Mathematical Modeling and Optimization of Anionic Dye Removal Using *Acacia nilotica* (leaves), *Terminalia arjuna* (nuts) and *Berri ptta* (capsule)

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Received 04 November 2019, Revised 11 May 2020, Accepted 21 May 2020

Abstract

Using cost effective and greener approach for water decontamination is the need of the time. Present work deals with the batch mode removal of anionic dye (Alizarin Red S) from water using biological materials *Acacia nilotica* leaves (KL), *Terminalia arjuna* nuts (AN) and *Berri ptta* capsule (BPC). Various parameters like pH, adsorbent dose, temperature, time were optimized to further conduct the isothermal, kinetics and thermodynamic studies. Isothermal studies revealed that $q_{\max}$ values were in the order. AN nuts (52.95 mg/g) > KL (42.546 mg/g) > BPC (40.60 mg/g) following pseudo second order kinetics model. The process of anionic dye removal is spontaneous and exothermic in nature. These biological materials proved very useful for water decontamination and therefore can be used on large scale.

Keywords: Decontamination; *Terminalia arjuna*, Isothermal study

Introduction

Dyes are the class of organic pollutants that are carcinogenic and mutagenic in nature and in most cases non-biodegradable. They are serious health risk for aquatic life and to human beings. Removal of such pollutants from water bodies is needed to lower health risks and to save lives. The process of dying, either in textile, leather, paper, and plastic industry, use synthetic dyes in various processes [1]. Effluents from these industries pose serious threats to the environmental natural balance [2]. The quantity of wastewater having processed dyes is constantly increasing. Industrial effluents containing different chemicals species, especially synthetic dyes are considered potential carcinogenic in nature. Some dyes undergo aerobic and anaerobic decomposition that results in the development of carcinogenic compounds. In addition, the colored pollutants reduce the penetration of light and prevent the process of

photosynthesis under water. The discharge of effluents from different dyeing industry to the water bodies is a main human concern. Removal of these dyes before discharging them to water bodies is very important. But in countries like Pakistan where the operational cost of any project is the deciding parameter it is required to use such methodology that can be used by people and at higher level for water purification keeping in view the cost effectiveness. Various techniques have been developed to eradicate this issue. Among all such techniques solid phase extraction can be recognized as effective to address such problems. Use of different materials based upon the need have facilitated scientist to get rid of pollutants in a very efficient way.

Alizarin red S dye is considered one of the dyes that produce purple and red colored solution

depending on the pH of water [3]. Alizarin red S dye is also known as 2-Anthraquinonesulfonic acid; 1,2-dihydroxy-9,10-anthra-quinonesulfonic acid sodium salt; ARS and Alias Mordant Red [3]. It is anionic, water soluble anthraquinone dye and an extensively used in industrial sector. It is a derivative of alizarin, which is considered as a natural dye extracted from the roots of *Rubia tinctorum* also known as madder and belongs to the family *Rubiaceae*. Alizarin red S is synthesized by sulfonation of alizarin [4].

Alizarin red S is also used as acid-base indicator, in stain microscopy and in determination of fluorine [5]. In textile industry alizarin red S is commonly used as a coloring agent. This dye is also utilized to stain biological specimens such as small invertebrate embryos and mineralized bones in vertebrate groups. This synthetic dye is stored away from humidity and heat because it is a strong oxidizing agent. It is a non-biodegradable and chemically stable hence, it cannot be fully mineralized by conventional processes of treatment. It is unaffected by degradation process due to its structure that offers high optical, physicochemical, and thermal stability [6].

Figure 1. Process of removal of dye from wastewater

Naturally, alizarin red S cannot be degraded because it has a complex arrangement of aromatic rings; hence it turns noxious and a potential toxic to the aquatic life and biota. The use of water having even trace quantity of toxic alizarin red S causes several harmful effects, such as malfunctioning of lungs, gastritis, painful

micturition, severe headache and methemoglobinemia [7]. It can be a source of eye and skin irritation, cytotoxicity, carcinogenicity, genotoxicity, and toxicity to freshwater organisms [8].

Biological materials are inexpensive, renewable, and nontoxic in nature. They contain cellulosic, lignocellulosic and hemicellulosic material in their structure. Ecofriendly and cost-effective properties make them material of choice for waste wastewater treatment by solid phase extraction. Stem, roots, leaves, barks, peels, and seeds of different plant materials are used for treatment of wastewater. *Acacia nilotica* leaves have been used for removing Cr (VI) from wastewater [9]. Good adsorption capacity of these leaves has been found for the removal of Rhodamine B and crystal violet from aqueous media [10]. For the removal of cationic / anionic dyes clays and plant materials have also been used [11, 12].

