

Biosorption of Phenol and Cyanide from Synthetic/Simulated Wastewater by Sugarcane Bagasse—Equilibrium Isotherm and Kinetic Analyses

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Abstract Sugarcane bagasse biosorbents were tested for biosorption of phenol and cyanide from synthetic/simulated wastewater. The influence of pH, biosorbent dose, temperature, contact time, and initial concentration of phenol and cyanide was investigated. At an optimum temperature 30 °C, pH 7, and the biosorbent dose of 40 g/L, 66.78% phenol and 79.30% cyanide were removed from binary aqueous solution containing 300 mg/L of phenol and 30 mg/L of cyanide. The equilibrium state was achieved after about 34 and 32 h, respectively, for phenol and cyanide at a temperature of 30 °C. The extended Freundlich model fits the binary equilibrium data suitably for both phenol and cyanide. The kinetic modeling results showed that fractal-like models and Brouser–Weron–Sototlongo for phenol and cyanide were capable to provide realistic explanation of biosorption kinetic. Biosorption of phenol and cyanide followed pseudo-second-order kinetics, indicating chemisorption to be the mechanism of biosorption. The present study provides a new insight for the removal of phenol and cyanide onto sugarcane bagasse.

Keywords Cyanide · Isotherm modeling · Kinetic modeling · Phenol · Sugarcane bagasse

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Introduction

Phenol and cyanide are discharged into an environment from numerous sources such as coke, iron–steel, pesticide, petroleum refining, mining, electroplating, wood-preserving chemicals, pharmaceuticals, and explosive-manufacturing industries [1–7]. Phenol and cyanide are measured persistent environmental pollutants, since they cannot degrade naturally. Exposure to even low concentrations of cyanide can cause heart pains, coma, breathing disorders, headaches, and even death. On the other hand, phenol exposure can lead to eye and skin injuries, headache, vomiting, lung, liver, kidney, and heart damage ultimately leading to death [8]. Therefore, it is important to remove phenol and cyanide from industrial wastewater and discharges. Both phenol and cyanide enter into water bodies due to unselective disposal of wastes from the industries [2, 5, 9]. Due to poisonous nature and environmental effects of phenol and cyanide, there are increasing concerns for the removal of these pollutants from wastewaters [10–14]. The concentration of phenol and cyanide in the wastewater generated from industries is usually much above the allowable limit specified by environmental protection agencies. Therefore, environmental protection agencies of many countries have suggested acceptable limit for phenol and cyanide in effluent. US Environmental Protection Agency (US EPA) and Minimal National Standard (MINAS) of Central Pollution Control Board (CPCB) limits for phenol in effluent as 0.5 mg/L and for cyanide as 0.2 mg/L [2–5].

Various treatment technologies have been suggested for elimination of phenol and cyanide. These methods include such as biosorption, ion exchange, leaching, oxidization, precipitation, biodegradation, membrane separation, and solvent extraction. Among these treatment techniques, biosorption using agricultural waste material has increased significant

attention because of its low cost, high efficiency, ease of handling, and more accessibility [12, 15]. Biosorption process has been considered by many researchers as a substitute to conventional treatment methods for the elimination of phenol and cyanide from wastewater [5, 11, 12, 16].

Most of the studies revealed that agricultural waste either in natural form or modified form is highly effective for the removal of pollutants. Even more notably, agricultural wastes have usually minor carbon footprint in their consumption, comparatively free from extensive price variations. However, in current years, sugarcane bagasse (*Saccharum officinarum* L.), the solid fibrous material, generating after crushing of the sugarcane stalk and juice extracting, has established rare commercial uses. Some literature has been made to directly use sugarcane bagasse as an adsorbent for the wastewater treatment [15]. The sugarcane bagasse was used for the biosorption of phenol and cyanide from synthetic/simulated aqueous solution. The ability of sugarcane bagasse to eliminate phenol and cyanide was examined as functions of pH, biosorbent dose, contact time, and initial concentration. The kinetic data of biosorption studies were verified using 14 kinetic models. The equilibrium data of biosorption studies were confirmed using five mono-component isotherm models and six binary component isotherm models. The field emission-scanning electron microscopy (FE-SEM) and Fourier transform infrared (FTIR) analyses before and after biosorption of phenol and cyanide onto sugarcane bagasse were also carried out to estimate the adsorption mechanism. The proposed model provides a better description of the biosorption of phenol and cyanide in the liquid phase. It is our belief that till date, our group has employed this biosorbent for simultaneous biosorption of phenol and cyanide in the liquid phase.

The purposes of the current study, distributed into four parts, were (1) to characterize the prepared fresh biosorbent (sugarcane bagasse) before and after loading with SEM and FTIR; (2) to examine the influence of operating parameters, viz., pH, contact time, biosorbent dose, temperature, and initial concentration for eliminating phenol and cyanide from synthetic/simulated wastewater; (3) to estimate the kinetics and mechanism of present biosorption process; and (4) to study the isotherms of biosorption to determine the mechanism of biosorption process.

Materials and Methods

Reagents

All AR-grade chemicals were used without further treatment and supplied by HiMedia Laboratories Pvt. Mumbai, India. Stock solution containing 100 mg/L cyanide was prepared by dissolving 0.0189 g of NaCN in 1 L of Millipore water (Q-H₂O, Millipore Corp. with resistivity of 18.2 MX cm). Stock

solution comprising 1000 mg/L of phenol was prepared by dissolving 1 g of pure phenol crystal in 1 L of Millipore water. The test solutions of various concentrations were prepared by diluting the stock solution [14].

Biosorbent Collection and Preparation

Sugarcane bagasse was collected from the local sugar mill. Sugarcane bagasse was washed with hot water (60 °C) and dried in sunlight followed by oven dried at 60 °C for 72 h. Biosorbent was soaked in 2 N H₂SO₄ solution to protonate the adsorption sites available on sugarcane bagasse surface [12]. The biosorbent was then washed several times with Millipore water and dried in hot air oven at 60 °C for 12 h to completely remove moisture. The dried sugarcane bagasse was sieved and stored in airtight plastic containers for further experimentation.

Biosorption Experiment

To study the biosorption as a function of dose 0.5–60 g/L of sugarcane bagasse for phenol and cyanide was considered, and pH (8), contact time (40 h), temperature (30 °C), and initial concentration (300 mg/L of phenol and 30 mg/L of cyanide) were kept constant. To evaluate the effect of pH, 2–12 pH range was used, whereas biosorbent dose, contact time temperature, and initial concentrations were kept constant. The effect of temperature was measured in the range of 20–50 °C. To evaluate equilibrium isotherm, the initial concentrations of phenol and cyanide, 100–1000 mg/L of phenol and 10–100 mg/L of cyanide concentrations, were used, while 40-g/L biomass dose, pH 8, temperature 30 °C, and contact time 40 h were constant [13, 14]. The contact time ranging from 2 to 50 h was used to evaluate kinetic modeling study, while other parameters were kept constant. Initial concentrations of phenol and cyanide were maintained at 300 and 30 mg/L, respectively, except in those where the initial phenol and cyanide concentration effects are to be studied. The volume of synthetic/simulated aqueous solution (100 mL), shaking speed (120 rpm), and biosorbent particle size (0.25 mm) were kept constant in all batch experiments [14]. The all batch experiments were carried out in a 250-mL round bottom flask with a working volume of 100 mL at 120 rpm in an incubator cum orbital shaker (Metrex, MO-250, India). The residual phenol and cyanide concentration were analyzed by colorimetric picric acid and 4-aminoantipyrene methods, respectively, by UV-Vis spectrophotometer (Hach, USA) [17].

