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Biosorption of oxybenzene using biosorbent prepared by raw wastes of *Zea mays* and comparative study by using commercially available activated carbonS. Lakshmi^a, Syed Baker^b, Chandan Shivamallu^{c,*}, Ashwini Prasad^d, Asad Syed^e, Ravindra Veerapur^{e,h}, Kollur Shiva Prasad^f, Abdulaziz A. Al-Kheraif^g, Darshan Devang Divakar^g, Abdallah M. Elgorban^e, M.N. Nagendra Prasad^{a,*}^a Department of Biotechnology, SJCE, JSS Science and Technology University, Mysore 570006, India^b Department of Microbiology, Krasnoyarsk State Medical University, Siberia, Russian Federation^c Department of Biotechnology and Bioinformatics, School of Life Sciences, JSS Academy of Higher Education and Research, Mysuru, Karnataka 570 015, India^d Department of Microbiology and Tissue Culture, School of Life Sciences, JSS Academy of Higher Education and Research, Mysuru, Karnataka 570 015, India^e Department of Botany and Microbiology, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia^f Department of Sciences, Amrita School of Arts and Sciences, Amrita Vishwa Vidyapeetham, Mysuru Campus, Mysuru 570 026, Karnataka, India^g Dental Biomaterials Research Chair, Dental Health Department, College of Applied Medical Sciences, King Saud University, P. O. Box: 10219, Riyadh 11433, Saudi Arabia^h Department of Metallurgy and Materials Engineering, Malawi Institute of Technology, Malawi University of Science and Technology, P.O. Box 5916 Limbe, Malawi

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ABSTRACT

Organic pollutants present in waste water have undesirable effect on the environment. Industry activities are the key sources of organic pollutants. Prime pollutants released from various sources react instantly with the environment and become derived (secondary) pollutants, which stay for an elongated time. The present research work has been carried out using biosorbent prepared from various *Zea mays* wastes for elimination of oxybenzene. Different parameters viz contact time, initial concentration; adsorbent dose, temperature and pH were optimized for the biosorption of oxybenzene on to the biosorbent samples. BCS (Baby corn silk) showed higher percentage of biosorption at optimum contact time of 3 h, pH between 5 and 6 and temperature at 25 °C. Analysis of equilibrium biosorption data in terms of several isotherm models revealed that Langmuir isotherm and Freundlich isotherm indicates better agreement with the experimental data. The kinetics of oxybenzene biosorption on to the biosorbents was described with the pseudo-first-order model. Thermodynamic parameters indicated that biosorption onto biosorbent was feasible in nature, spontaneous, and endothermic for some biosorbents, but on contrary not feasible, exothermic and non spontaneous for other biosorbents. The result of this study showed that the biosorbent derived from *Zea mays* can be used as a prospective biosorbent for oxybenzene in wastewater and also can be an alternative for the commercially activated carbon.

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Abbreviations: NCH, Normal corn husk; NCS, Normal corn silk; BCH, Baby corn husk; BCS, Baby corn silk; CAC, Commercially available activated carbon.

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1. Introduction

Oxybenzene is the major pollutant, present in the wastewater released from different process industries like tanning, plastics, textile, pulp, gas, pharmaceutical, paper, ferrous industries, coke manufacturing, rubber and petroleum refinery industries (Girish et al., 2016). Environmental regulation has considered oxybenzene as a precedence pollutant. Its bearable concentration should be less than 0.1 mg/L before it is released into the aquatic environment (Ahmaruzzaman et al., 2005). Oxybenzene and its derivatives are poisonous and most eugenic at elevated concentrations and may be absorbed by plants, human beings and aquatic animals. The

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abolition of oxy benzene is a major obligation for environmental protection (Amin et al., 2010). Different techniques (biological, chemical and physical methods) have been used to eradicate oxybenzene from contaminated water (Girish et al., 2012). A variety of treatment methods like biodegradation (enzymatic and microbial), electrochemical and advanced oxidation processes, membrane separation process (pervaporation), extraction (using different solvents) and biosorption on activated carbon are used to treat oxybenzene compounds from wastewater. Application of treatment methods like biodegradation, electrochemical and advanced oxidation processes, membrane separation process (pervaporation) and extraction processes are limited, due to its economical or practical limitations. Biosorption is the feasible method for removal of oxybenzene if the oxybenzene concentration is at lower concentration (Farooq et al., 2010; Sud et al., 2008). Oxybenzene can be treated using biological methods. However, at upper concentrations, extraction should be made using solvents and biosorption can be effectual for the treatment of oxybenzene in the middle concentrations (Jadhav et al., 2004). Amongst all the types of methods, biosorption has been extensively used because of its effectiveness (Babel et al., 2004).

For removal of oxybenzene from wastewater, the use of activated carbon (commercially available) is considered as an efficient method due to its large surface area, high biosorption, microporous nature, high purity and capacity (Omri et al., 2012). The use of effective commercial activated carbons to control pollution is unjustified and cost-intensive based on relatively expensive and depleting source materials. Therefore, it is very significant to identify and scrutinize the viability of using cheaper raw materials to prepare activated carbon. Several agri-waste based biosorbents such as agricultural waste material, seed coat of palm (Rengaraj et al., 2002), rubber seed coat (Rengaraj et al., 2001) coconut shell pulp of beet (Dursun et al., 2005), jute stick (Habib et al., 2008), bamboo (Hameed et al., 2006) and corn-cob (Tseng et al., 2005) have been reported for the removal of oxybenzene as a substitute to expensive commercial activated carbon.