Berri pttia capsule is a medicinal plant. It is high deciduous tree that has long incurved seed pods also called capsules that are wasted after ripening. They have also proved useful for the removal of alizarin red S. *Terminalia arjuna* is medicinally very important plant that has been used for the Ayurvedic treatment of cardiovascular diseases. Its fruit showed good removal capacity for Pb (II) [13]. Its plant material proved useful for removal of methylene blue dye from contaminated waters [14].

Although adsorption is extensively worked technique but still there are so many materials available that can be applied as adsorbent and may function far better than those explored so far [15]. Therefore, the present work has used novel species that showed good potential for anionic dye removal. Fig.1 represents the steps involved in the removal of anionic dye from wastewater. These species based upon their morphology and availability of functional groups can be used as such or modified chemically for increasing the active sites for providing the attaching sites for a wide variety of polluting species.

Materials and Methods

Reagents used

Alizarin dye from Sigma Aldrich was used for making standard solutions. Sodium hydroxide, hydrochloric acid, nitric acid, sodium carbonate, zinc chloride, calcium chloride, methanol, and ethanol (Merck) were used for preparing solutions for chemical modification of adsorbents selected for present study. Doubly distilled water was used throughout this work. All glassware used in this study was of Pyrex, Germany. Chromic acid was used to wash the glassware. Washed glassware was dried in oven at 70°C for 4 h prior to adsorption studies.

Preparation of adsorbents

Plant material used in present study were collected from University of the Punjab, New Campus, Lahore. Collected material was separately washed and dried in day light under shade. Dried material was grinded and powdered was sieved to 40 ASTM mesh size. Prepared material was stored in glass jars and tightly covered and tagged KL (for *Acacia nilotica* leaves), AN (*Terminalia arjuna* nuts) and BPC (Berri patta capsule).

Instrumentation

During study the following instrumentation is employed for conducting necessary experimentation and characterization; Electronic weighing balance (Shimadzu Corporation Japan); Orbital shaker (Yellow line OS 10control, Japan); pH meter (Hanna); Spectrophotometer (Hitachi U1800); SEM (JSM 5910, JEOL Japan); FT-IR (Fourier-transform infrared spectroscopy) spectrometer (Jasco, USA)

Adsorbents selected for alizarin red S adsorption

To conduct the adsorption study for alizarin, adsorbents were subjected to the initial experiment for dye removal. 0.2 g of each adsorbent was added separately to the 50 mL of 25 ppm dye solution. Solutions were shaken for 30 min at 150 rpm at room temperature. After

filtration, the remaining dye was estimated spectrophotometrically at 423 nm.

Parameters optimization

Batch mode solid phase extraction studies were conducted by optimizing the following parameters. For this purpose, 50 mL of 25 ppm dye solution was used, after prescribed procedure the left-over dye concentration was then checked by using spectrophotometer.

Time span was varied from 5 to 70 min with the regular interval of 5 min and agitation speed of 150 rpm at room temperature. As little as 0.2 g of the adsorbents were added in the said amount of the solution. After treatment, the solutions were filtered and checked for the remaining dye concentrations spectrophotometrically.

Greater the number of adsorption sites higher is the adsorption rate. Increasing the adsorbent dose proportionally increases the number of adsorbing sites. Effect of varying adsorbent dose was studied by varying the adsorbent dose from 0.2 to 2 g at previously optimized time and agitation speed. Remaining dye concentration helped to find out the most suitable adsorbent dose for dye removal.

Quality of adsorption process depends upon the pH of the working solution. pH was varied from 3 to 11 to study the behavior of selected dye in acidic and basic medium. pH of the solution was adjusted by using 0.1 M sodium hydroxide and 0.1 M hydrochloric acid solution.

Varying the temperature from 10°C to 60°C under the optimized conditions of contact time, agitation speed, adsorbent dose, and pH, helped to find out the temperature dependence of this study.

Chemical treatment

Acid and alkali treatment of adsorbents was carried out by using 0.01 M solution of sodium hydroxide, hydrochloric acid, nitric acid and sodium carbonate. Treatment of adsorbents with organic solvents was carried out by using

50% v/v solution of methanol and ethanol. Treatment of adsorbent by zinc chloride and calcium chloride was carried out by using 0.01 M solution of both separately.

