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Extensive investigation on the study for the adsorption of Bromocresol Green (BCG) dye using activated *Phragmites karka*

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Removal of Bromocresol green (BCG) dye from aqueous solution has been investigated using activated bio-sorbent *Phragmites karka* (PK). Batch adsorption method has been adopted and different parameters such as; *p*H of the solution, contact time, agitation speed, APK/BCG dose and temperature has been studied. From the resulted adsorption data the process is optimised and the transportation mechanism of BCG onto APK phase is proposed. In this study the bio-adsorbent PK is charred using H_2SO_4 to produce activated *Phragmites karka* (APK) which appears as an effective adsorbent on enhancing the loading efficiency of BCG than PK without activation. The BCG adsorption efficiency is increased from 16.05 to 84.2 % with increasing in acidity of the solution and maximized at *p*H 0.5 of solution. Maximum loading capacity of 392.3 mg/g is resulted using APK as adsorbent while removing BCG at ambient condition. The PK, APK, BCG loaded APK, and BCG are characterized by SEM, UV-vis and FTIR to ascertain the adsorption process as well as mechanism. The absorption peak obtained at 3450 cm^{-1} due to ν (O-Hstr) of BCG was shifted to a broad band at 3270 cm^{-1} shows the conjugation of BCG on surface of the APK, confirming the transporation of BCG to APK Phase as resulted from FTIR analysis. From the adsorption kinetics study, the rate of BCG adsorption shows well fit to the pseudo second order model than pseudo first order kinetic model. The positive value of, ΔH^o 2.49 kJ/ mole obtained by thermodynamic study reveals the endothermic nature of adsorption and and ΔS^o 24.87 $J.K^{-1}mol^{-1}$ shows the increase in degrees of freedom of BCG during adsorption. Equilibrium data are analysed by Langmuir, Freundlich and Tempkins adsorption isotherm to establish adsorption mechanism and the results shows best fit with Freundlich (R^2=0.99) isotherm and reveals that the adsorption is of chemisorptions type.

Keywords: Bromocresol Green (BCG), *Phragmites karka*, Adsorption, Kinetics, Isotherm

Uses of organic dyes are extensive in several domestic as well as other industrial products. These dyes are being applied as the dying agent for the products manufactured from various industries: textiles, plastics, rubber, leather, paper, cosmetics and food[1,2]. However, there is the issue of the low content of azo dyes found in indusial effluent, discharged from the textile industries and dye manufacturing sectors during production process. These effluents containing dyes get contaminated to the underground and other water bodies of the environment. Most of these dyes can cause potential threat because they are of toxic, mutagenic or carcinogenic in nature. Thereby, its contamination with the fresh water bodies of environment not only become serious threat to the aquatic life but also to the human lives[3,4]. It is therefore urged to develop relevant process to remove dyes from waste effluent in environmental prospect. As reported by the literatures[4,5], the production cost of dye manufacturing industry is lost by 15-20 % of dye in the form of effluent as per the estimation reported by World Bank.

Dyes are of various kinds based on their chemical nature, they are broadly classified into three different categories based on ionization property in aqueous solution. They are of anionic (acidic, direct and reactive dyes), cationic (basic dyes) and nonionic (disperse dyes) dyes [5]. Dyes used in the dye/textile industries are of synthetic and complex chemical structure which makes them exist in environment for a long period of time due to their high stability towards light, oxidation and biodegradation. In consequences of which it become difficult to remove the dye molecules from the aqueous media. Intensive studies have been devoted by the researchers for the removal of dyes where they describe that the waste water having dye molecules discharged into aqueous system that promotes the eutrophication and also affects the photosynthetic process in aquatic ecosystem because of the reduction of penetration of light[6,7]. However, some dyes basically azo dyes which constitute 60–70% of the total commercial dye stuffs decompose to produce about 20 kinds of carcinogenic aromatic amines[8,9] leading to cause on changing in DNA structure of animals also induced lesions and cancer. One such dye namely Bromocresol Green (BCG) (2,6-dibromo-4-[7-(3,5-dibromo-4-hydroxy-2-methyl-phenyl)-9,9-dioxo-8-oxa-9λ6thiabicyclo[4.3.0] nona-1,3,5-trien-7-yl]-3 methyl-phenol) is a triphenylmethane (anionic) and usually used as *p*H indicator and as a DNA tracer for agarose gel electrophoresis. In addition, it also used in textile industry for dying purposes[10]. In acidic media, BCG remains as light brown solid; while in alkaline *p*H (sodium salt) it become dark green solid. It is again found as a pollutant in the environment due to its changeable color property with different *p*H level of water such as in aqueous solution they dissociate to monoanionic form (pK_a of 4.8) and get yellow color and at higher *p*H, it changes to dianionic form (blue- colour)[10]. Thus, removal of dye from waste contaminated water is warranted before they are discharged into fresh natural water bodies of the environment.

