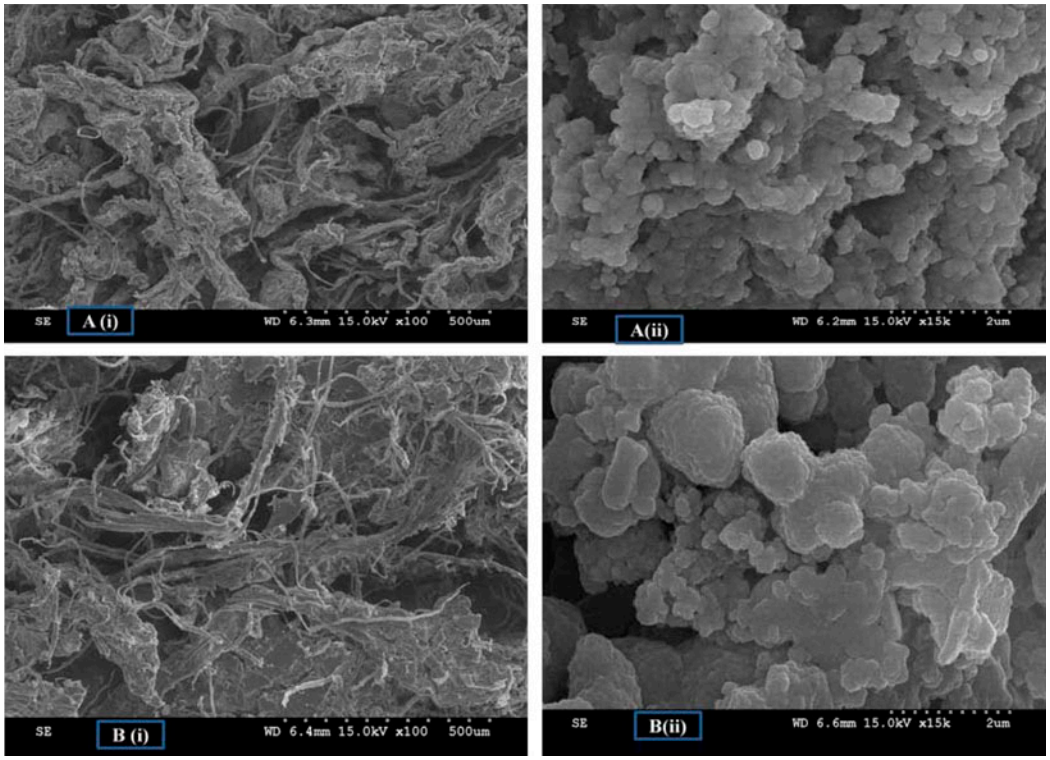

Fig. 5. (A(i)) SEM images of (GBPs) before phenol adsorption (A(ii)) close view (B(i)) SEM images of (GBPs) after phenol adsorption (B(ii)) close view.

Table 1
Effect of concentration on phenol removal from aqueous solution by UTBPs, AcBPs, BBPs, GBPs, and AlBPs

Phenol (mg/L)	UTBPs (%)	AcBPs (%)	BBPs (%)	GBPs (%)	AlBPs (%)
50	53	62	57	70	64
60	67	78	72	84	80
70	78	90	85	95	87
80	78	90	85	95	87
90	78	90	85	95	87

Table 2
Effect of adsorbent dose on phenol removal from aqueous solution by UTBPs, AcBPs, BBPs, GBPs, and AlBPs

Adsorbent dose (g)	UTBPs (%)	AcBPs (%)	BBPs (%)	GBPs (%)	AlBPs (%)
1.0	29	24	23	30	28
2.0	47	51	50	58	54
3.0	65	73	70	82	75
4.0	70	84	81	96	83
5.0	70	84	81	96	83

3 h. Further increase in shaking time up to 6 h brings no significant change in the equilibrium concentration. The increase in phenol removal with increase in shaking time is due to the increase in interaction chances between the sorbent surface and phenol molecules which may be fully saturated in 3 h [63].