The amount of phenol and cyanide adsorbed onto sugarcane bagasse was calculated by the concentration difference method [5, 15]. The biosorption capacities of sugarcane bagasse of phenol and cyanide were predicted using the amount of pollutant retained on unit mass of biosorbent.

The total amount of phenol and cyanide adsorbed per unit mass of the biosorbent at equilibrium (Q_e) and at time t (Q_t) was designed by using the following equation:

$$Q_e = (C_i - C_e)V/M \quad (1)$$

$$Q_t = (C_i - C_t)V/M \quad (2)$$

The percent removal of phenol and cyanide was calculated as follows:

$$\text{Percentage removal} = ((C_i - C_f)/C_i) \times 100 \quad (3)$$

where

Q_e is the amounts of phenol and cyanide adsorbed on to the per unit mass of biosorbent at equilibrium (mg/g),

Q_t is the uptake of phenol and cyanide at time t (mg/g),

C_f is the final concentration of phenol and cyanide (mg/L),

C_t is the liquid phase concentration of phenol and cyanide at time t (h),

C_i is the initial pollutant concentration (mg/L),

C_e is the concentration of adsorbate at equilibrium (mg/L),

V is the volume of the solution (L),

M is the mass of the biosorbent (g).

Surface Analysis of Biosorbent

To determine the surface morphology of sugarcane bagasse and its composition, FE-SEM (FE-SEM Quanta 200 FEG) analytical instrument was used. The biosorbent before and after biosorption of phenol and cyanide was subjected to analysis by the instrument. The elemental analysis for sugarcane bagasse was also conducted by energy-dispersive X-ray spectroscopy. Spectral analysis using FTIR (Nicolet 6700, USA, coupled with OMNIC software version 6.2) was used to explain the functional groups present onto the surface of the sugarcane bagasse before and after biosorption. The characterization of biomass was achieved by proximate and ultimate analyses. The proximate analysis of biomass provides volatile content, moisture content, free residual carbon, ash content in the sample, and high heating value, whereas the ultimate analysis provides information about the weight percentage of hydrogen, carbon, and oxygen as well as nitrogen and sulfur [18]. Table 1 shows the proximate and ultimate analyses of sugarcane bagasse. The Brunauer–Emmett–Teller (BET) surface area of sugarcane bagasse is 67 m²/g. The technique for estimating surface area is the BET method [19].

Isotherm and Kinetic Analyses

To design an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curves.

Table 1 Proximate and ultimate analyses of sugarcane bagasse

	Sugarcane bagasse (wt%)
A. Proximate analysis	
Moisture	8.1
Fixed carbon	12.5
Volatile matter	82.1
Ash content	3.9
Heating value (MJ kg ⁻¹)	18.5
B. Ultimate analysis	
Carbon	43.8
Hydrogen	5.23
Oxygen	45.4
Nitrogen	0.34
Sulfur	0.01
Calorific value (kcal/kg)	4410

Therefore, the equilibrium adsorption data for phenol and cyanide from mono-component and binary component systems onto sugarcane bagasse have been used to test the applicability of various mono- and multi-component isotherm equations. The equilibrium data of biosorption studies were confirmed using five mono-component isotherm models (Langmuir, Freundlich, Redlich–Peterson, Toth, and Fritz–Schlunder) and six binary component isotherm models (non-modified Langmuir, modified Langmuir, extended Langmuir, extended Freundlich, non-modified Redlich–Peterson, and modified Redlich–Peterson models). The kinetic data of biosorption studies were verified using 14 kinetic models (fractional power model; pseudo-first order; pseudo-second order; Elovich model; Avrami model; modified second-order model; Ritchie second-order model; exponential kinetic model; mixed first-, second-order model; fractal-like mixed first-, second-order model; fractal-like first-order model; fractal-like second-order model; fractal-like exponential model; and Brouser–Weron–Sototlongo mode).

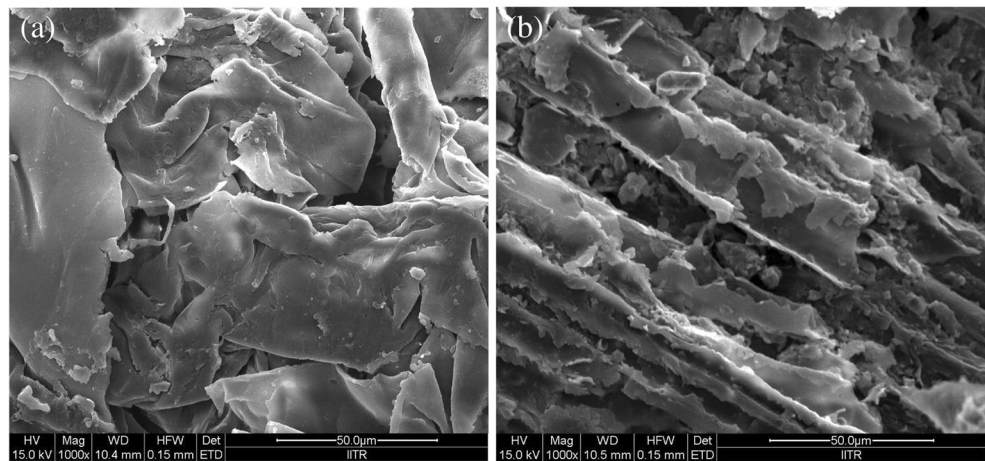
Results and Discussion

Biosorbent Characterization

FE-SEM Analysis of Sugarcane Bagasse

Sugarcane bagasse is a non-conducting biomaterial. Unloaded and loaded samples were also visualized through SEM to take into account the changes in surface morphology due to the adsorption of phenol and cyanide. For scanning electron microscopy analysis, biosorbent was coated with gold in the occurrence of argon. The images were taken with an

Fig. 1 Surface micrographs of sugarcane bagasse samples **a** before biosorption and **b** after biosorption (FE-SEM analysis)



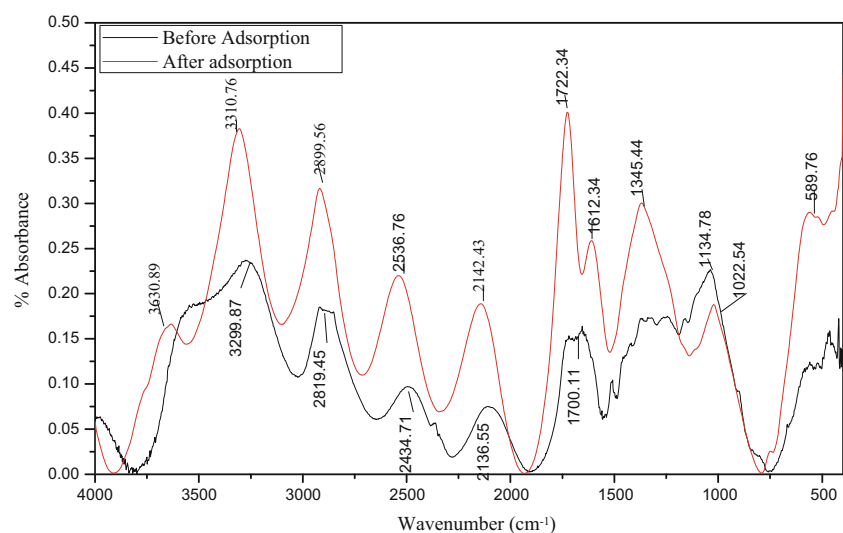
accelerator voltage = 15 kV and an emission current = 100 IA by the tungsten filament. The surface morphologies of sugarcane bagasse are revealed in Fig. 1a, b. A change in surface morphology from being smooth to rough and occupation of pores indicates biosorption of phenol and cyanide onto the surface and pores of sugarcane bagasse giving it a rough texture (Fig. 1b).