Agriculture is one of the strong markets of the Indian financial system and accounts for 18.5 per cent of the country's gross domestic product. *Zea Mays* is a common grain and it is now being accepted as staple diet and its demand is increasing year by year. In India, maize is the third important cereal crop after rice and wheat in terms of area. Currently, 49 per cent of maize output is used as poultry feed, 12 per cent as animal feed, 25 per cent as food, 13 per cent in starch and other industries, and 1 per cent as seed. The by-products from maize are value added products which include maize husk, maize silk, starch, liquid glucose, dextrose monohydrate, anhydrous dextrose, sorbitol, corn gluten to name a few.

In this study biosorbent was prepared using silk and husk of *Zea Mays* variants, which are considered as inexpensive biosorbents for treating oxybenzene. *Zea mays*, commonly known as maize, belongs to the member Poaceae grass family. With production, the waste that also comes from the crop which is going futile. Being an abundant source of carbonaceous agri-waste, it can be developed as a cheaper and feasible biosorbent for the removal of oxybenzene. High contents of Peroxidases enzyme (oxybenzene degrading enzyme) are found in *Zea mays*, which diminishes the problem of disposal of adsorbed oxybenzene (Lakshmi et al., 2018). The kinetics, thermodynamics and isotherms of oxybenzene biosorption were studied and compared with activated carbon (commercially available) to evaluate the effect of several parameters such as biosorbent dosage, pH, contact time, initial ion concentration, temperature and agitation speed on the biosorption process. The Scanning electron microscope studies (SEM) was performed to assess the surface morphology, pores volume and chemical form of the biosorbent, Fourier Transform Infrared (FTIR) was used to detect functional group and characterizing

covalent bonding information after biosorption. The equilibrium data were analyzed using different isotherms. The kinetics and thermodynamics of biosorption were interpreted theoretically using different models.

2. Methods

2.1. Plant material

Zea mays samples were obtained from the local market in the city of Mysore, Karnataka. *Zea mays* is commercially available as normal corn and baby corn in the market. From the samples corn silk and corn husk were segregated. The detection of plant material for adsorption was chosen as per (Elliger et al., 1980) and for detoxification using enzymes as per (Lakshmi et al., 2018). For simultaneous adsorption and detoxification studies this plant was selected. Voucher specimen of this material has been not deposited in a publicly available herbarium as it is locally available plant.

2.2. Chemicals

The AR grade chemicals and supplier details are as follows: Oxybenzene (Nice Chemicals, Mumbai, India), Anhydrous sodium carbonate (Rankem, Mumbai, India), Potassium hydrogen phosphate (s.d.Fine Chem Ltd, Bengaluru, India), Sodium Bicarbonate (Rankem, Mumbai, India), Copper sulphate, sodium potassium tartrate (Merck, Pune, India), 4-aminoantipyrine, Boric acid, Potassium ferricyanide, Potassium dihydrogen phosphate (Hi media laboratories, Bengaluru, India), di-sodium hydroxide (Merck, Pune, India), Sodium bicarbonate, and Folin reagent (Merck, Pune, India).

2.3. Biosorbent preparation

Husk and silk samples were sun-dried for few days to take away the moisture content. The Samples were further subjected to grinding and shredding to form a fine powder. Each sample was stored in appropriate air tight containers to avoid contamination. Thus the obtained samples were further segregated and named as NCH (Normal Corn Husk), NCS (Normal Corn Silk), BCH (Baby Corn Husk) and BCS (Baby Corn Silk).

2.4. Instrument/equipment

Computer interfaced UV-Visible spectrophotometer (Cary 60 UV-Vis, Agilent Technologies) was used. Cuvette, crusher, shaker, pH meter, stirrer were used. Scanning electron microscopy (SEM) images and X-ray mapping were recorded on Zeiss microscope.

2.5. Oxybenzene analysis

The amount (concentration) of oxybenzene in the aqueous solution was determined using a UV-Visible spectrophotometer at a wavelength of 510 nm based on a modified 4-AAP method. Prior to analysis, calibration curve was plotted and its regression factor was calculated, which showed a linear relationship between the concentrations ranges used in this work.

2.6. Batch biosorption kinetic studies

Stock solution of oxybenzene was prepared and stored in brown bottles. Batch biosorption experiments were carried out in flasks (conical) by using an accurately weighed amount of NCH, NCS, BCH, BCS, and CAC (Commercially available activated Carbon). Batch experiments were conducted by using specified amounts of

biosorbent dosage with oxybenzene at different agitation time periods until equilibrium was achieved. Initial concentrations of oxybenzene were held between 20 and 100 mg/l. RPM (revolutions per minute) as a measure of agitation speed of interaction between the biosorbent particles and oxybenzene molecules of various values was used to determine their attributes. Temperature has been set to three different conditions on an hourly basis. Kinetics of biosorption of oxybenzene on biosorbents was carried out in batch experiments by using an orbital shaker manufactured by Shalom Instruments. All the pH based batch experiments were set up by using citrate buffer and acetate buffer in EUTECH Instruments with model no pH/Ion 510 (bench pH/Ion/mV meter), Singapore. For every batch study conducted, filter paper (Whatman No. 5) was used to remove the biosorbent and other fine particles. Each experiment has been repeated three times and the mean values were considered.