Table 3
Effect of contact time on phenol removal from aqueous solution by UTBPs, AcBPs, BBPs, GBPs, and AlBPs

Time (h)	UTBPs (%)	AcBPs (%)	BBPs (%)	GBPs (%)	AlBPs (%)
1	22	34	27	29	38
2	39	45	49	58	54
3	50	64	68	72	70
4	66	70	72	90	82
5	72	81	79	94	88
6	72	81	79	94	88

3.9. Effect of pH on phenol removal

Different pH from 2 to 10 were tested for each adsorbent at phenol concentration 70 mg/L and agitated with 300 rpm at 25˚C for 3 h. The phenol adsorption was lower at low pH because at lower pH the H^+ ions in the solution interact with the negatively charged groups of adsorbents (UTBPs), (AcBPs), (BBPs), (GBPs), (AlBPs), and decrease its interaction with phenol molecules. Change in pH affects the surface charge of the adsorbents and the degree of ionization of the phenol, increasing the pH up to 8 has increased the phenol removal (Table 4). Further increase in the solution pH from 8, the removal of phenol decreases because at higher pH, OH^- ion concentrations are much higher, which increase the hindrance to the diffusions of phenol ions and thus reduce its adsorption [64,65].

3.10. Comparison of phenol removal by UTBPs, AcBPs, BBPs, AlBPs, and GBPs

The results in Fig. 6 show that the adsorption of phenol on UTBPs is lower than other adsorbents like AcBPs, BBPs, AlBPs, and GBPs. In UTBPs, the peptic materials and lignin have blocked the pores and reactive sites of cellulose. The phenol removal capacity of BBPs is much lower than AlBPs and GBPs, because during bleaching, the surface active groups are removed which are responsible for binding the adsorbate molecules. The adsorption capacity of AlBPs has the higher phenol removal than UTBPs, AcBPs, and BBPs, because during alkali hydrolysis, the lignin and peptic compounds completely removed from the adsorbents. Alkali treatment breaks the cellulose main skeleton and exposes the reactive functional groups which facilitate the interaction between phenol molecules and adsorbents. Similarly, the phenol removal capacity of GPBs is highest among all adsorbents due to the additional side chain (CH_2=CH–C≡N) which

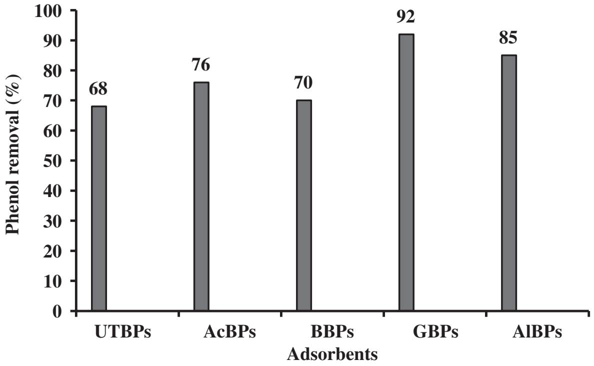

Fig. 6. Comparison of phenol removal by UTBPs, AcBPs, BBPs, GBPs, and AlBPs.

Table 4
Effect of pH on phenol removal from aqueous solution by UTBPs, AcBPs, BBPs, GBPs, and AlBPs

pH	UTBPs (%)	AcBPs (%)	BBPs (%)	GBPs (%)	AlBPs (%)
2.0	25	33	39	34	30
4.0	40	50	54	52	41
6.0	52	63	61	73	70
8.0	72	74	77	96	85
10.0	65	68	60	75	67
12.0	55	59	55	67	51

has increased its interaction with adsorbate molecules. The incorporation of arylonitrile (CH_2=CH–C≡N) monomer to cellulosic skeleton enhanced its interaction with phenol [66,67].

3.11. Adsorption isotherm study

In the current study, the Freundlich and Langmuir adsorption models were used to study the interaction of phenol with the selected adsorbents (UTBPs, AcBPs, BBPs, GBPs, and AlBPs).

3.11.1. Freundlich adsorption isotherm

The linear form of Freundlich adsorption isotherm is given in (Eq. (8)) [68].

$$\ln q = \ln K + \frac{1}{n} \ln C_e \tag{8}$$

By plotting $\ln q$ vs. $\ln C_e$ linear plots were obtained with slope $1/n$ as shown in (Fig. 7). The "n" and "K" (adsorption capacity) for phenol adsorption were calculated from (Fig. 7). The values of "n" show that surfaces are heterogeneous and possess great affinity for phenol, the adsorbents are effective and adsorption have been taken place.

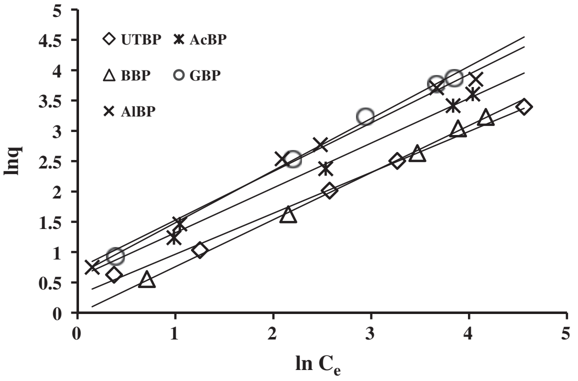

Fig. 7. Freundlich adsorption isotherm for phenol adsorption onto UTBPs, AcBPs, BBPs, AlBPs, and GBPs.