Many researchers[5,11-13] have investigated the removal of dye from waste contaminated water and as per degree of this pollution level and numerous physical/chemical/ biological approaches are being adopted for the removal of dyes from waste contaminated waters. The methods such as coagulation–flocculation, membrane filtration, photocatalytic oxidation, biological treatments and adsorption process are quite familiar and being commonly practiced by authors[4,5,14,15]. To overcome several issues such as incomplete removal of said dye, usage of high cost reagent and high energy generation of toxic sludge or other waste products, high operating costs of these processes in above processes, an effective method like adsorption appears to be promising and environmental friendly. Other salient features such as high loading efficiency, cost-effective, simple design process and effortless operation shows its potential for application in separation of dyes from numerous sources[5,7,16]. However, selection of the suitable adsorbent in adsorption process becomes vital in context of their effectiveness towards higher loading efficiency. Bio-adsorbent such as walnut and poplar woods[6], olive stones[7], apricot stones[16], rice husks[17], orange peels[18], bamboo charcoal[19], *Ziziphus nummularia*[20] etc. appears to be promising and are successfully used for removal of methylene blue and methyl orange, acid red 18, rhodamin B, acid orange 7 and Bromocresol Green dyes. But the above adsorbent applied as it is seems to be less effective, therefore they are either modified or activated by chemical/ physical mean to improve the adsorption efficiency[21]. In addition, the activated carbon form of above bio adsorbents is most widely used because of their characteristic features like high adsorption efficiency due to high specific surface areas, favourable pore size distribution and high degree of surface reactivity and amphoteric nature, ascertaining their potential usages for removal of both cationic and anionic pollutants from waste contaminated water[21-23]. Numbers of commercially activated carbons are available as adsorbents for dye removal but due to the issue of high preparation cost as they are derived from non-renewable source of expensive starting materials such as lignocellulosic materials and coal[24], thus alternate source with viable methods for preparation of AC is urged. Chemical activation includes treatment with different chemicals have great advantage over the physical activation process e.g., chemical activation acquires only one step, lower temperatures for pyrolysis, high yield, very high surface area, etc. However, the activated carbon prepared from plant wastes or agricultural by-products, such as saw dust, wood, banana pith, fruit stones, coconut husks, rice husks, citrus fruit peels etc. are great interest due to their advantages of low cost (or even free of cost), easy accessible, and eco-friendly[10].

Present investigation is aimed to produce low cost, more effective and environmentally friendly activated carbons from bio adsorbent *Phragmites karka* for efficient removal of BCG. In this study activated *Phragmites karka* was applied for BCG removal and adsorption data were investigated by fitting the kinetics, adsorption isotherm and thermodynamic results. Typical solid sample (s) of the experiments including the activated *Phragmites karka* was characterized by FT-IR, UV-VIS, SEM and the adsorption mechanism was proposed and reported.

Experimental Section

Materials

Bromocresol Green (BCG) with the molecular formula $C_{12}H_{14}Br_4O_5S$ having molecular mass 698.05

was procured from Himedia chemical reagent Ltd. Hydrochloric acid (Fisher Scientific) and sodium hydroxide (Merck) used in this experiment were of analytical grade (AR). The stock solution of BCG and different BCG concentration with subsequent dilution was prepared using double distilled water.