2.7. Characteristics studies

Scanning electron microscope (SED 20.0 kV WD10.5 mm Std-PC 40.0) was used to study the surface texture and porosity of the sample. Fourier transform infra-red spectroscopy was used to analyze the samples after biosorption of oxybenzene.

3. Results

3.1. Effect of biosorbent dosage on the removal of oxybenzene

Fig. 1 represents the removal of oxybenzene as a function of biosorbent dosage ranging from 0.5 to 2.0 g of biosorbents and commercial activated carbon. Apparently in all the cases, the biosorption percentage (adsorption of oxybenzene on adsorbent) increases in the beginning and after certain time, the biosorption percentage doesn't show any significant increase due to the fact that the biosorption equilibrium was achieved. This result seemed to be similar to that of the experiment conducted by (Zhang et al., 2010).

The analysis was extended to enlighten the comparison of biosorbent dosage against percentage biosorption between NCH, NCS, BCH, BCS, and CAC. Customarily, CAC proved its efficacy with the highest percentage biosorption followed by BCS which showed

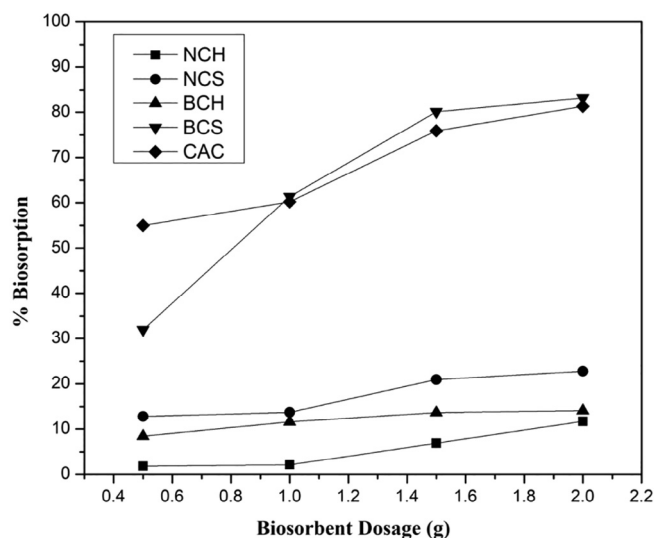


Fig. 1. Effect of biosorbent dosage on the removal of oxybenzene by NCH, NCS, BCH, BCS and CAC (initial concentration of oxybenzene = 100 ppm; pH = 6.56; equilibrium time = 3 h).

comparable results as CAC with % biosorption of 63 ± 24.1 (standard deviation of 24.1). The least efficacy was shown by NCH when compared to other samples.

3.2. Contact time

The dependency for the oxybenzene removal with the agitation time is depicted in Fig. 2. After continuous agitation the results were analyzed over a contact time range of 1–3 h. Apparently, the contact time seems to be insensitive for shorter time period but a significant difference in the biosorption percentage can be seen only in the 3rd hour for all the samples studied. Increase in biosorption rate from 2nd hour pointed to the conclusion that extended periods of biosorption contact time increased the collision frequency between the adsorbate and biosorbent material to cause increased biosorption of oxybenzene on the sample material (Mittal et al., 2009). But there are reports (Yousef et al., 2011) that due to formation of repulsion among oxybenzene molecule the vacant surface sites are difficult to occupy. This shows a steady biosorption rate and they were well shown by the straight horizontal line from the 1st hour.

3.3. Time versus amount adsorbed per gram

At varying time intervals, the amount adsorbed per gram of biosorbent is represented in Fig. 3. The amount of oxybenzene adsorbed, q_e (mg/g) at equilibrium was calculated by the following equation:

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

where, C_e and C_0 equilibrium and initial concentrations of oxybenzene solutions (mg/L), W is the weight of the biosorbent used in grams and V is the volume of the solution in liters and Fig. 1.2 shows that the highest biosorption percentage is achieved by the biosorbent sample BCS compared to CAC which is theoretically not possible. By Fig. 1.3, the reason for that anomaly can be clarified that CAC shows the highest oxybenzene uptake followed by BCS sample with the amount adsorbed (mg/g) as 2.6 ± 0.1 . This is due to the influence of weight of biosorbent used for biosorption studies (Mittal et al., 2009).

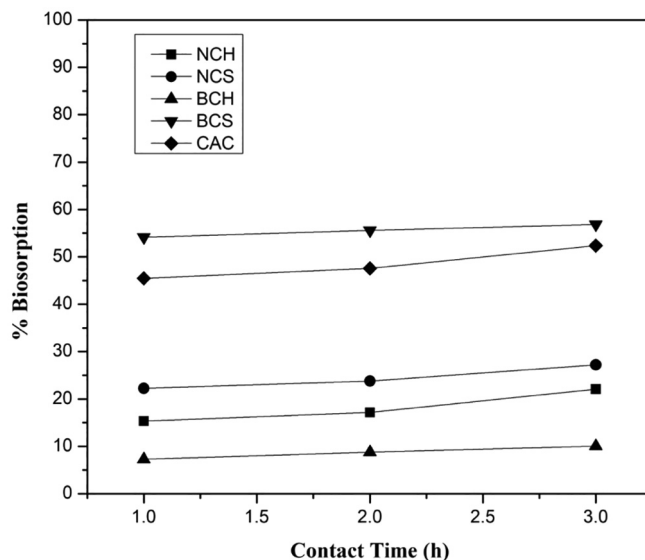


Fig. 2. Effect of contact time on the removal of oxybenzene by NCH, NCS, BCH, BCS and CAC (initial concentration of oxybenzene = 100 ppm; pH = 6.56).