FTIR Spectroscopy of Sugarcane Bagasse

To understand the biosorption process, chemical structure of the biosorbent is of significant importance. For identifying the functional group's presence on biosorbent surface, the FTIR method is a significant tool. The samples of sugarcane bagasse were taken before and after biosorption and dried at 60 °C in an oven. The pellet to be analyzed was obtained by compressing a mixture of sample and KBR in a ratio of 1:10 in hydraulic press at 15-t pressure for 30 s. The FTIR spectra of sugarcane bagasse are revealed in Fig. 2. Several strong and

weak peaks were detected in the region of 4000–400 cm^{-1} . The region between 3125 and 3575 cm^{-1} indicated the stretching of O–H from cellulosic basis [20]. The peak detected at 3299.87 cm^{-1} was recognized as O–H stretching, which shifted to 3310.76 cm^{-1} after phenol and cyanide biosorption. The peak at 2536.76 cm^{-1} is indicated carboxyl group. The FTIR spectra showed broad peaks at about 1612.34 cm^{-1} , conforming to stretching from ketones and aldehydes. The band in the area of about 1600 cm^{-1} indicated the occurrence of carbonaceous materials. Therefore, a stretch detected at 1612.34 cm^{-1} seemed in Fig. 2 [21]. The peaks at about 589.76 cm^{-1} show the occurrence of Si–H. Peak at 1612.34 cm^{-1} corresponds to –CH stretching due to the presence of conjugated hydrocarbon groups, aromatic hydrocarbons, carboxylic groups, and carboxyl and carbonate structures indicating adsorption of phenol, whereas peak at 1345.44 cm^{-1} corresponds to inorganic nitrates marking a potential adsorption site for cyanides. It could be detected from Fig. 2 that some peaks are shifted and broadened,

Fig. 2 FTIR spectra of sugarcane bagasse before and after biosorption



representing that the functional groups existing on the sugarcane bagasse surface were involved in biosorption of phenol and cyanide.

Effect of Operating Parameters

Effect of pH

Figure 3 illustrates the effect of biosorption on phenol and cyanide removal efficiency. The pH of the biosorption system significantly influences the pollutant ion speciation, surface chemistry of the biosorbent surface, and adsorption of adsorbate onto adsorbent surface. At acidic pH range (4–7), the cyanide removal rate is high. The percentage removal of cyanide increases with the increase in pH up to pH 7. Beyond pH 7, the removal percentage of cyanide becomes constant. Sugarcane bagasse generally contains some anionic groups such as carbonyl, phenolic, and phosphate, which are accountable for negative surface charge on the sugarcane bagasse. Sugarcane bagasse also comprises oxides like CaO, SiO₂, and Al₂O₃. These oxides react with H⁺ or OH⁻ and S⁻ ions of the aqueous solution and can produce both negative and positive charges on the biosorbent surface. As in sugarcane bagasse, the concentration of CaO is high; at pH <7.0, biosorbent surfaces reveal positive charge and responsible in the biosorption of cyanide [15, 22]. The biosorption of cyanide is due to the surface charges on biosorbent surface and cyanide behavior in water. At pH values above 7.0, high negative surface charge grows on the biosorbent surface. The increase in biosorption of cyanide was observed beyond pH 7 in NaCN solution. Higher adsorption of cyanide occurred in pH range of 7–10 [23]. This is owing to the fact that cyanide is hydrolyzed in aqueous solution to form HCN. The pKa value of hydrocyanic acid is 9.4. So, at pH <9.4, cyanide exists in HCN; however, at pH >9.4, HCN dissociates to CN⁻ ions

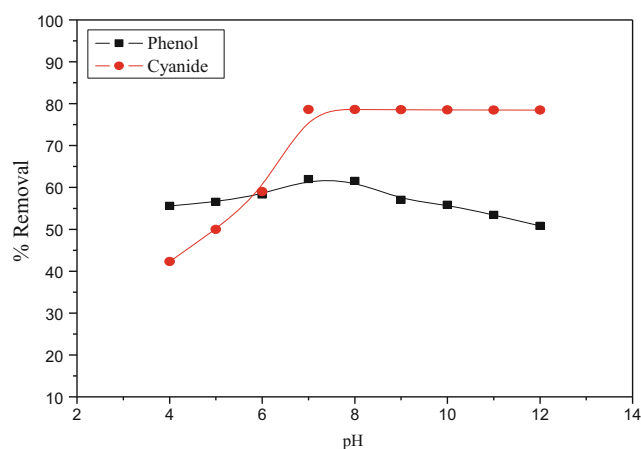


Fig. 3 Effect of pH on the biosorption of 300 mg/L of phenol and 30 mg/L of cyanide using 40 g/L sugarcane bagasse, during orbital shaking of 120 rpm at 30 °C temperature for 40 h

[24]. Since CN⁻ is a nucleophilic ion and when in interaction with the negatively charged biosorbent, it fixes with the anionic functional groups existing on the biosorbent surface and thus increases rate of biosorption. Figure 3 signifies that the biosorption of phenol remains nearly constant in an acidic pH range, where the phenol remains in undissociated forms. Phenol is a weak acid with acid dissociation value (pKa) of 9.8, and it dissociates into phenoxide ion when pH > pKa. At lower pH values, phenolic compounds are present as the unionized acidic compound [25]. However, a reduction is observed in percentage removal at pH greater than its pKa (9.96), representing the biosorption of phenol in its undissociated form and pH 7 to be most suitable for biosorption of phenol [25]. However, as the pH increased, the biosorption start to decrease likely owing to the electrostatic repulsions between the negatively charged phenol anion and the surface site or by the phenol anions in the aqueous solution [26]. All further batch studies were achieved at pH 7, which is the optimum value for both the phenol and cyanide.

Effect of Biosorbent Dose

Figure 4 indicates the effect of biosorbent dose on percentage removal of phenol and cyanide in the range of 0.5–60 g/L. The percentage removal of both phenol and cyanide increases with an increase in biosorbent dose up to 40 g/L, and beyond this dose, the percentage removal becomes constant. This is due to the fact that the phenol and cyanide concentrations onto biosorbent surface and concentrations of phenol and cyanide in solution come into equilibrium with each other. The increase in removal percentage of phenol and cyanide at initial stage is owing to the increase in biosorbent dose. This is owing to fact that with the increase in biosorbent dose, the number of active sites on the biosorbent surface in unit volume of aqueous solution increases; thus, there is an increase in the removal percentage of phenol and cyanide. Therefore, the