Procedure for analysis of dye solution

The desired concentration (100 mg/L in most of the study unless otherwise specified) of BCG used in this investigation resembles to the concentration profile of industrial discharge waste effluent was prepared for the experimental investigation. The estimation of BCG solution for each of the samples resulted after adsorption experiment was performed by colour metric method using a UV-Visible spectrophotometer (UV- 1800, Shimadzu, Japan) while measuring absorbance at wavelength of 442 nm. The *p*H of the respective solution was measured by Systronics *p*H meter (μC *p*H system 361, India) and the *p*H adjustments were made using dilute NaOH and HCl solutions. Fourier transform infrared (FT-IR) analysis for *Phragmites karka* was performed by Shimazdu, IRAffinity-1S FTIR spectrophotometer (Shimadzu Co. Tokyo, Japan).

Preparation of activated *Phragmites karka*

The adsorbent materials were collected from Chilika lake area, Odisha, India and first washed with distilled water to remove dirt and impurities and water soluble materials and then dried to remove the water content. The dried *Phragmites karka* was crushed in a laboratory mill and sieved to obtain particles ranging 1–2 mm. Desired weighed quantity of precursor was treated with amount of 25% (V/V) sulphuric acid at room temperature for 3 hr. The sample was further washed several times with double distilled water and filtered. This cycle was repeated till to obtain the *p*H of filtrate in neutral (*p*H= 7) range. Thereafter, the residue was dried at 100°C overnight and crushed followed by sieving to produce the particle size in the range of 100-150 mesh. The final product obtained was stored in a closed container for experimental use.

Experimental procedure

The adsorption of BCG onto activated *Phragmites karka* (APK) was carried out in batch experiments. Adsorption experiments were carried out in 250 mL (volume) Erlenmeyer flasks containing 100 mL of BCG solutions and to that the desired dose of APK was charged and placed in a thermo-stetted shaking incubator (LSI-3016R, Labtech, Korea). To determine the efficiency of adsorption on APK, experiments were carried out while varying the parameters such as: *p*H, temperature, particle size, amount of adsorbent, initial concentration of dye, contact time and shaking speed. The temperature was controlled during the experiment and overall change of temperature was observed to be ± 2°C. The *p*H of the solution was adjusted by adding 0.1 mol/L NaOH / HCl. To study the adsorption equilibrium, a definite amount of adsorbent was equilibrated with desired dye solution at room temperature for definite time periods. At the end of the predetermined time intervals, the adsorbent was removed by simple filtration. The filtrate was analyzed for the residual (unadsorbed) BCG using double beam UV-Vis spectrophotometer (Shimadzu, UV-1800, Japan) at 442 nm. The amount of BCG dye adsorbed by APK at equilibrium q_e (mmol g^{-1}), and q_t (mmol g^{-1}) at time t were obtained according to equation (1) and (2) respectively, as follows:

$$q_e = \frac{(c_o - c_e).v}{m} \qquad \ldots(1)$$

$$q_t = \frac{(c_o - c_t).v}{m} \qquad \ldots(2)$$

In addition, the percentage of BCG dye adsorbed from aqueous solution with the APK was calculated using Eq. (3).

$$\%M = \frac{(c_o - c_t)}{c_o} \times 100 \qquad \ldots (3)$$

where C_o and C_e (mol.L^{-1}) are initial and equilibrium concentration of APK dye in aqueous phase, respectively, C_t (mol.L^{-1}) is the concentration of BCG at time t; V (mL) is the volume of the solution and m (g) is the mass of APK.

The adsorption kinetics study was carried out within the contact time range of 1-300 min, while keeping the APK amount constant. The adsorption isotherm was studied at varying BCG dye concentration. The APK amount was varied from 0.1-1.0 g in the batch test adsorption study. The temperature of the solution was maintained at 303 K in most of the experiments unless otherwise specified. The shaking speed was kept fixed at 250 rpm in most of the batch test experiments except when the effect of rpm that was changed in the range of 50-250 rpm.