3.11.2. Langmuir adsorption isotherm

The linear form of Langmuir adsorption isotherm is given in (Eq. (9)):

$$\frac{C_e}{q} = \frac{1}{q_{\max} K} + \frac{C_e}{q_{\max}} \tag{9}$$

By plotting C_e/q against C_e, straight lines were obtained with intercept $1/q_{\max}K$ and slope $1/q_{\max}$ where $q_{\max}$ is the amount of adsorbate (mg/g) corresponding to a complete monolayer coverage and K (L/g) is the binding energy constant (Fig. 8). The isotherm constants were calculated from the linear regression of the experimental data. The isotherm constants and regression values (R^2) in Table 5, which shows that the adsorption data are well fitted by Langmuir isotherm model.

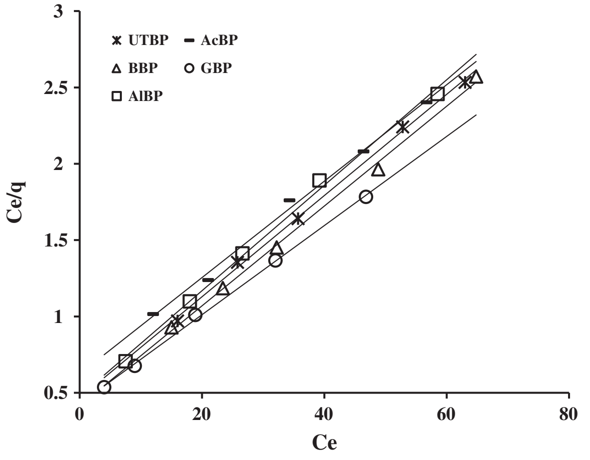

Fig. 8. Langmuir adsorption isotherms for phenol adsorption onto UTBPs, AcBPs, BBPs, AlBPs, and GBPs.

Table 5
Freundlich and Langmuir isotherms parameters for phenol adsorption onto UTBPs, AcBPs, BBPs, GBPs, and AlBPs

		Adsorbents				
Isotherm	Parameters	UTBPs	AcBPs	BBPs	GBPs	AlBPs
Freundlich	$1/n$	0.6370	0.9394	0.7719	0.9668	0.7910
	K_F (mg/g)	3.84060	3.6804	3.3271	3.911	3.1710
	R^2	0.991	0.992	0.999	0.995	0.991
Langmuir	$q_{\max}$ (mg/L)	23.9808	32.2580	21.2765	43.1034	34.5161
	K (L/mg)	0.9186	0.9046	0.9124	0.8968	0.9012
	R^2	0.998	0.997	0.987	0.992	0.984

3.12. Adsorption kinetics

In this study pseudo-first-order, pseudo-second-order kinetics, and intraparticle diffusion models were used to test the experimental data of the adsorption of phenol by UTBPs, AcBPs, BBPs, AlBPs, and GBPs.

3.12.1. Pseudo-first order model

The linear form of Lagergren pseudo-first-order rate expression is given by (Eq. (10)):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{10}$$

where q_e and q_t are the amount of phenol adsorbed (mg/g) on adsorbent at equilibrium and at time t, respectively and K_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The plot of $\ln(q_e - q_t)$ vs. t, gives a straight lines as shown in the (Fig. 9). The rate constant k_1 (min^{-1}) can be calculated from the slop of the linear plots [69,70].

3.12.2. Pseudo-second-order model

The linear form of pseudo-second-order model may be described as in (Eq. (11)):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

where K_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order kinetic equation, q_e and q_t are the amount of phenol adsorbed (mg/g) onto the selected adsorbents (UTBPs, AcBPs, BBPs, AlBPs, and GBPs) at equilibrium and at time t, respectively. The rate constant K_2 (g mg^{-1} min^{-1}) and equilibrium adsorption capacity q_e were calculated from the slope and intercept of the linear plot of t (time) vs. t/q_t (Fig. 10). The results show that the second-order model is more suitable than first-order model to describe the adsorption kinetics of phenol onto UTBPs, AcBPs, BBPs, AlBPs, and GBPs.