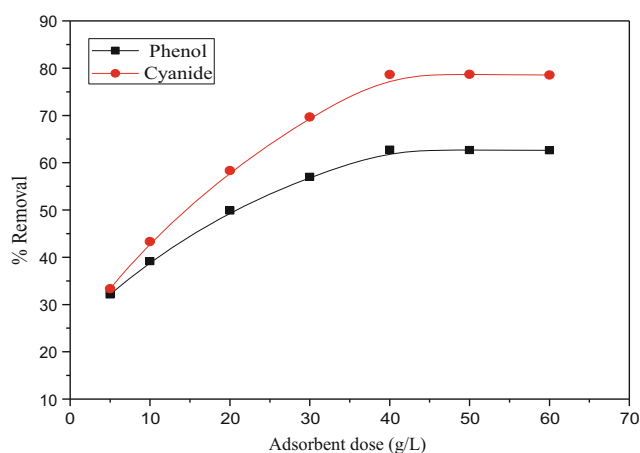
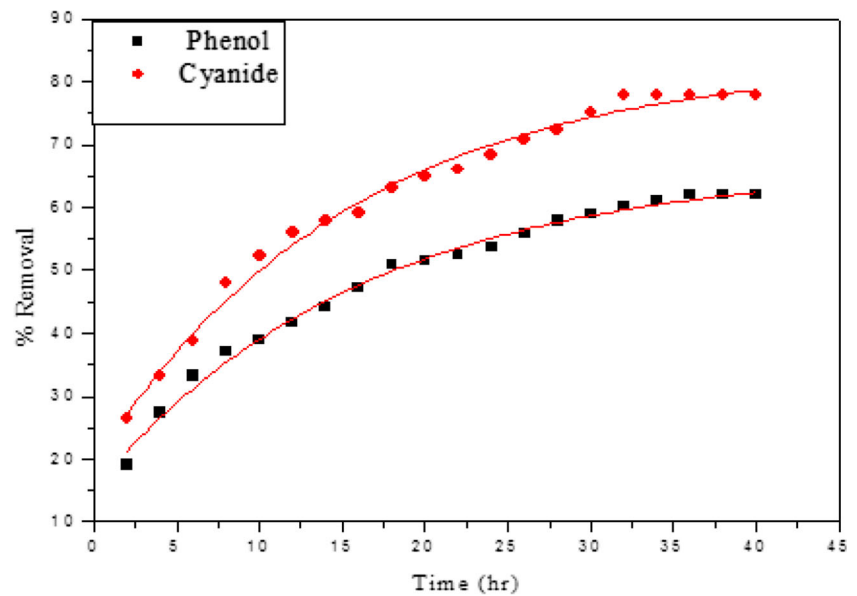


Fig. 4 Effect of biosorbent dose on the biosorption of 300 mg/L of phenol and 30 mg/L of cyanide using pH 7, during orbital shaking of 120 rpm at 30 °C temperature for 40 h

Fig. 5 Effect of contact time on the biosorption of 300 mg/L of phenol and 30 mg/L of cyanide using pH 7, biosorbent dose 40 g/L during orbital shaking of 120 rpm at 30 °C temperature



optimum dose of sugarcane bagasse for removal of phenol and cyanide can be chosen as 40 g/L for biosorption process.

Effect of Contact Time

The biosorption data for the percentage removal of phenol and cyanide versus contact time are revealed in Fig. 5. The removal percentage of both phenol and cyanide were fast at the initial stage of biosorption process, owing to fact that at initial stage, more sites were available for biosorption, and as time passes, the rest of biosorption sites were hard to be adsorbed for the reason that of repulsive forces between molecules of bulk phase and solid [26]. The mass transfer resistance between biosorbent and bulk phase is overcome through energy provide by contact time. This energy is used to transfer substrate species from bulk solution to the energetic sites existing on biosorbent surface; as a result, at initial stage of process, the percentage removal of phenol and cyanide is high. The figure indicates that the percentage removal becomes constant after 34 h in the case of phenol and 32 h in the case of cyanide.

Effect of Temperature

Figure 6 shows the results achieved from phenol and cyanide biosorption when temperature was increased from 20 to 40 °C. The percentage removal increases from 56.31 to 58.52 and from 58.67 to 80.33% in case of phenol and cyanide, respectively, on increasing temperature of phenol and cyanide from 20 to 40 °C (Fig. 6). As the temperature rises, the rate of diffusion of the phenol and cyanide molecules through the exterior boundary layer and in the inner pores of the biosorbent increase due to the reduction in the viscosity of the aqueous solution. The thermal energy of molecules also

increases with temperature. The increasing of temperature may enhance the affinity of aggregation and therefore the uptake of the phenol and cyanide [5]. The removal of cyanide is increased up to 30 °C slightly, and after that, it becomes constant. Biosorption of phenol was decreased with increasing temperature (Fig. 6). This could be due to the increased tendency of desorption of phenol at increased temperature, resulting owing to weakening of adsorptive forces between adsorbate and active sites of adsorbent as well as between the nearby molecules of adsorbate [15]. A decrease and constant in the adsorption rate of both cyanide and phenol, respectively, with increasing temperature are related to the increasing Brownian movement of molecules in solution [27]. The optimum temperature of the aqueous binary solution was carefully chosen as 30 °C for both phenol and cyanide.

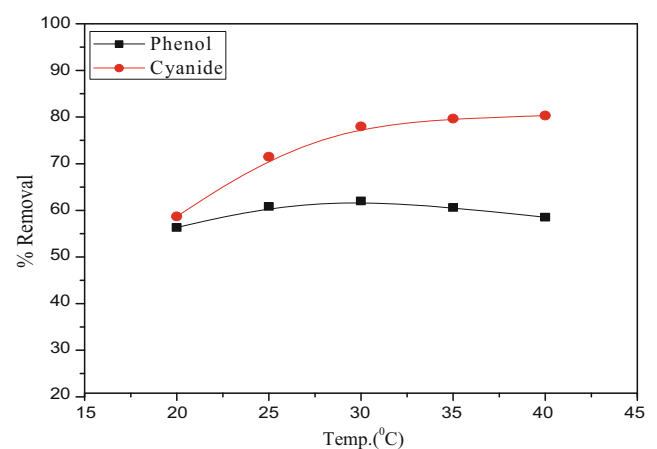


Fig. 6 Effect of temperature on the biosorption of 300 mg/L of phenol and 30 mg/L of cyanide using pH 7, biosorbent dose 40 g/L during orbital shaking of 120 rpm for 40 h

Effect of Initial Concentrations of Phenol and Cyanide

The effect of initial concentrations of phenol and cyanide on biosorption was evaluated from 100 to 1000 mg/L of phenol and 10–100 mg/L of cyanide, and the additional operating parameters such as shaking speed (120 rpm), biosorbent dose (40 g/L), pH (7), and contact time (40 h) remain constant. The percentage removal of phenol and cyanide onto sugarcane bagasse were found to decrease at higher concentrations. The surface of sugarcane bagasse turn out to be saturated after some time; as a result, the removal percentage is higher at initial stage of operation. This is owing to the fact that at initial stage, the enough number of active binding sites is vacant on the surface of biosorbent. But, at higher initial concentrations, the number of phenol and cyanide ions are comparatively high than existing biosorption sites on the surface of sugarcane bagasse. A similar statement has been well defined by Mondal and Balomajumder (2007) [22]. When the initial concentration of phenol was increased from 100 to 1000 mg/L, the uptake capacity increased from 1.5 to 5.64 mg/g and the percentage removal decreased from 75.00 to 28.21 mg/L for sugarcane bagasse (Fig. 7a). In case of cyanide, similar tendency was detected. The percentage removal was decreased from 81.01 to 43.87 mg/L for the initial cyanide concentration of 10–100 mg/L, and uptake capacity increased from 0.16 to 0.88 mg/g (Fig. 7b).

Equilibrium Isotherm Modeling

The comparisons of equilibrium isotherm models for phenol and cyanide onto sugarcane bagasse are presented in Figs. 8 and 9. The equilibrium isotherm data were fitted into the

several mono- and multi-component isotherm models (Table 2). Mono-component isotherm modeling was carried out to find the best fit model and estimation of parameters for multi-component adsorption studies. The best model is chosen on the basis of error function Marquardt's percent standard deviation (MPSD).