Selected adsorbents (100 g) each were agitated in a flask with 500 mL of treating agent at 100 rpm for 3 hours. Later, the solution was filtered, and adsorbents were washed with doubly distilled water to remove excess of modifying reagents. Washed adsorbents were dried in oven for 5 hours at 70°C and stored properly.

Desorption

Regenerating of adsorbents was also studied that favors the applicability, usability on large scale and environment friendly nature of selected adsorbents. Desorption of adsorbed dye was done by using 0.1 M sodium hydroxide and sodium bicarbonate.

Isothermal study

For isothermal studies, the dye concentration was varied from 5 to 35 ppm with regular interval of 5 ppm. 50 mL of each concentration of dye solution was used under the previously optimized parameters of time of contact, agitation speed, pH, adsorbent dose, and temperature. Remaining alizarin concentration in each set of experiment was determined spectrophotometrically.

$$\text{Adsorption (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

'C_e' and 'C_o' are the concentrations of alizarin dye before and after adsorption, respectively. Langmuir, Freundlich and Temkin were used for exploring the adsorption mechanism.

Langmuir adsorption isotherm was studied using the equation 2.

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (2)$$

Linearity of the plot between 1/q vs. 1/C_e revealed the applicability of the adsorption model.

Dimensionless factor 'R_L' (equation 3) helps to determine the favorability of adsorption process.

$$R_L = \frac{1}{(1 + bC_e)} \quad (3)$$

Freundlich adsorption model was studied to investigate the heterogeneous nature of adsorption process using equation 4.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Linear plot of 'log q' vs. 'log C_e' indicates the applicability of Freundlich adsorption model. Freundlich constant 'n' shows the quality of adsorption.

Temkin adsorption isotherm model (equation 5) deals with the uniform distribution of energy throughout the adsorbent surface.

$$q = B_T \ln C_e + B_T \ln K_T \quad (5)$$

Linearity of the plot 'q' vs. 'ln C_e' reveals the applicability of this model. Temkin isotherm constant B_T gives information about the nature of interaction between adsorbent and alizarin dye.

Kinetics study for alizarin red S removal

To conduct the kinetics study 50 mL of 25 ppm solution of alizarin was used and agitated for 5 to 70 minutes keeping the optimized conditions under consideration. Filtrate obtained in each case was subjected to the dye estimation by using spectrophotometry. Pseudo first and pseudo second order kinetics models are used for studying the kinetic behavior of alizarin adsorption process using equation 6 and 7 respectively.

$$\log(q_e - q_t) = \log q_e - \left\{ \frac{k_1}{2.303} \right\} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \left\{ \frac{1}{q_e} \right\} t \quad (7)$$

Value of regression coefficient (R²) in case of plotting a graph between log (q_e-q_t) vs. 't' and 't/q_t' vs. 't' helpful in concluding the suitable applicability of pseudo first and pseudo second order reaction kinetics.

Thermodynamic study for alizarin red S removal

Thermodynamics study was conducted by varying temperature of the dye solution from 10°C to 60°C. Previously optimized parameters were employed. Enthalpy (ΔH°) and entropy (ΔS°) of the adsorption process were calculated by the regression analysis of the linear plot of $\ln K_D$ vs. $1/T$. Thermodynamic parameter Gibbs free energy (ΔG°) was then calculated using equation 9.

$$\Delta G^\circ = IRT \ln(K) \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

$$\ln(K) = -\left(\Delta H^\circ \frac{1}{RT}\right) + \Delta S^\circ \frac{1}{R} \quad (10)$$

Negative values of enthalpy and Gibbs free energy reveal that adsorption is exothermic and spontaneous in nature. Whereas, the positive value of entropy reveals the randomness in the system due to the interaction between alizarin dye and the adsorbent.

Results and Discussion

In present work, alizarin red S was removed from aqueous media by solid phase extraction using three novel biosorbents.

Characterization of adsorbent

Selected adsorbents were characterized before and after adsorption by spectroscopic techniques including scanning electron micrographs and Fourier transform infrared spectroscopy.

SEM images of adsorbents after alizarin red S adsorption

Surface morphology of plant material was explored by SEM images of adsorbents before and after the adsorption of alizarin dye. Alizarin adsorbed adsorbent surface was coated with gold through gold sputter by applying accelerating voltage of 15kV. SEM micrographs of adsorbents before adsorption are represented in Fig. 2.