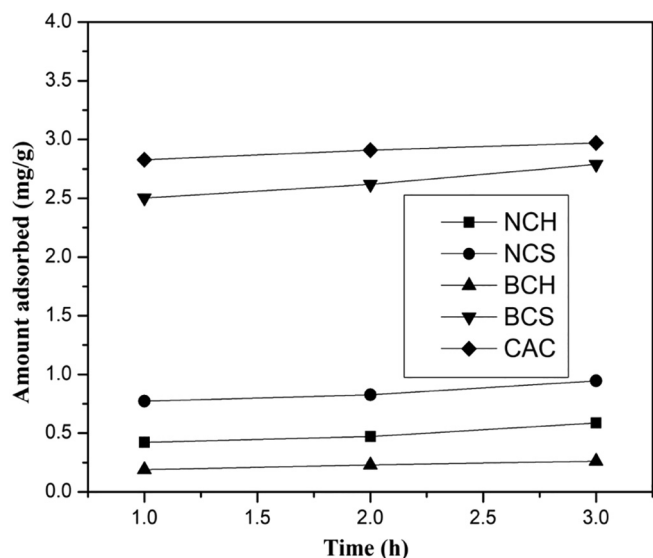


Fig. 3. Equilibrium uptake of oxybenzene at different contact time and initial concentration at 100 mg/l.

3.4. Concentration of the adsorbate

The test results for the effect of initial adsorbate concentration for oxybenzene removal is shown in Fig. 4. The common experimental studies have been reported that adsorbate concentration is proportional to the biosorption rate. For NCH, BCH, and CAC, the biosorption percentage of oxybenzene increased with the increase of the initial adsorbate concentration. The important motivating force to beat all mass transfer limitations of oxybenzene between the aqueous and solid phases is the initial oxybenzene concentration

Therefore at higher initial oxybenzene concentration rate of biosorption is more. A similar trend was also observed (Dursun et al., 2005) for removal of oxybenzene by AC. As far as NCS is considered, there was a decrease in biosorption percentage of oxybenzene with the increase of the initial adsorbate concentration.

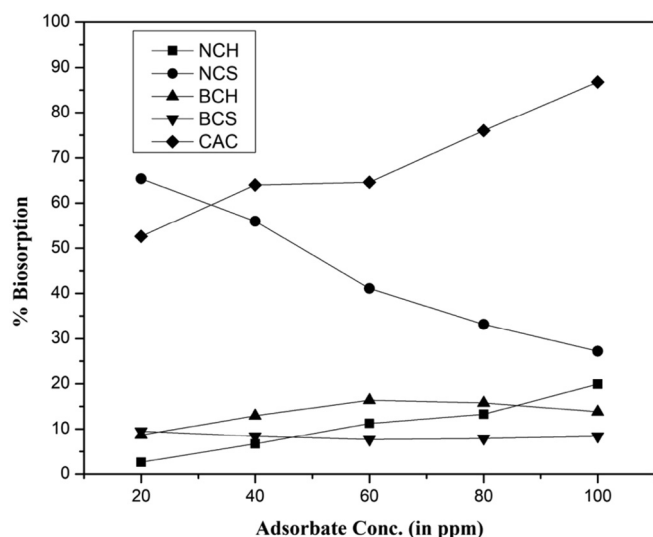


Fig. 4. Effect of initial adsorbate concentration on the removal of oxybenzene by NCH, NCS, BCH, BCS and CAC (pH = 6.56; equilibrium time = 3 h).

3.5. Biosorption isotherms

To explain the data obtained from various experiments in biosorption, isotherms models have been commonly employed (Mittal et al., 2009).

In the present work, the experimental data for the biosorption of oxybenzene on biosorbent samples and commercially available activated carbon were best fitted to Langmuir models and Freundlich models and the correlation coefficients were calculated. Table 1 depicts the values of correlation coefficient (R^2) obtained for different samples under each isotherm. The linear forms of Freundlich and Langmuir models are represented by the equations:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^0 b}\right) + \left(\frac{1}{Q^0}\right) C_e$$

where q_e is the equilibrium amount of oxybenzene adsorbed, K_f , $1/n$ and b are characteristic constants, C_e is the concentration at equilibrium (mg/l), and Q^0 is the concentration of solid phase corresponding to complete coverage of available biosorption sites. For relative measurement of biosorption capacity the value of K_f has been used, b and $1/n$ are related to enthalpy and intensity of biosorption (Maarof et al., 2004). The Langmuir model suggests the biosorption process to be monolayer. According to Langmuir isotherm the surface of biosorbent material contains a number of active sites where the adsorbate attaches itself.

But in the case of Freundlich model heterogeneity was observed due to porosity. This implies that the model is based on the assumption that heterogeneous biosorption due to surface having unevenly available sites with various biosorption energies (Mittal et al., 2009).

3.6. RPM studies

Biosorption that is influenced by the speed (rpm) of the shaker was varied and its results are given in the Fig. 5. As seen in the image, biosorption percentage reduced as the rpm have increased in most of the samples. At a higher rpm, the energy (kinetic) of the biosorbent particle and adsorbate molecules increase in an adequate amount when, they have a collision with both rapidly. This results in the disengagement of the limply (loosely) bound adsorbate molecules. Added to that, at higher rpm, the suspension of the sample is no more homogenous and is found to form small clusters, which randomize the particles and molecules movement (Omri et al., 2012).