Results and Discussion

Effect of contact time and agitation speed

Effect of contact time for the study of adsorption of BCG is important factors which illustrates the adsorption capacity of adsorbent as well as establish the adsorption kinetics. Adsorption of BCG was studied using 0.1g of APK in 100 mL aqueous solution containing 100 mg/L of BCG at varying contact time from 0 to 360 min. where rest of the parameters were: shaking speed 250 rpm, temperature 303 K and *p*H 0.5. As shown in Fig. 1(a), the adsorption of BCG at the initial contact time was high due to the availability of more active sites on the adsorbent surface and the solution concentration was also high, which lead to fast electrostatic force of interaction of the anionic BCG with APK. The adsorption equilibrium of BCG on APK was attained at 300 min of contact time and beyond that the plateau value was reached. Therefore, the contact time of 300 min. was kept fixed for further experimental studies.

It is well known that in adsorption process the rate of adsorption was controlled either by film diffusion or pore diffusion, depending upon the degree of agitation of the fluid particle system. At the lower agitation speed, the fluid film around the particle is thicker and the film diffusion seems to be rate limiting step. The adsorption kinetics is influenced by low mass transfer of adsorbate to the internal surface of particle. In contrast, at higher agitation speeds, the film diffusion increases to a maximum value and pore diffusion thus becomes the rate controlling step[4,10,16]. In this investigation, influence of shaking speed on adsorption of BCG dye was carried out within the range of 50-250 rpm using 0.1 g of APK with a solution of volume 100 mL, temperature 303 K and 100 mg/L of BCG concentration. From Fig. 1, It was assured that the percentage of BCG adsorption was increased from 60.61 to 99.99 % with increase in shaking speed from 50-250 rpm and thereafter it remains same. In addition, adsorption efficiency of BCG followed increasing trend up to 300 min. of contact time at the above studied agitation speed range. From this result, it was ensured that percentage removal of BCG at 250 rpm was found to be maximum and indicating that adsorption process is of diffusion controlled. From this study, the suitable condition of agitation speed of i.e. 250 rpm was kept fixed for further experiments.