3.12.3. Intraparticle diffusion

The intraparticle diffusion model was used to investigate the diffusion mechanism of phenol into the adsorbents. The adsorbate species transferred from solution bulk into the solid phase during intraparticle diffusion process [71]. The intraparticle diffusion can be represented as, (Eq. (12)):

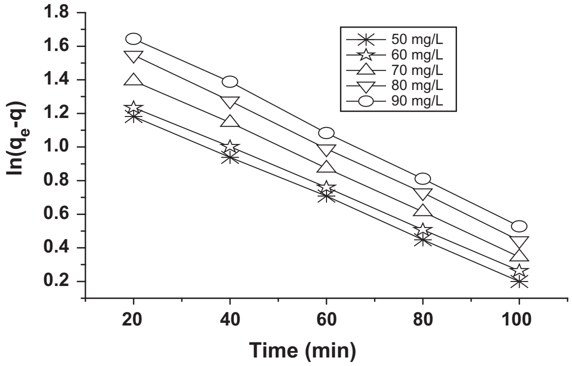

Fig. 9. Pseudo-fist order plot for phenol adsorption onto GBP.

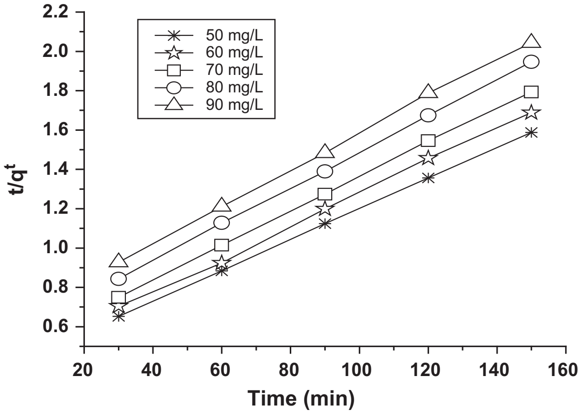

Fig. 10. Pseudo-second order plot for phenol adsorption onto GBP.

Table 6
Pseudo-first-order, pseudo-second-order, and intraparticle diffusion values for phenol adsorption onto GBPs

	Pseudo-first-order calculated			Pseudo-second-order calculated			Intraparticle calculated	
C_o (mg L^{-1})	q_e (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (mg g^{-1})	K_2 (g mg^{-1}min^{-1})	R^2	K_i (mg g^{-1} min$^{-1/2}$)	R^2
50	34.18	0.0498	0.993	37.14	0.0425	0.997	1.738	0.9969
60	48.26	0.0562	0.997	51.68	0.0480	0.996	2.375	0.9971
70	62.32	0.0694	0.998	64.72	0.0531	0.999	3.832	0.9990
80	71.91	0.0615	0.998	75.35	0.0487	0.997	4.290	0.9882
90	82.33	0.0502	0.997	84.29	0.0463	0.998	4.543	0.9959

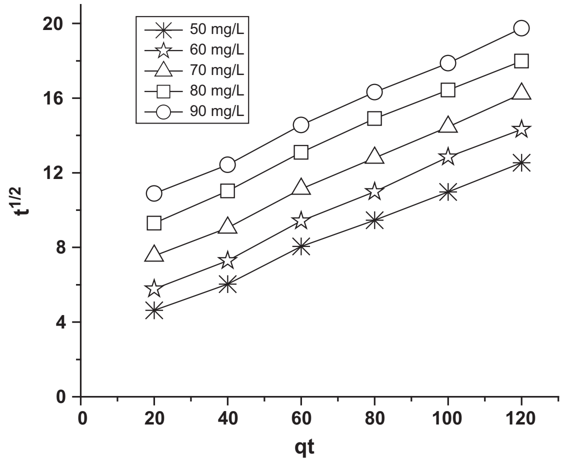

Fig. 11. Intra-particle diffusion plot of phenol adsorption onto GBPs.

$$q_t = K_P t^{0.5} + C \tag{12}$$

where q_t is the amount of phenol adsorbed onto the adsorbents (UTBPs, AcBPs, BBPs, AlBPs, and GBP) at time t (mg g^{-1}), K_P (mg g^{-1} min$^{0.5}$) is the intraparticle diffusion rate constant, and C is the intercept. The boundary layer effect is directly proportional to the intercept and it can be determined from the values of intercept. The kinetic parameters of phenol onto these selected adsorbents are given in (Table 6). The plots are linear, which show the applicability of all three models. From (Table 6), it is clear that R^2 for the pseudo-second-order kinetic model is 0.99 and the calculated q_e values are nearly close to the experimental q_e values. The intraparticle diffusion rate increased constantly with increase in phenol concentration as shown in (Fig. 11).