Some samples show that an increase in biosorption percentage with increasing speed of agitation. The diffusion rate of oxybenzene molecules from the bulk liquid to the surroundings of the activated carbon particles becomes higher due to improved turbulence and a decrease in the depth of the liquid boundary layer (Kusmierek et al., 2015).

Table 1
 R^2 values for Freundlich and Langmuir isotherms for oxybenzene biosorption.

Sample	R^2 value to biosorption isotherms	
	Freundlich	Langmuir
NCH	0.98877	0.97169
NCS	0.84835	0.97995
BCH	0.96487	0.9598
BCS	0.99633	0.98281
CAC	0.95501	0.97854

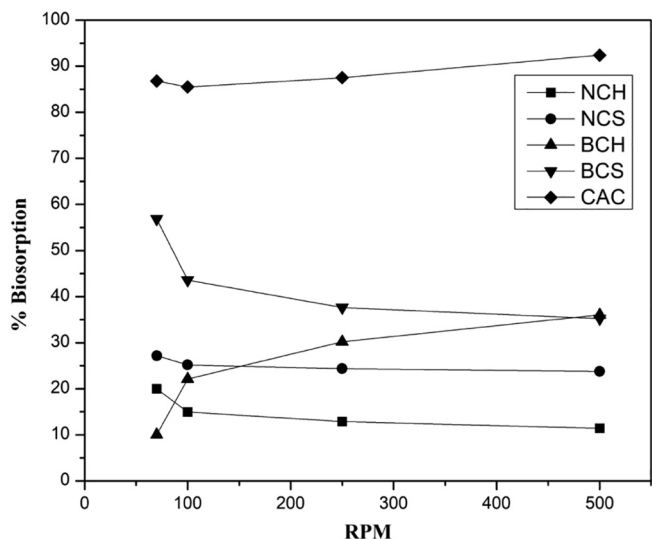


Fig. 5. Effect of RPM on the removal of oxybenzene by NCH,NCS,BCH,BCS and CAC (initial concentration of oxybenzene = 100 pp; pH = 6.56; equilibrium time = 3 h).

3.7. Kinetic studies

The biosorption rate data for the biosorption of oxybenzene onto the biosorbent samples and activated carbon were analyzed using kinetic models. i.e., zero-order-equation, first-order-equation, and pseudo-first-order-equation were tested respectively using the formulas given below:

$$q_e - q_t = kt$$

$$\frac{1}{q_t} - \frac{1}{q_e} = kt$$

$$\ln(q_e - q_t) = \ln q_e - kt$$

where, q_e and q_t are the amounts adsorbed at equilibrium and at time t , and k is the rate constant. Table 2 depicts the correlation coefficient values obtained for different samples under the kinetic models. The above models have checked based on the regression factor. From the table, it is clear that the majority of the samples followed pseudo-first-order-equation and only in the BCS case the kinetic model fitting is at the first order. Similar reports have been reported in the biosorption of oxybenzene from waste water using biomass materials (Hameed et al., 2008).

3.8. Temperature studies

Temperature dependent biosorption studies were carried out on an hourly basis at 3 various temperatures, i.e. 25, 30, and 35 °C. The temperature effect on the biosorbents samples and

Table 2
Biosorption kinetic parameters for the biosorption of oxybenzene onto biosorbent samples and commercial activated carbon are based on the rate equations.

Samples	R ² value to corresponding order of reaction		
	Zero	First	Pseudo first
NCH	0.8974	0.8629	0.9016
NCS	0.9086	0.9028	0.9095
BCH	0.98	0.9938	0.9942
BCS	0.9898	0.9919	0.983
CAC	0.9206	0.8951	0.9783

commercial activated carbon for the removal of oxybenzene is given in Fig. 6, Fig. 7 and Fig. 8. The biosorption percentage exhibits either raise or decline with an increase in temperature. The biosorption percentage increases with an increase of temperature, owing to quick buildup in the rate of diffusion of the adsorbate molecules along the boundary layer (external) and within the pores (internal) of the biosorbent molecule. This is followed by a decline in the stickiness (viscosity) of the solution (Pirbazari et al., 2014). The highest percentage of adsorption 51 ± 3 was observed for BCS at a temperature 25 °C

3.9. Studies on thermodynamic feasibility

Thermodynamic parameters, i.e., free energy (ΔG^0), enthalpy (ΔH^0), and entropy changes (ΔS^0), calculated using the following equations, are given in Table 3:

$$\Delta G^0 = -RT \ln K_1$$

$$\Delta H^0 = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \frac{K_2}{K_1}$$

And,

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

Here K_1 and K_2 are the Langmuir constants corresponding to temperatures 27 °C and 30 °C, respectively.

3.10. pH studies

The effect of study of the pH on the biosorption ability of biosorbent samples and activated carbon for oxybenzene, experiments were conducted at room temperature and with oxybenzene' s initial concentration of 100 mg/L at varied pH values from 3 to 9. Fig. 9 shows that the percentage oxybenzene elimination was maximum with value 36.3 ± 24.5 when the initial pH is 5–6 for oxybenzene solution.