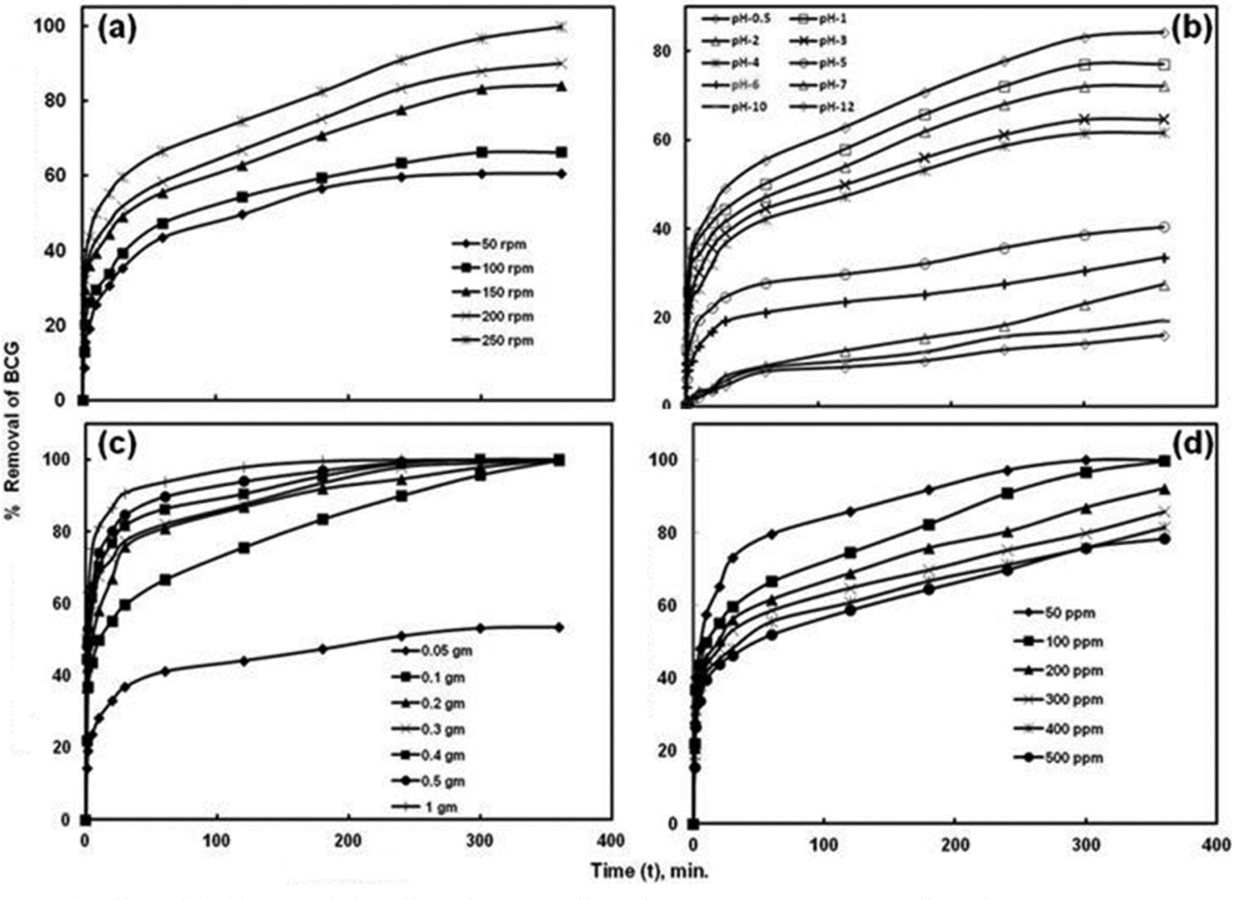

Fig. 1 — (a) Effect of shaking speed (b) Effect of *p*H (c) Effect of adsorbent dose and (d) Effect of initial dye concentration, on adsorption of BCG by APK.

Effect of *p*H on BCG adsorption

The solution *p*H and its effect is a very important factor in adsorption process, since the variation in *p*H leads to the variation in the degree of ionization and dissociation of the adsorbate molecule which is most probably influence on the surface properties of the adsorbent. Removal of BCG was studied as a function of *p*H at a definite concentration (100 mg/L) of dye using 0.1 g of *Phragmites karka*. From Fig. 1(b), it can be seen that the maximum removal of BCG dye (99.9%) was observed at *p*H 0.5 and under alkaline or neutral conditions, the change of initial *p*H had no significant effect on the adsorption for BCG onto APK. Adsorption of BCG was favoured by lowering the *p*H of the solution which may be due to the strong ionization of BCG to become anionic form and leading to increase the electrostatic interaction with adsorbent site[5,10]. The adsorption efficiency was reduced at higher *p*H this may be caused as the *p*H of the system increases, the number of negatively charged binding sites would increase and due to electrostatic repulsion the negatively charged surface of the adsorbents will not adsorb the anionic BCG dye[16,25,27].

Effect of adsorbent

In this study, amount of adsorbent APK dosages was varied from 0.05 to 1.0 g where other parameters were: dye concentration 100 mg/L, *p*H 0.5, contact time 5h., temperature 303 K, agitation speed of 250 rpm and solution volume 100 mL. As shown in Fig. 1(c), the adsorption of BCG was increased from 52.12 to 99.9 % with increase in resin dosage from 0.05 to 1.0 g. As can be seen from the above results, there is the rise in adsorption efficiency with increase in APK dose and in addition, the adsorption rate was also significantly increased at higher sorbent (APK) amount level. The enhancement of the adsorption efficiency at higher adsorbent dose can be caused due to the increase in active sites of the APK which become available with the increase in mass of APK per unit volume solution[28,29]. In consequences of which adsorption equilibrium was attained in short span of time.

Effect of the initial concentration amount

The initial dye concentration also plays an important role to know the adsorption capacity of adsorbents. The investigation on the adsorption of BCG on to APK was carried out while varying BCG concentrations from 50-500 mg/L where other parameters such as *p*H, APK dose, temperature and agitation speed were kept fixed at 0.5,0.1 gm, 303 K and 250 rpm, respectively. The adsorption percentage of BCG was found to be of decreasing trend from 99. 99 % to 78.46 % with increase in the initial BCG dye concentration from 50-500 mg/L, respectively, and the results are as shown in Fig. 1(d). The observation attributes to the lack of available active sites required for the high initial concentration of the dyes and on the other hand, the adsorption sites are absorbed the available solute more quickly at lower concentration of the dye[27,28,29]. Furthermore, the adsorption data resulted in this study was interpreted while studying different adsorption isotherms as discussed later sections.