3.13. Thermodynamic studies

The thermodynamic parameters such as entropy change (ΔS), enthalpy change (ΔH), and Gibb's free energy (ΔG) were determined to evaluate the feasibility and nature of adsorption by using (Eq. (13)):

$$K_c = \frac{C_a}{C_s} \tag{13}$$

where C_a and C_s are the equilibrium concentration of solutes on adsorbent and in solution, respectively, and K_c is the equilibrium constant. The Gibb's free energy change (ΔG) is related to equilibrium constant by the following equation, (Eq. (14)):

$$\Delta G = -RT \ \ln K_c \tag{14}$$

The Gibb's free energy change is also related to entropy change (ΔS) and enthalpy change (ΔH) at constant temperature by the using (Eq. (15)):

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{15}$$

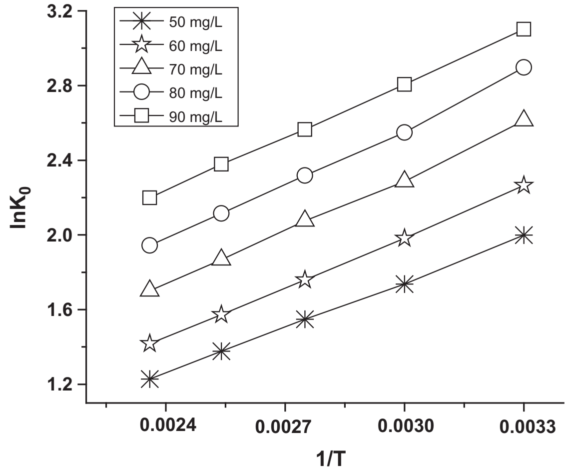

Fig. 12. Von't Hoff plot of temperature effect on phenol initial concentration.

Table 7
Equilibrium constants and thermodynamic parameters values for phenol adsorption onto UTBPs, AcBPs, BBPs, AlBPs and GBPs

Adsorbents	$K_0 \times 10^{-4}$ (m^3 mol^{-1})				$-\Delta G^0$ (kJ mol^{-1})				ΔS^0 (kJ mol^{-1} K^{-1})	ΔH^0 (J mol^{-1})
	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K		
UTBPs	46.47	42.32	38.90	35.25	43.29	45.98	48.34	52.30	0.076	48.93
AcBPs	57.87	53.46	48.95	43.92	44.51	47.14	51.67	55.20	0.087	60.27
BBPs	52.34	47.18	44.53	40.36	42.87	45.90	47.10	48.62	0.089	55.81
AlBPs	59.78	55.14	50.32	45.75	44.83	49.25	52.90	57.43	0.089	60.30
GBPs	65.70	62.40	54.69	50.03	54.30	58.86	61.34	63.67	0.097	67.70

The values of ΔH and ΔS were calculated from the plot of K_c vs. $(1/T)$ as shown in (Fig. 12). The values of K_c, ΔH, ΔG, and ΔS for the adsorption of phenol onto AcBPs, BBPs, AlBPs, and GBPs at various temperatures are given in (Table 7). The negative values of ΔG and ΔH show that the adsorption is feasible, spontaneous, and exothermic in nature [72]. The negative values of ΔG implied that the adsorption process is spontaneous and does not require an external energy source. The ΔG values decreases with increase in temperature indicating the decline in the feasibility of adsorption at higher temperature. The ΔS values are positive, which suggested that the randomness increased at solid/liquid interface during the adsorption of phenol onto UTBPs, AcBPs, BBPs, AlBPs, and GBPs.

4. Conclusion

Agricultural products and by-products have the potential functional groups which have great affinity for heavy metals and organic compounds like dyes and phenols. The efficiency of the agricultural adsorbents can be further increased by chemical treatment such as acid and alkali hydrolysis, and grafting copolymerization. Chemical treatment of banana peels with dilute acids, bases, or bleaching agents such as $NaClO_3$ remove the peptic and viscous compounds like lignin, pectin, etc. which are embedded in cellulose fibers. The adsorption efficiency of chemically treated and GBPs is much higher than untreated peels. The adsorption capacity of GBPs for phenol is much higher than other adsorbents (UTBPs, AcBPs, BBPs, and AlBPs), which means that the incorporation of ($–CH_2=CH–C\equiv N$) group onto cellulosic chain has increased its interaction with phenol. The grafting yield depends upon initiator ($FeSO_4$) amount, temperature, monomer (acrylonitrile), and time. Among these five adsorbents, GBPs have highest adsorption capacity for phenol (92%). The order of phenol removal by these adsorbents is GBPs > AlBPs > AcBPs > BBPs > UTBPs. Owing to their high adsorption efficiency and low cost, GBPs, AlBPs, and AcBPs can be used as an alternative to the expansive activated carbon for the removal of phenol and its derivatives from wastewater.

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