A similar tendency of pH effect was reported for the biosorption of oxybenzene for the biomass, which was used to prepare activated carbon (Hameed et al., 2008). Normally, the surface charge of biosorbent and degree of ionization of the oxybenzene mole-

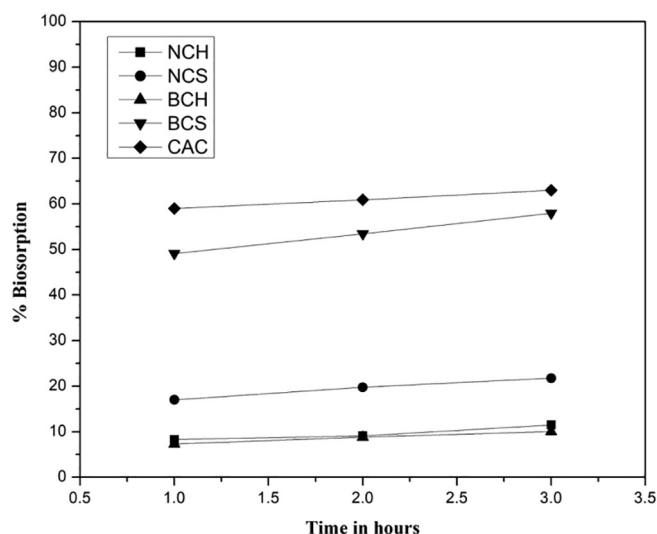


Fig. 6. Effect of temperature (25 °C) on the removal of oxybenzene by NCH,NCS, BCH,BCS and CAC (Initial concentration of phenol = 100 ppm; RPM = 70; pH-6.56).

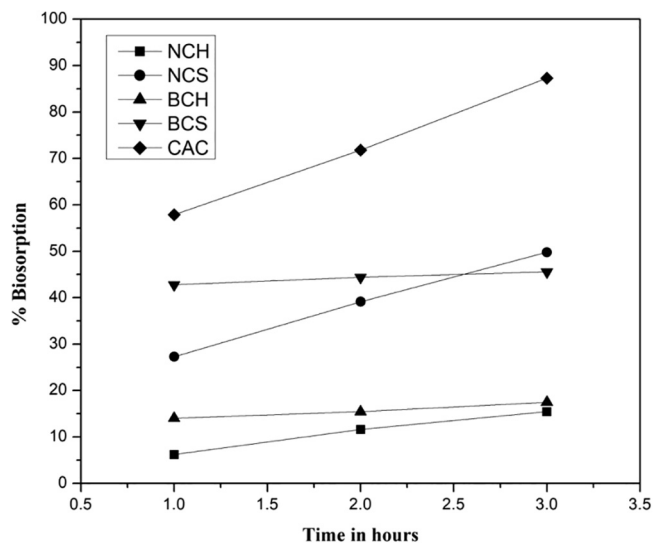


Fig. 7. Effect of temperature (30 °C) on the removal of oxybenzene by NCH,NCS, BCH,BCS and CAC (Initial concentration of phenol = 100 ppm; RPM = 70; pH=6.56).

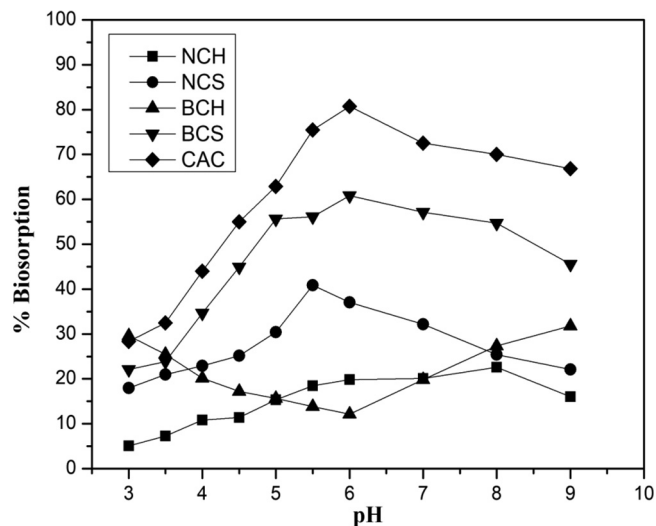


Fig. 9. Effect of pH on the removal of oxybenzene by NCH, NCS, BCH, BCS and CAC (Initial concentration of phenol = 100 ppm; RPM = 70; Temperature = 25 °C).

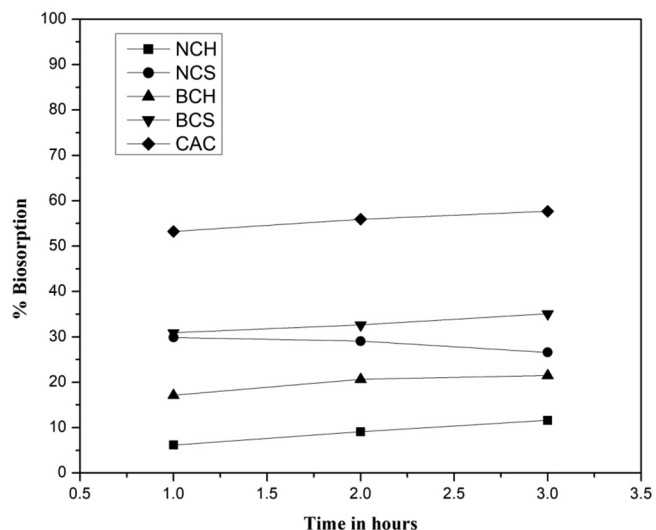


Fig. 8. Effect of temperature (35 °C) on the removal of oxybenzene by NCH,NCS, BCH,BCS and CAC (Initial concentration of phenol = 100 ppm; RPM = 70; pH=6.56).