Figure 2. SEM. image of raw adsorbents; (a) (KL (acacia nilotica leaves)), (b) (AN (terminalia arjuna nuts)), (c) (BPC (berri ptta capsule))

SEM analysis of the samples revealed change in the surface morphology of all the biological adsorbents. This means that raw form of all the adsorbents was suitable for the adsorption of ARS on the surface due to which alizarin red S interacted well and further brought the change in the surface morphology of the adsorbents.

SEM micrographs of adsorbents after adsorption are represented in Fig. 3.

Figure 3. SEM. image after adsorption: a (Acacia nilotica leaves (KL)), b (Terminalia arjuna nuts (AN)), c (Berri pitta capsule (BPC))

FT-IR analysis

FT-IR spectra of KL (Fig. 4) showed absorption bands at 2918, 1720, 1603, 1194, 1028 and 758 cm^{-1} . The peak 2918 cm^{-1} corresponds to C-H stretching vibrations of alkanes. The peak 1720 cm^{-1} corresponds to C=O stretching vibration of aldehydes. The peak 1603 cm^{-1} corresponds to C=C of alkenes. The peak 1194 cm^{-1} is

characteristic of C-N of amines. The peak 1028 cm^{-1} corresponds to C-O stretching of carboxylic acids or phenols. The bands at 758 cm^{-1} corresponds to C-X where "X" denoted any halogen element.

Figure 4. FT-IR spectrum of acacia nilotica leaves

FT-IR spectra of AN (Fig. 5) showed absorption bands at 3289, 2159, 1340, 1235, 1152, 1105.85, 1032, 1364 and 663 cm^{-1} . The band at 3289 cm^{-1} corresponds to O-H alcohols, phenols of H-bonded or carboxylic acids. The band at 2159 cm^{-1} corresponds to C≡C stretching vibrations. The band at 1340 cm^{-1} corresponds to amines having C-N group. The band at 1235, 1152, 1105, 1032 cm^{-1} is characteristic of C-O stretching vibrations of alcohols or carboxylic acids. The band 1364 and 663 cm^{-1} corresponds to C-X where "X" denoted any halogen element.

Figure 5. FT-IR spectrum of terminalia arjuna nuts

FT-IR spectra of BPC (Fig. 6) showed absorption bands at 2928, 1704, 1637, 1375, 1239 and 1035 cm^{-1} . The band at 2928 cm^{-1} is characteristic of C–H stretching vibrations of alkanes. The bands at 1704 corresponds to C=O stretching of aldehyde. The band at and 1637 cm^{-1} refers to C=C vibrations in alkenes. The band 1375 cm^{-1} corresponds to C–X where “X” denoted any halogen element. The band 1239 and 1035 cm^{-1} corresponds to stretching vibrations of C–O of carboxylic acids or phenols.

Figure 6. FT-IR spectrum of Berri ptta capsule

Parameters optimized

The earlier mentioned parameters were optimized to explore adsorption behavior. Mechanism of the adsorption process was explored by applying the isothermal models. Kinetics and thermodynamic studies showed the time and temperature dependence of adsorption study.

Effect of contact time

Selected adsorbents (0.2 g) were used for alizarin adsorption study at constant agitation speed of 150 rpm. Comparative analysis revealed that AN showed maximum removal efficiency (87.92%) after 5 minutes. This reveals that more effective adsorption sites were offered by AN that allowed the interaction with the adsorbate ions and maximum removal efficiency was attained. Whereas, in case of KL and BPC it took a bit long that might attribute to the slow attachment of

adsorbate ions to the adsorbent surface as shown in Fig. 7.

Figure 7. Effect of contact time on removal of alizarin red S using; KL (acacia nilotica leaves), AN (terminalia arjuna nuts) and BPC (berri ptta capsule)

Effect of adsorbent dose

Effect of adsorbent dose was studied at the optimized values of time of contact and shaking speed. Adsorbent dose was varied from 0.2 to 2 g. Removal efficiency tends to increase and reach the maximum value after equilibrium was attained. The results are graphically represented in Fig. 8. Maximum removal efficiency in case of AN is attributed to establishment of equilibrium and maximum adsorbate-adsorbent interaction at 0.4g of dose. Further by increasing the adsorbent dose showed no remarkable effect on removal efficiency.