Mono-Component Modeling

The individual Langmuir, Freundlich, Redlich–Peterson, Toth, and Fritz–Schlunder isotherm model parameters for phenol and cyanide were studied to explain the biosorption process. Out of these isotherms, Langmuir and Freundlich are two-parameter models, Redlich–Peterson and Toth are three-parameter models, and Fritz–Schlunder model is four-parameter model. Langmuir model relies on the assumptions that a mono-layer of biosorbate is biosorbed above homogeneous surface of biosorbent at a constant temperature, there is no contact between the biosorbed molecules and all vacant sites on biosorbent surface, and all active sites are of same intensity [28]. The Freundlich model is based on biosorption on heterogeneous surfaces [28]. Redlich and Peterson model include three parameters into an isotherm and then can be applied both in heterogeneous or homogenous systems, owing to the high adaptability of the equation [29]. The Fritz–Schlunder model is empirical three-parameter isotherm combining the Langmuir and Freundlich isotherms [29]. The parameters of the five mono-component isotherms and the values of their corresponding MPSD are presented in Table 2, whereas Fig. 8 offers the comparison between the isotherm models for phenol and cyanide. When the initial concentration increases from 10 to 100 mg/L for cyanide

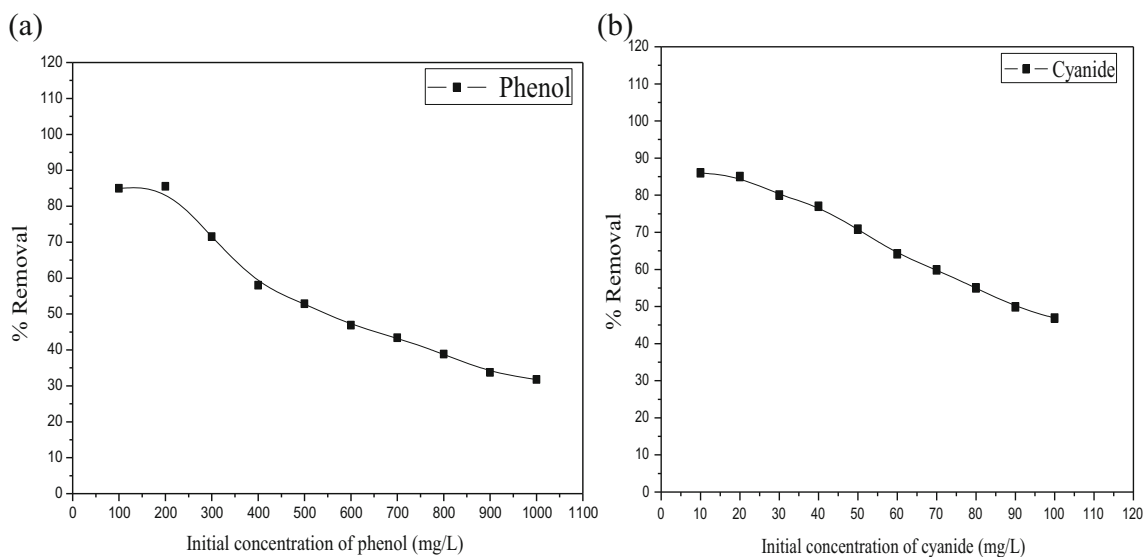


Fig. 7 Effect of initial concentration on the biosorption of phenol and cyanide using pH 7, biosorbent dose 40 g/L during orbital shaking of 120 rpm at 30 °C temperature for 40 h contact time. **a** Phenol. **b** Cyanide

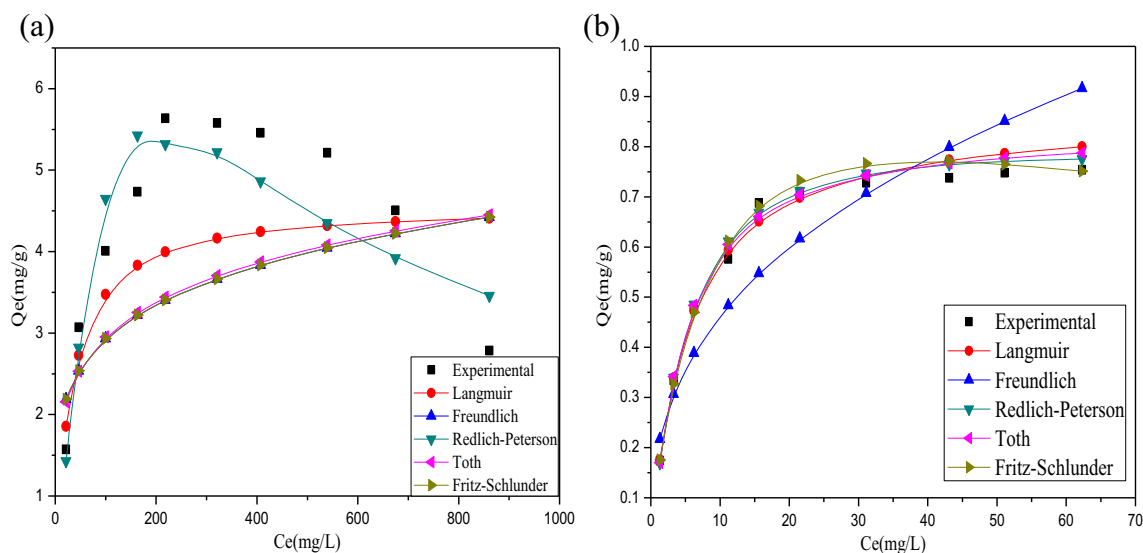


Fig. 8 Comparison of different mono-component isotherm models on sugarcane bagasse. **a** Phenol. **b** Cyanide

and 100 to 1000 mg/L for phenol, the biosorption capacity of sugarcane bagasse increases from 0.17 to 0.75 mg/g for cyanide and from 1.57 to 4.50 mg/g for phenol in mono-component system. The initial concentration provides the necessary driving force to overcome the resistances to the mass transfer of phenol and cyanide between the aqueous and the solid phases. The increase in initial concentration also increases the interaction between the pollutant in the aqueous phase and the sugarcane bagasse [28]. Therefore, an increase in initial concentration of phenol and cyanide enhances the adsorption uptake of the phenol and cyanide. Also, it is observed that the adsorption capacity of bagasse for phenol is greater than that for cyanide. The main purpose to carry out single-component adsorption studies is to evaluate the best

model among the abovementioned models and to estimate the parameters of the models used in binary component adsorption studies. Based on the results revealed in Table 2 and Fig. 8, best fit isotherm models for phenol are observed in the order of Redlich–Peterson > Langmuir > Toth > Fritz–Schlunder > Freundlich and for cyanide in the order of Fritz–Schlunder > Redlich–Peterson > Toth > Langmuir > Freundlich. K_F and n , the mono-component Freundlich constants, show the adsorption capacity and adsorption intensity, respectively. The higher the value of n is, the higher will be the affinity and the heterogeneity of the biosorbent surface are. It is found from Table 2 that the sugarcane bagasse shows greater heterogeneity for phenol than that for cyanide. Between the two-parameter model, the Langmuir model provides a better