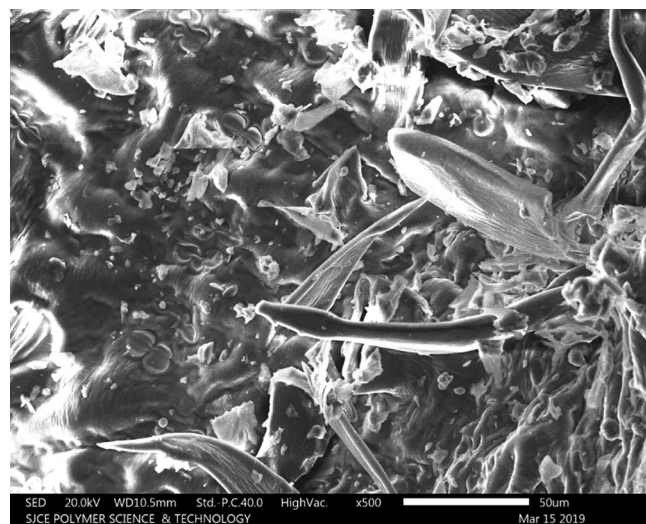


Fig. 10. Scanning electron micrograph of biosorbent sample NCH.

cules is affected by pH (Aksu et al., 2003). Oxybenzene $pK_a \approx 9.89$ as it is a weak acid compound (Sivanesan et al., 2007) is dissociated at $pH > pK_a$.

3.11. Characteristics of samples

3.11.1. SEM analysis

Fig. 10 and Fig. 11 represent the SEM micrographs of sample NCH and BCS taken at 500x magnification. Both the micrographs clearly show irregular patterns of cavities, indicating that the

porosity was generated due to removal of H_2O during the drying process. During this activation period, there was significant increase in carbon content as the volatile matter content decreased.

The pyrolytic effect explains in a better way that, most of the organic substances have been degraded and discharged as gas and liquid tars leaving the material with high carbon purity (Omri et al., 2012).

Table 3
Thermodynamic parameters for the biosorption of oxybenzene.

Sample	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)	Inference
NCH	7772.6	2320280.95	-23157.06	Not feasible, endothermic and non-spontaneous
NCS	3676.06	1098307.18	-10025.76	Not feasible, endothermic and non-spontaneous
CAC	-1530.4	-457202.6	4224.1	Feasible, exothermic and spontaneous
BCH	-222.78	-66548.55	620.22	Feasible, exothermic and spontaneous
BCS	361	110,267	-1283	Not feasible, endothermic and non-spontaneous

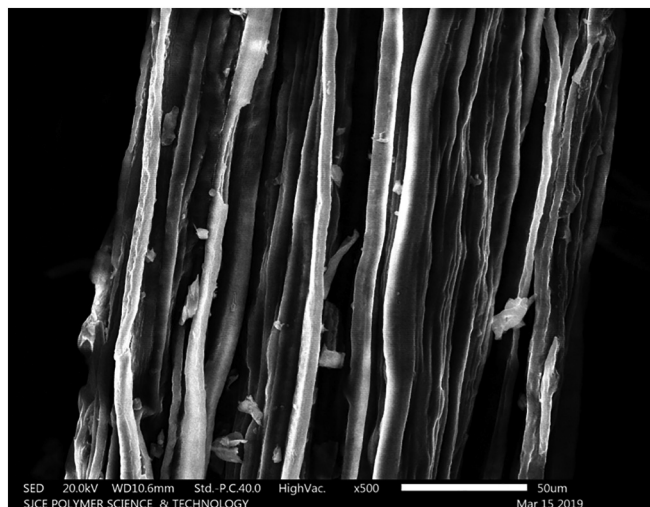


Fig. 11. Scanning electron micrograph of biosorbent sample BCS.

3.11.2. FTIR analysis

The FTIR spectrum of biosorbent samples after biosorption of oxybenzene are illustrated in Fig. 12 [(a), (b), (c) & (d)]. A broad absorption band at 3000–3600 cm^{-1} is accountable to (O–H) stretching vibrations in hydroxyl groups.

The maximum biosorption band for NCH, NCS, BCH, and BCS are about 3324, 3410, 3389, and 3356 cm^{-1} (Omri et al., 2012). In all the FTIR spectrum of different samples showed a shoulder at 1080 cm^{-1} that can be attributed to C–OH stretching of oxybenzene groups.

4. Discussions

The results obtained support the fact that, with a gradual rise in the biosorbent amount, there was an increase in the adsorptive surface area which provides numerous vacant sites for biosorption. The important motivating force to beat all mass transfer limitations of oxybenzene between the aqueous and solid phases is the initial oxybenzene concentration. Results obtained showed that both Freundlich and Langmuir models as most prominent. The increase in temperature causes a decline in biosorption due to the diminished attractive forces between the adsorbate and biosorbent, and to a certain extent due to the development adsorbate thermal energies, which makes biosorbent weak to hold the adsorbed molecules at required sites (Larous et al., 2012). The negative values of ΔG° indicate the feasibility nature of oxybenzene biosorption on the biosorbent samples and commercial activated carbon. The change in enthalpy ΔH° for oxybenzene biosorption on the biosorbent samples was both positive and negative. The positive value indicates biosorption is endothermic in nature and the negative value indicates that the biosorption is exothermic in nature (Singh et al., 2007). The positive value of entropy ΔS° demonstrates the improved randomness inferring natural (spontaneous) biosorption and the negative value of entropy demonstrates non-spontaneous type of biosorption.