Effect of temperature

The effect of temperature on adsorption is one of the key parameter especially to ascertain the thermodynamic conditions of the adsorption process such as to know the nature of adsorption whether the dye adsorption process is endothermic or exothermic. Nevertheless, in practical case study most of the textile dye effluents are discharged at relatively high temperatures which would directly be taken up for removal studies. In this study the effect of temperature on the adsorption of BCG was investigated at the temperature range of 293-333 K. where other parameters were kept fixed; the adsorbent mass 0.1g, agitation speed 250 rpm, initial dye concentration 100 mg/L and a constant solution *p*H 0.5. From the Fig. 2(a), it was observed that while increasing the temperature of the solution, adsorption capacity as well as the rate of BCG adsorption with APK increases. The rate of adsorption with increase in temp was more pronounced within initial 30 min. of contact time and thereafter it was steady. The reason of the increasing trend of BCG adsorption with rise in temperature may be due to (i) the mobility of the dye molecule increases which enhances the adsorbate to penetrate into the pores of adsorbent, (ii) the increase in the chemical interactions between the adsorbate, and the surface functionalities of the adsorbent, (iii) the change in chemical potentials, related to the solubility of the adsorbate species. The adsorption process at any interface between two phases can be regarded as an equilibrium process which suggests that the adsorption process is of endothermic in nature and was further confirmed by the ΔH^{o}(kJ mol^{-1}) value resulted as described below [5,10,16]. The adsorption between two phases can be regarded as an equilibrium process at any condition.

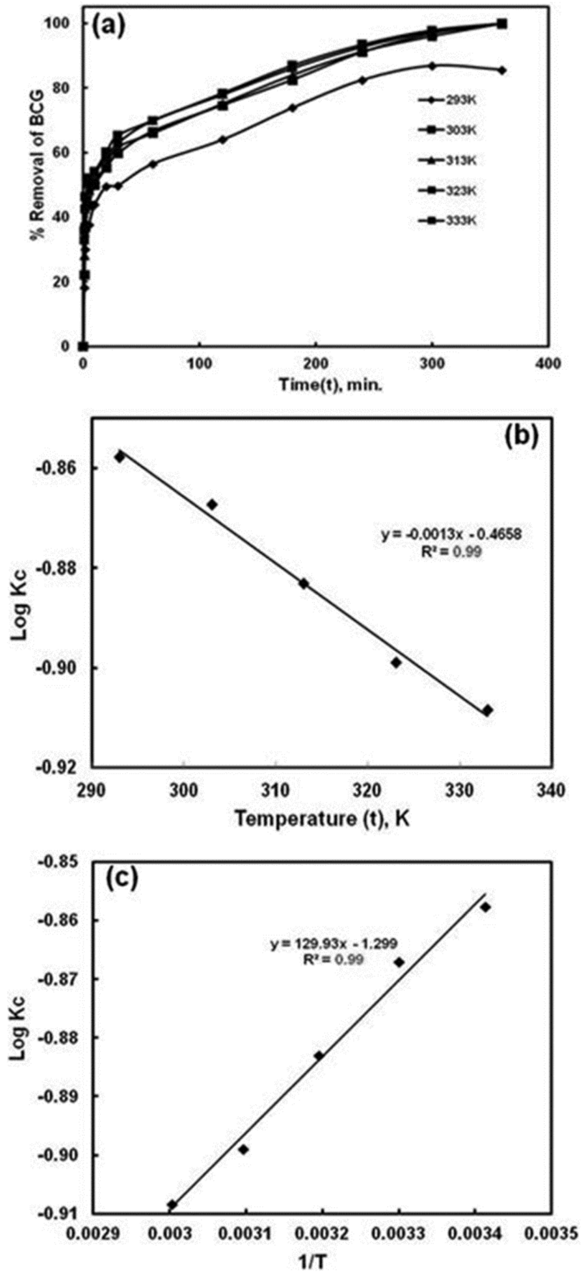

Fig. 2 — (a) Effect of temperature on adsorption of BCG (b) Equilibrium constants for BCG on APK as function of temperature (c) Van't Hoff plot for exchange of BCG with APK.