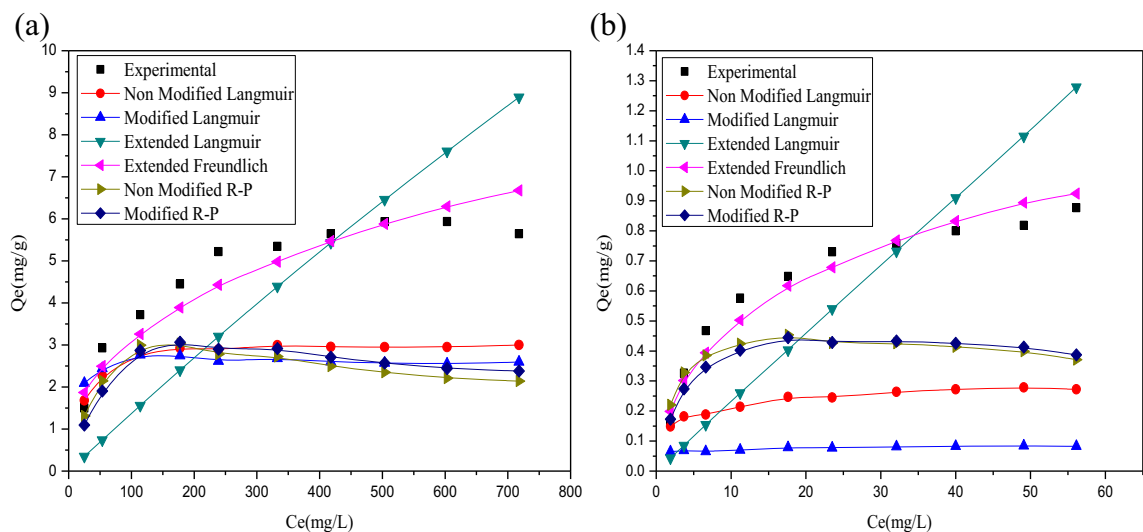


Fig. 9 Comparison of different binary component isotherm models on sugarcane bagasse. **a** Phenol. **b** Cyanide

fit than the Freundlich model. The features of Langmuir isotherms can be described by a separation factor [30].

$$R_L = \frac{1}{(1 + bC_0)} \quad (4)$$

Separation factor R_L explains the feasibility of adsorption process. An adsorption process is favorable when $R_L < 1$, unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable for $0 < R_L < 1$, and irreversible when $R_L = 0$. In this study, the value of R_L was found to be 0.10 and 0.14, respectively, for phenol and cyanide. This shows a greatly favorable biosorption ($R < 1$).

Binary Component Modeling

The presence of more than one component in an aqueous solution causes interference and competition for adsorption sites, which leads to a more complex mathematical formulation of the equilibrium. In general, amount of component adsorbed may increase, decrease, or remain unchanged in the presence of other component(s). Therefore, the relationships between the adsorbed quantity of one component and the concentrations of all other components present in the aqueous solution are described by multi-component adsorption isotherms [23]. The binary component experimental adsorption data of phenol and cyanide onto sugarcane bagasse have been examined by non-modified Langmuir model, modified Langmuir model, extended Langmuir, extended Freundlich model, non-modified R-P model, and modified R-P model. The values of model parameters with MPSD are specified in Table 2. The comparisons of binary component models for phenol and cyanide in the aqueous solution are shown in Fig. 9a, b. The binary component extended Freundlich model indicates a better fit to the experimental data with a low MPSD value for both phenol and cyanide (MPSD = 14.96 and MPSD = 12.14, respectively). This is predictable as sugarcane bagasse has a heterogeneous surface. It is evident that the modification of the Freundlich equation as given by the extended Freundlich model takes into account the interactive effects of individual pollutant between and among themselves and also the biosorbent sugarcane bagasse reasonably well. Therefore, the binary adsorption of phenol and cyanide onto sugarcane bagasse can be represented satisfactorily and effectively by the extended Freundlich model. The values of the correction factors are less than 1.0 for modified Langmuir model (Table 2), representing that the modified Langmuir model could predict the binary adsorption equilibrium data [31]. When the initial concentration increases from 10 to 100 mg/L for cyanide and 100 to 1000 mg/L for phenol, the loading capacity of sugarcane bagasse increases from 0.16 to 0.88 mg/g for cyanide and from 1.50 to 5.64 mg/g for phenol in binary

Table 2 Comparison of mono-component and binary component isotherm model parameters for phenol and cyanide onto sugarcane bagasse

	Parameters	Phenol	Cyanide
Mono-component isotherm models			
Langmuir	Q_o	4.57	0.87
	b	0.03	0.20
Freundlich	MPSD	29.46	5.09
	K_F	1.22	0.19
	n	5.25	2.69
Redlich–Peterson	MPSD	37.94	18.67
	K_{RP}	0.069	0.15
	a_{RP}	0.0003	0.13
	β	1.63	1.06
	MPSD	15.73	4.43
Toth model	q_{to}	282.04	0.83
	a	0.31	6.94
	n	0.048	1.15
	MPSD	37.47	4.78
Fritz–Schlunder model	a_1	0.58	4.32
	a_2	−0.53	28.59
	b_1	0.19	−0.36
	b_2	−0.0005	−1.11
	MPSD	37.90	3.45
Binary component isotherm models			
Non-modified Langmuir	MPSD	44.54	66.60
	Modified Langmuir	$\eta_{i,j}$	0.37
Extended Langmuir	MPSD	51.50	80.69
	$Q_{o,i}$	94.25	5.46
	b_i	0.0001	0.0003
Extended Freundlich	MPSD	53.58	54.79
	x_i	−0.49	−0.48
	y_i	1.17	0.11
	z_i	−0.13	0.40
	MPSD	14.96	12.14
Non-modified R-P model	MPSD	51.72	43.51
Modified R-P model	$n_{i,j}$	1.29	1.37
	MPSD	50.27	42.11

component system. Biosorption of phenol followed the trend of better fit models as extended Langmuir < non-modified Redlich–Peterson < modified Langmuir < modified Redlich Peterson < non-modified Langmuir < extended Freundlich, whereas biosorption of cyanide followed the trend as modified Langmuir < non-modified Langmuir < extended Langmuir < non-modified Redlich Peterson < modified Redlich Peterson < extended Freundlich. Comparisons of specific uptake for biosorption of phenol and cyanide on different biosorbents are shown in Table 3.

In binary component aqueous solution, the components present in solution may have three types of sorption interaction effects such as if the adsorption of the adsorbate decrease when there are additional adsorbates present in the binary component mixture (antagonism $Q_{mix}/Q_i < 1$), the adsorption of the adsorbate increase when there are another adsorbates present in the binary component mixture (synergism $Q_{mix}/Q_i > 1$), and if the binary component mixture has no effect on the adsorption of each adsorbate (non-interaction $Q_{mix}/Q_i = 1$) [32], where Q_i is the biosorption capacity of

Table 3 Comparison of specific uptake for biosorption of phenol and cyanide on different biosorbents

Serial no.	Biosorbent	Initial concentration (mg/L)	Specific uptake (mg/g)	Component	Reference
1	Activated carbon	200	28.2	Cyanide	[24]
2	Lignified activated carbon and iron impregnated activated carbon derived from Gölbas, lignite	100, 100	64.02, 62.04	Cyanide	[39]
3	Moderate density fiber board saw dust (MDFSD)	100	1.4	Cyanide	[40]
4	Pistachio green hull	156	1.56	Cyanide	[41]
5	Rice husk, activated carbon, impregnated activated carbon by silver and copper	100	0.401	Cyanide	[42]
6	<i>Lantana camara</i>	250	25	Phenol	[14]
7	Olive mill waste	700	25	Phenol	[43]
8	Modified fly ash	30–80	30	Phenol	[44]
9	Sugarcane bagasse fly ash	200	30	Phenol	[15]
10	Sugarcane bagasse	300	94.24	Phenol	Current study
11	Sugarcane bagasse	30	5.46	Cyanide	Current study

component present alone in the solution and Q_{mix} is the biosorption capacity of one component in the presence of the other component in binary component aqueous solution. The values of Q_{mix}/Q_i are established to be 20.62 for phenol and 6.27 for cyanide as existing in Table 2, founding the fact that both phenol and cyanide show synergism effects.