Figure 8. Effect of adsorbent dose on alizarin red S adsorption using; KL (acacia nilotica leaves), AN (terminalia arjuna nuts) and BPC (berri ptta capsule)

Effect of pH

Greater removal efficiency for the dye is observed in the acidic range. Highest values of adsorption were obtained for AN at pH 3. Results are graphically represented in Fig. 9. Acidic medium might have increased the effective adsorption site by creating charge on the adsorbent surface which further facilitated the dye to get attached with the adsorbent surface.

Figure 9. Effect of pH on alizarin red S adsorption using; KL (acacia nilotica leaves), AN (terminalia arjuna nuts) and BPC (berri ptta capsule)

Effect of temperature

Temperature has a remarkable effect on adsorption process as it effects the movement of molecules and further increases collision of adsorbate molecules with adsorbent surface. Its effect on the adsorption of alizarin red S was studied at optimized conditions of time of contact, agitation speed, adsorbent dose, and pH. Results obtained are graphically presented in Fig. 10.

Figure 10. Effect of temperature on alizarin red S adsorption using; KL (acacia nilotica leaves), AN (terminalia arjuna nuts), BPC (berri ptta capsule)

Effect of chemical treatment

In addition to the use of raw adsorbents for alizarin red S removal various chemical treatment were also tested to enhance the adsorption capacity of the adsorbents. 1 g of each treated adsorbent was added to the solution and adsorption study was conducted at the previously optimized conditions of: time of contact, agitation speed pH and temperature. All the selected adsorbents were treated chemically to get some better results of dye removal. It has been found that acidic, alcoholic and zinc chloride treatment showed comparatively good results. Zinc chloride treatment for KL was in accordance with [16]. AN showed better response for acid treatment than alcoholic. Results for the effect of chemical treatment are graphically represented in Fig. 11.

Figure 11. Effect of chemical treatment on alizarin red S adsorption using; KL (acacia nilotica leaves), AN (terminalia arjuna nuts) and BPC (berri ptta capsule)

Effect of desorbing reagent

Regeneration of the adsorbent is very important as it affirms its reusability and ecofriendly nature. Adsorbents can be re-employed for removal of toxic species after regeneration. Desorption studies were carried out using 0.1g of each adsorbent in 50mL of the desorbing solution. The solution was agitated at 100 rpm for 30 minutes. For desorption of alizarin red S; sodium hydroxide (0.1 M) and Sodium carbonate (0.1 M) solutions were used. Sodium hydroxide is found more effective in desorbing the alizarin red S from the adsorbents as compared to Sodium carbonate. This might be because formation of sodium salt of dye facilitated

desorption of alizarin from the adsorbent surface. Results for desorption studies of alizarin red S are graphically represented in Fig. 12.

Figure 12. Effect of desorbing agent on alizarin red S adsorbed biological adsorbent

Isothermal modeling for alizarin red S

Three isothermal models as discussed earlier were employed for isothermal modeling to explore the adsorption mechanism. Parameters for 'Langmuir adsorption isotherms' are given in Table 1.

Value of regression coefficient (R^2) is approaching unity in case of those adsorbents where Langmuir adsorption isotherm holds good and is dominating model to explain the adsorption of alizarin red S. It is also clearly suggested from the data that there are fixed number of adsorption sites uniformly distributed on adsorbent surface and alizarin has equal affinity towards adsorption sites with no lateral interaction among dye molecules. Moreover, the $Q_{\max}$ value is also indicative of the fact that among the biological

adsorbent arjun nuts showed greater tendency for dye adsorption.

Langmuir parameter 'b' was used to determine the value of dimensionless constant R_L . It was depicted that for all the adsorbents the value of this dimensionless constant is below 1. This suggested that adsorption of alizarin red S by the adsorbents selected for this study was favorable process and these adsorbents can be used for large scale removal of alizarin red S from wastewater [17].

Multilayer adsorption on the heterogeneous surface of adsorbent was explored by applying the Freundlich isotherm. This multilayer adsorption can be further explained by the lateral interaction among the alizarin molecules. It has been revealed that nonlinearity of the system increased with the increased value of 'n' that is associated with the increased heterogeneity of the adsorbent surface. Value of 'n' from 2 to 10 indicates the better adsorption whereas from 1 to 2 predict good adsorption. Higher values of K_f indicated the effective bonding of dye on the adsorbent surface.

Temkin isotherm model explains the equal distribution of binding energies on the adsorbent surface. Value of ' B_T ' below 8 revealed the weak interaction that can be interpreted as physisorption. Lower B_T values are indicative of the fact that adsorbents can be easily regenerated after desorption. Higher K_T values are indicative of the fact that stronger interactions are present between the adsorbent surface and alizarin dye.