The equilibrium constant Kc for adsorption was calculated using the Eq. (4)

$$K_c = \frac{C_{Ae}}{C_e} \qquad \ldots (4)$$

where C_{Ae} and C_e are the concentrations of BCG in adsorbent phase (g/L) and in solution (g/L) at equilibrium. As shown in Fig. 2(b) and Fig. 2(c), the value of Kc decreased with an increase in temperature from 293 to 333 K. The values of ΔG^o (kJ mol^{-1}), ΔH^o (kJ mol^{-1}) and ΔS^o (J mol^{-1}K^{-1}) can be calculated by following thermodynamic relationships in Eqs. (5), (6), and (7).

Table 1 — Thermodynamic results of BCG dye adsorption by APK

Initial dye concentration (mg/L)	Temperature, K	ΔG^o, kJ mol^{-1}	ΔH^o, kJ mol^{-1}	ΔS^o, J mol^{-1}K^{-1}
100	293	-4.8	2.49	24.87
	303	-5.04		
	313	-5.29		
	323	-5.54		
	333	-5.79		

$$\Delta G° = -RTLn\, K_c \qquad \ldots(5)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad \ldots(6)$$

$$\log K_c = \frac{\Delta S^{\circ}}{2.303R} - \frac{\Delta H^{\circ}}{2.303RT} \qquad \ldots(7)$$

where ΔG^o is the standard free energy, ΔH^o and ΔS^o are the enthalpy and entropy change of adsorption process. The thermodynamic co-relation of rate constant K_c with standard free energy (ΔG^o) was described in Eq. (5) and (6). The plot of the $\log K_c$ as a function of 1/T, based on the Vant Hoff relationship as given in Eq. (7), gave straight lines was shown in Fig. 2(b). The value of ΔH^o and ΔS^o were calculated from the slope and intercept, respectively, and listed in Table 1. The thermodynamics constants determined from the experimental study appear to be consistent and independent of initial dye concentration of the solution. The negative value of ΔG^o indicated the feasibility of the adsorption process and the spontaneous interaction of dye ion with active sites of the adsorbent. The positive value of ΔH^o (+2.49) corresponds to an endothermic nature of the adsorption process and the positive values of ΔS^o (+24.87) reveals the increased randomness of the dye and adsorbent interface during adsorption process[1,5,20,25].

Kinetics model

The rate of the adsorption of BCG on to APK and the mechanism can be established based on kinetics study results. In general, dye adsorption on the solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of dye molecules on the adsorbent surface, and (2) Relatively slow intraparticle diffusion. To analyze the adsorption kinetics of dye, the first-order, the pseudo second-order, and intraparticle or film diffusion models were applied to data obtained from the experiments[6,16,28,30].

Pseudo first-Order and second order Kinetics

The kinetic data for the adsorption of BCG with APK was fitted with both first order / second order kinetic model by referring the Lagrange equations. Pseudo first-order kinetics can be described by the equation (8) as given below.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right).t \qquad \ldots(8)$$

where q_e and q_t are the amounts ($mg.g^{-1}$) of adsorbate at equilibrium and at time t (min), respectively, and k_1 is the rate constant (min^{-1}).

Plotting the values of log (q_e-q_t) versus ‘‘t’’ as shown in Fig. 3(a) gives a linear relationship and from which k_1 and q_e was determined from the slope and intercept values, respectively. The values of correlation coefficient R^2, q_e and rate constant k_1 are reported in Table 2 and from which it was found that the calculated values of q_e was significantly lower than the experimental values which indicates that the adsorption of BCG onto APK is not a first-order reaction.