The experimental equilibrium sorption data obtained for the mono-component and the binary systems show that the adsorption capacity of sugarcane bagasse for phenol is, in general, more than that of cyanide. There are possible interaction effects between different pollutants in the solution and, in specific, possible interactions on the surface depending on the adsorption mechanism. The factors that affect the sorption preference of biosorbent for different kinds of adsorbates may be associated to the characteristics of the binding sites (e.g., surface properties, functional groups, and structure), the properties of the adsorbates (e.g., ionic size, concentration, ionic weight, molecular structure, ionic charge, ionic nature, or standard redox potential), and the solution chemistry (e.g., ionic strength, and pH). Though, it is difficult to find a common denominator from the physical and chemical properties of phenol and cyanide, which describes the interactive mechanism and the increase in the selectivity for sorption of an adsorbate from the binary mixtures.

Kinetic Modeling

Kinetic modeling was recognized in order to found the mechanism of biosorption onto biosorbents. Kinetic study distributes the fact about the mechanism of biosorption that includes the diffusion (external, intraparticle, and bulk) and chemical reactions. In general, the adsorbate transport follows in the few steps: (1) the transport of pollutants in the bulk solution, (2) the external diffusion from the bulk solution to the exterior surface of the biosorbent, (3) the transport of the pollutant

through the boundary layer, (4) the transfer of pollutant in the pores of the biosorbent and finally uptake of pollutant molecules by the active sites, and (5) the biosorption and desorption of pollutant [33]. To estimate the dynamic biosorption behavior of phenol and cyanide on sugarcane bagasse, numerous kinetic models were used in this study, assuming that concentrations of adsorbate on the adsorbent surface are equal to the measured concentrations. (The details of kinetic equations are provided in the [supplementary material](#).) Among them, fractional power model, pseudo-first order, and pseudo-second order are empirical models, though their major shortcoming is that they may only define the adsorption kinetics at some situations [34]. Elovich kinetic model, fractional power, Ritchie second order, and exponential kinetic models are two-parametric empirical models to analyze kinetic data. Other three-parametric kinetic models, for example, Avrami; modified pseudo-second-order; and mixed first-, second-order equations, have been suggested for adsorption kinetics at the solid/solution interface.

A non-linear regression analysis technique was used to solve adsorption kinetic models. Table 4 demonstrates the values of kinetic model parameters for the biosorption of phenol and cyanide on surface of sugarcane bagasse. The best fit model was determined on the basis of error function MPSD. High error values recommend that these models (pseudo-first order, Avrami, and exponential) are not appropriate for both phenol and cyanide. On the basis of the lowest error function values of MPSD, the perfect fitting of the experimental results was achieved by using Brouser–Weron–Sototlongo model and fractal-like models such as fractal-like pseudo-first order; fractal-like pseudo-second order; fractal-like exponential; and fractal-like mixed first, second order (Fig. 10a, b) for both phenol and cyanide among all the tried kinetic models.

The better fit of Brouser–Weron–Sototlongo kinetic model specifies that the removal of both phenol and cyanide onto

Table 4 Kinetic model parameters for biosorption of phenol and cyanide onto sugarcane bagasse

Kinetic models	Parameters	Phenol	Cyanide
Fractional power model	k_{fp}	1.59	0.21
	ν	0.39	0.37
	MPSD	0.85	0.94
Pseudo-first order	q_e	5.72	0.72
	k_1	0.15	0.15
	MPSD	1.96	1.99
Pseudo-second order	q_e	6.93	0.87
	k_2	0.023	0.19
	MPSD	1.132	1.29
Elovich model	a_{el}	1.71	5.31
	b_{el}	0.59	4.79
	MPSD	0.49	0.80
Avrami model	q_e	5.72	0.72
	k_{av}	0.26	0.37
	n_{av}	0.55	0.40
Modified second-order model	MPSD	1.96	1.99
	q_e	7.96	1.016
	k_{1m}	0.09	0.084
Ritchie second-order model	b_{1m}	1.15	1.17
	MPSD	0.52	0.62
	q_e	6.93	0.87
Exponential kinetic model	k_{1R}	0.16	0.16
	MPSD	1.13	1.29
	q_e	5.92	0.75
Mixed first-, second-order model	k_{ex}	0.097	0.099
	MPSD	1.49	1.59
	q_e	6.79	0.87
Fractal-like mixed first-, second-order model	k_m	0.0046	0.003
	f_2	0.97	0.98
	MPSD	1.13	1.29
Fractal-like, first-order model	q_e	7.72	0.97
	f_{eq}	-18.38	-13.16
	k_{fin}	1.68	1.48
Fractal-like, second-order model	α	0.26	0.28
	MPSD	0.48	0.66
	q_e	8.05	1.03
Fractal-like exponential model	k_{ff}	-0.18	-0.19
	a	0.57	0.55
	MPSD	0.45	0.69
Brouser–Weron–Sototlongo model	q_e	10.83	1.44
	k_{fs}	0.013	0.10
	a	0.63	0.59
Brouser–Weron–Sototlongo model	MPSD	0.45	0.71
	q_e	8.55	1.12
	k_{rex}	0.10	0.11
Brouser–Weron–Sototlongo model	a	0.62	0.59
	MPSD	0.45	0.70
	q_e	11.19	0.93
Brouser–Weron–Sototlongo model	$t_{bws,\alpha}$	23.82	14.63
	n_{bws}	1.98	2.25
	a	0.59	1.22
Brouser–Weron–Sototlongo model	MPSD	0.45	0.60

sugarcane bagasse followed chemisorption interaction type, indicating that the rate-controlling step might be chemical adsorption including valency forces over exchange or distribution of electrons between phenol and cyanide anions and sugarcane bagasse. Additionally, the Brouser–Weron–Sototlongo kinetic model states other notable data, which is the time significantly to adsorb half the maximum amount ($t_{bws,\alpha}$). Brouser–Weron–Sototlongo kinetic model has a good fitting performance; it states such quality data (i.e., biosorption capacity close to

experimental data, $q_e(BWS)$, and the time of half reaction ($t_{bws,\alpha}$) [35, 36]. As presented in Table 3, with respect to initial phenol and cyanide concentrations, 23.82 and 14.63 h (the lowest value) were suitable for sugarcane bagasse to achieve half of the phenol and cyanide uptake capacities, respectively, which is important as well as valuable parameter for computing the reaction speed. As for BWS model itself, it has a good fitting performance and more implicitly, which were estimated aimed at industrial treatment design purposes [36]. Avrami

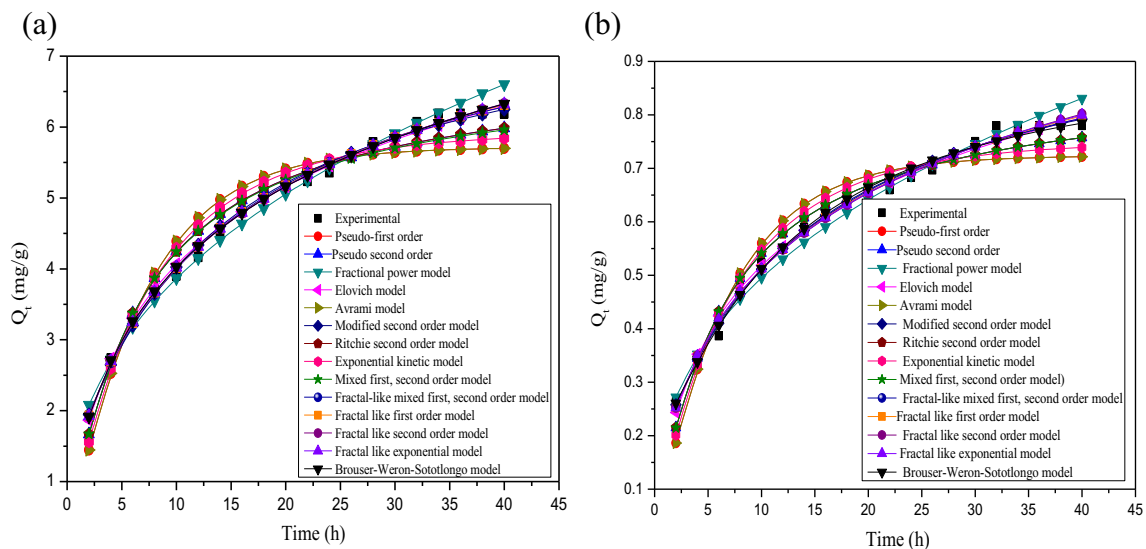


Fig. 10 Comparison of kinetic models for biosorption onto the sugarcane bagasse. **a** Phenol. **b** Cyanide