The rate of biosorption declines at high pH values due to ionization of adsorbate molecules. The cause could be also due to the electrostatic repulsions between the oxybenzene anions and negative surface charge interactions. While when the solution is at acidic state the percentage removal was superior because oxybenzene was undissociated and the scattering interaction was predominated. From FTIR analysis it is evidently proved that biosorbent used successfully removed oxybenzene.

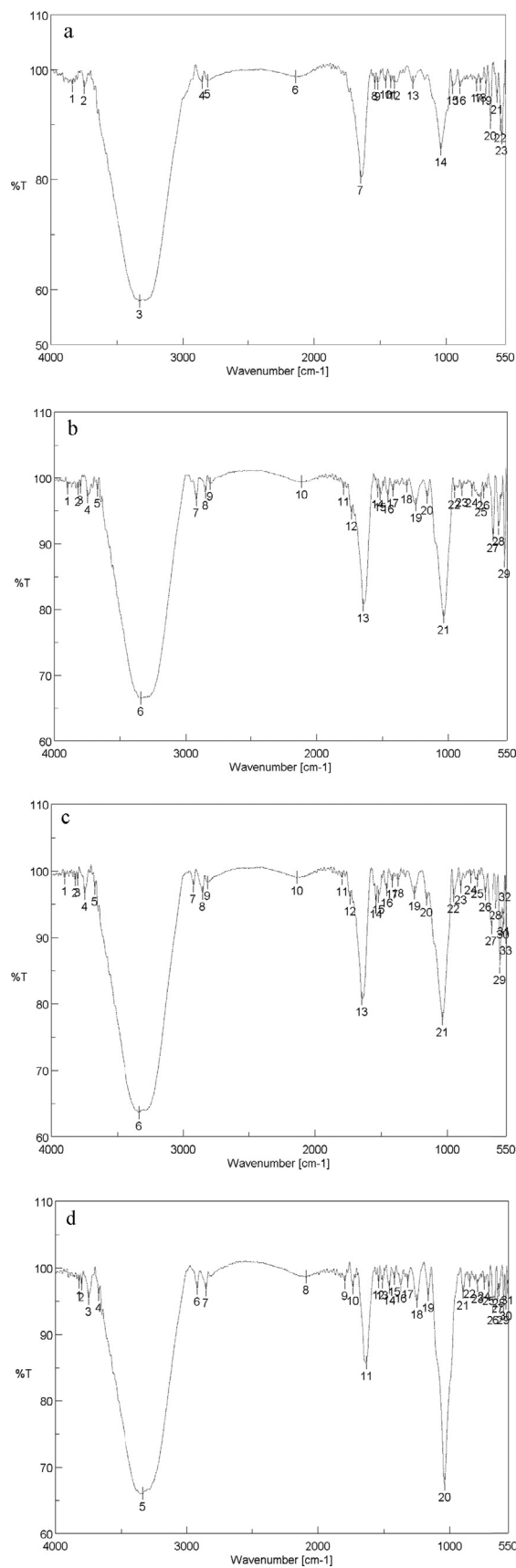


Fig. 12. FTIR spectrum of biosorbent samples after biosorption of oxybenzene (a) NCH (b) NCS (c) BCH (d) BCS.

5. Conclusion

Biosorption using various biosorbent is very important to treat organic pollutants that are released during various human activities. Biosorbent samples obtained from *Zea mays* along with commercial activated carbon were characterized for various physical and chemical properties and studied for the biosorption of oxybenzene under different conditions. The observations indicated that the biosorption capability of the biosorbent was significantly affected by the dosage of the adsorbent, contact time, oxybenzene initial concentration, agitation speed, temperature, and initial pH. Each biosorbent displayed optimum values under each parameter and exploiting that value for the removal of oxybenzene from the wastewater displayed efficient biosorption.

The kinetic and thermodynamic parameters for the oxybenzene biosorption onto biosorbent samples were also determined. The value of ΔG° indicates the feasibility and natural (spontaneous) nature of the biosorption process. The ΔS° values indicate the randomness of molecules and the values of ΔH° shows that the biosorption is either endothermic or exothermic in nature. The Langmuir and Freundlich biosorption equations were used to test the experimental data at equilibrium. The data were well explained by both the models. The kinetic models have been used to analyze data obtained for biosorbent samples. The results showed that the biosorption data better fitted for pseudo-first order equation.

Among all the biosorbent samples, BCS has showed significant capacity in removal of biosorption falling short only marginally to that of the activated carbon. A combination of the biosorbent samples can be used for the maximum biosorption. The biosorption capacities of biosorbent samples used are higher than agricultural wastes or waste materials which undergo high temperature and chemical treatment. Added to it, the *Zea mays* derived biosorbents contains a rich source of peroxidase which is an oxybenzene degrading enzyme, due to which, the disposal and secondary treatment of the adsorbed material is avoided saving huge energy and expenses. Thus, the results of this study show that the biosorbents derived from *Zea mays* can be used as possible biosorbent for the removal of oxybenzene in wastewater and an alternative choice for the commercial activated carbon.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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