Table 1. Adsorption isothermal parameters for alizarin red S adsorption study.

Adsorbent	Langmuir Isotherm Parameters				Freundlich Isotherm Parameters			Temkin isotherm Parameters		
	R^2	$Q_{\max}$ (mg/g)	b (L/g)	R_L	R^2	n	K_f (mg/g)	R^2	B_T (kJ/mol)	K_T (L/mg)
KL	0.860	42.546	0.005	0.888	0.879	0.754	0.122	0.813	2.386	0.338
AN	0.993	52.951	0.006	0.869	0.989	1.034	0.320	0.949	3.035	0.505
BPC	0.987	40.601	0.007	0.851	0.984	0.925	0.249	0.907	2.718	0.441

Table 2. Kinetic study for adsorption of alizarin red S.

Adsorbent	Pseudo First Order Kinetics Parameters			Pseudo Second Order Kinetics Parameters			Q_{exp} (mg/g)
	R^2	K_1 (min^{-1})	Q_t (mg/g)	R^2	K_2 (g/mg/min)	Q_t (mg/g)	
KL	0.8082	0.020	1.050	0.9989	0.744	1.384	1.70
AN	0.6789	0.043	5.744	0.9843	0.200	1.955	2.05
BPC	0.9009	0.044	5.133	0.9988	0.185	4.705	4.69

Kinetic study for alizarin red S adsorption

Kinetics study showed the removal of alizarin red S as a function of time and data obtained is tabulated in Table 2. The dependence of experimental data on time was investigated by applying pseudo first and pseudo second order kinetics models.

When maximum alizarin was adsorbed the adsorbent becomes saturated thereby revealing the adsorption capacity of each adsorbent for alizarin. Theoretical and experimental adsorption capacities represented as Q_t and Q_{exp} are shown in the Table 2. Better applicability of the kinetic model was checked by using equations 6 and 7 for pseudo first and pseudo second order kinetics model respectively. Comparison of the regression coefficient (R^2) values showed that pseudo second order model is more in accordance with the data.

In all the cases the R^2 values for pseudo second order kinetics model are approaching unity. Theoretical and experimental adsorption capacity values were not in agreement with each other for pseudo first order kinetics model. Whereas, in the case of pseudo second order kinetics model theoretical and experimental adsorption capacity for alizarin were in accordance

with each other which showed the better applicability of this model.

Thermodynamic study for alizarin red S adsorption

Thermodynamics study for adsorption process of alizarin was conducted by keeping all the parameters constant and varying the temperature from 10 °C to 60 °C. Thermodynamic parameters like; ΔG° , ΔH° and ΔS° were calculated by using equations 9 and 10 and are tabulated in Table 3.

Negative values of ΔG° indicate the spontaneous nature and thermodynamic feasibility of adsorption of alizarin using all the adsorbents. Increased negative value of ΔG° with temperature indicates the increased alizarin removal at high temperature. Negative values of ΔH° revealed the exothermic nature of alizarin adsorption process, whereas, the positive ΔH° values revealed endothermic nature of alizarin adsorption. For significant adsorption of alizarin the negative values of ΔG° must be accompanied with the negative values of ΔH° as shown in case of KL, AN and BPC. Positive values of ΔS° showed that when alizarin interacted with the adsorbent surface, this interaction imparted randomness to the system.

Table 3. Thermodynamic parameters for adsorption of alizarin red S.

Adsorbents	Thermodynamic Parameters			
	R^2	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
KL	0.934	-2.754	-4.970	0.643
AN	0.955	-1.384	-3.390	0.812
BPC	0.849	-0.744	-0.822	0.147

Conclusion

Present study revealed that comparative analysis of three biosorbents to check their abilities to remove alizarin red S from water proved very effective. All the three selected biomaterials significantly removed alizarin red S from water. Out of these the AN (terminalia arjuna nuts) proved more efficient in removing alizarin red S from water. Surface characterization of adsorbents also revealed the presence of different adsorbing sites that very effectively removed the dye from water. Isothermal, kinetics and thermodynamics studies revealed that adsorption followed Langmuir monolayer pattern, pseudo second order reaction kinetics model. The thermodynamic parameters including Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), showed the adsorption process was exothermic and spontaneous. Keeping in view the regenerability of the biosorbents, it is therefore recommended to be used on large scale for column studies for water purification.

Conflict of interest

The authors have no conflict over the publication of this research article.

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