exponent (n_{av}) (0.55 for phenol and 0.40 for cyanide) is a fractionary number connected with the possible variations of the biosorption mechanism that happens all over the biosorption process [37, 38]. The value of low error values (MPSD) for pseudo-second-order model estimates that possible route or mechanism of biosorption of phenol and cyanide on sugarcane bagasse is chemisorption. It is understood that the mixed first-, second-order rate equation is linear in the Lagergren coordinates near to the equilibrium and slightly in the initial portion of the experiment. Specifically, we may conclude that it contains two linear sections linked with a curved one. The second-order equation shows linear performance in the initial stage of the experiment also; however, the linear section is relatively short. On the other hand, mixed first-, second-order rate equation may be treated as Langmuir equation for energetically homogeneous surfaces or as only empirical equation for energetically heterogeneous surfaces. The vital theory of modified second-order model was that a number of surface sites are used by both phenol and cyanide. It was supposed that the pre-adsorbed phase occurred on sugarcane bagasse biosorption. The vital theory of Ritchie second-order model was that one adsorbate was adsorbed on two surface sites. It was supposed that the pre-adsorbed phase has not occurred on sugarcane bagasse biosorption. The sugarcane bagasse surface cover age has been usually supposed to be zero. For fractal-like models such as fractal-like pseudo-first order; fractal-like pseudo-second order; fractal-like exponential; and fractal-like mixed first, second order, the rate coefficient for biosorption is measured as a function of time by using the fractal-like idea. One of the probable physical meanings of fractal-like kinetics was that biosorption of phenol and cyanide occurred at solid/solution edge. In this methodology, it was specified that by passing time, a number of paths for phenol and cyanide biosorption on biosorbent surface seems [35]. The

error values MPSD for fractal-like models and Brouser–Weron–Sototlongo kinetic model were better than that other kinetic models for phenol and cyanide. Fractal-like mixed first-, second-order kinetic model representing the rate of adsorption was dependent on initial concentration of adsorbate in solution and rate of agitation. Also, on the basis of the fractal-like concept, the fractal-like equations can be used for investigating the kinetic data for biosorption systems with heterogeneous solid surfaces. However, the Brouser–Weron–Sototlongo kinetic model revealed the complex mechanism of removal process. Figure 10a, b demonstrates the comparison of kinetic models for phenol and cyanide removal, respectively.

Conclusions

The current study demonstrates that the sugarcane bagasse is an effective biosorbent for the elimination of phenol and cyanide from synthetic/simulated wastewater. Maximum biosorption for both 300 mg/L of phenol and 30 mg/L of cyanide was found to occur at pH 7.0, biosorbent dose 40 g/L, and temperature 30 °C. The Redlich–Peterson model and Fritz–Schlunder model for phenol and cyanide, respectively, indicate good fit with the experimental equilibrium data for mono-component aqueous solution. In the binary component solution, the affinity of the sugarcane bagasse for phenol was greater than that for cyanide, for both the mono-component and binary component solutions under the similar experimental environment. On the basis of MPSD error function, the extended Freundlich equilibrium isotherm model revealed the best fit to the binary component data. The effect of presence of phenol and cyanide on each other was also calculated, and it was found to be synergistic. By applying 14 kinetic models, the Brouser–Weron–Sototlongo model and fractal-

like models such as fractal-like pseudo-first order; fractal-like pseudo-second order; fractal-like exponential; and fractal-like mixed first-, second-order models were found suitable for predicting the kinetic of biosorption of both phenol and cyanide onto sugarcane bagasse. The kinetic study experimental data also indicated better fit with pseudo-second-order model very well; therefore, it can be established that chemisorption was the potential route of biosorption on sugarcane bagasse. In conclusion, it may be established that sugarcane bagasse may be used for the separate and simultaneous elimination of phenol and cyanide from synthetic/simulated wastewater.

Q_o , Langmuir model constant (mg/g); b , Langmuir model constant; $Q_{e,i}$, amount of i th component adsorbed per gram of adsorbent at equilibrium (mg/g); $Q_{o,i}$, constant in modified Langmuir model for i th component (mg/g); $C_{e,i}$, concentration of i th component in the binary mixture at equilibrium (mg/L); K_F , Freundlich model constant (mg/g); n , Freundlich, Toth model constant; $K_{F,i}$, extended Freundlich model constant (mg/g); K_{RP} , Redlich–Peterson model constant (L/g); a_{RP} , Redlich–Peterson model constant (L/mg); β , Redlich–Peterson model constant; $\eta_{RP,i}$, binary component Redlich–Peterson model constant (L/g); $a_{RP,i}$, binary component Redlich–Peterson model constant (L/mg); β_j , binary component Redlich–Peterson model constant; x_i, y_i, z_i , constant in modified Redlich–Peterson model; N , number of observations in the experimental isotherm; P , number of parameter in regression model; $Q_{e,i}^{exp}$, experimental value of Q_e (mg/g); $Q_{e,i}^{cal}$, predicted value of Q_e (mg/g); α_1 , constant in Fritz–Schlunder isotherm (mg/g)/(mg/L) $^{\beta_1}$; α_2 , constant in Fritz–Schlunder isotherm (mg/L) – β_2 ; β_1, β_2 , constants in Fritz–Schlunder isotherm; k_{fp} , fractional power model rate constant (mg g $^{-1}$ h $^{-1}$); v , adjustment parameter; k_1 , pseudo-first-order adsorption rate constant (h $^{-1}$); k_2 , pseudo-second-order adsorption rate constant (g mg $^{-1}$ h $^{-1}$); a_{el} , Elovich coefficient representing the initial adsorption rate (g mg $^{-1}$ h $^{-1}$); b_{el} , Elovich coefficient representing desorption constant (g mg $^{-1}$); k_{av} , Avrami kinetic rate coefficient (h $^{-1}$); n_{av} , constant corresponding to the mechanism of adsorption; k_{1m} , modified second-order rate coefficient (h $^{-1}$); b_{1m} , constant; k_{1R} , Ritchie second-order rate coefficient (h $^{-1}$); k_{ex} , exponential rate coefficient (mg/g); k_m , mixed first-, second-order rate coefficient (h $^{-1}$); f_2 , involvement of pseudo-second-order model; k_{fm} , fractal-like mixed first-, second-order rate coefficient (h $^{-1}$) $^\alpha$; t^α , fractal time; k_{ff} , fractal-like pseudo-first-order kinetic rate coefficient (h $^{-1}$); k_{fs} , fractal-like, pseudo-second-order kinetic rate coefficient (h $^{-1}$); k_{fex} , fractal-like exponential rate coefficient (h $^{-1}$); $t_{bws,\alpha}$, time required for adsorbing half the maximum amount; n_{bws} , fractional reaction order

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