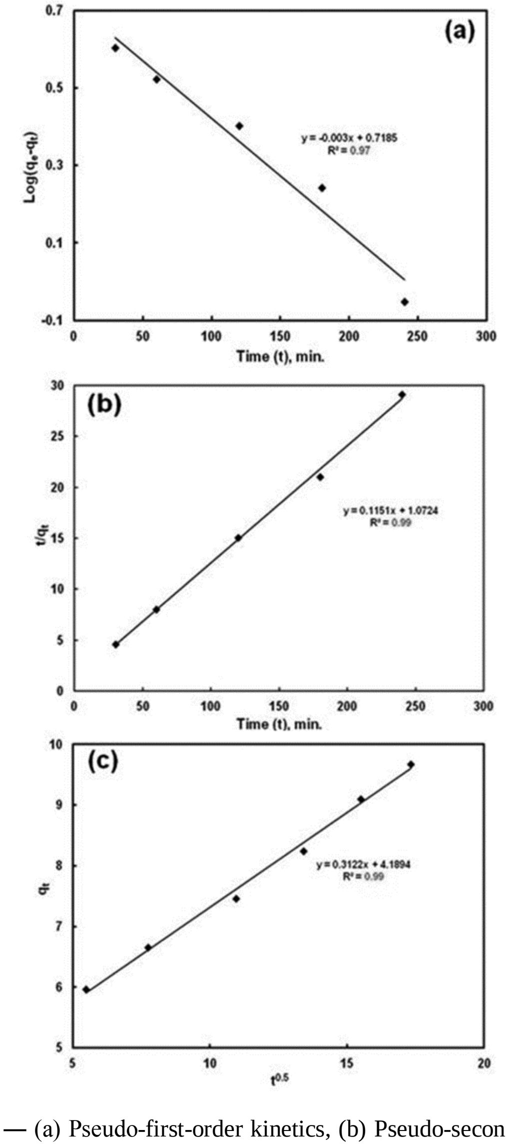

Fig. 3 — (a) Pseudo-first-order kinetics, (b) Pseudo-second-order kinetics and (c) intra particle diffusion model for adsorption of BCG by APK.

The pseudo second-order model is represented by the equation (9).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \ldots(9)$$

where k_2 ($g.mg^{-1}.min^{-1}$) is the rate constant of pseudo–second order adsorption and the other terms have the same meaning as described in Eq. (8). The validity of second order kinetics can be evaluated if the plot of t/q_t as the function of t (min) gives a linear relationship shown in Fig. 3(b). The values of slope (q_e) intercept (k_2) and correlation coefficient (R^2) were calculated using the straight line of the graph and also listed in the Table 2. The calculated values of q_e from pseudo-second order reaction appears to show reasonable agreement with the experimental q_e values from Fig. 3(b). From the above analytical data it was presumed that the pseudo-second-order model provides better correlation of adsorption than the pseudo-first-order model, suggesting that the rate limiting step may be of chemical sorption type[20,30,31].

Intra-particle diffusion

Furthermore, the adsorption process would not only occur at the external surface of the APK but it might also diffuse into it’s the inner porous layer. Thus, the intra-particle diffusion can be explained using Weber-Morris model equation[16, 30,31] on the rate of BCG dye adsorption with APK as described by Eq. (10).

$$qt = X_i + k_p t^{1/2} \qquad \ldots(10)$$

where q_t is the concentration of BCG dye adsorbed at

Table 2— Kinetic results for BCG adsorption by APK

q_e exp (mg/g)	9.99
Pseudo first order model k_1	0.007
q_e cal (mg/g)	5.23
R^2	0.97
Pseudo second order model	
K_2	0.2349
q_e cal (mg/g)	11.814
R^2	0.99
Intra particle diffusion model	
k_p	0.3122
R^2	0.99

a given time t (min.), k_p (mg/g. $min^{0.5}$) is the intra particle diffusion rate constant and X_i is the intercept. To study the effect of the intra particle diffusion model for this experimental investigation, the resulted experimental data of the plot q_t vs $t^{0.5}$ was shown in Fig. 3(c), where the straight line trend of the plot indicated about the control of adsorption by intra particle diffusion of the BCG dye within the pores of APK to the adsorption sites. From the slope of the plot, the k_p values was calculated and shown in Table 2.

Mechanism of adsorption

Form kinetic results for the adsorption of BCG from the synthetic solution using APK appears to follow increasing trend with increase in the contact time and it was also observed that the adsorption process was very first at the initial period of contact time and then attained plateau value with the increase in contact time up to 500 min . Therefore, the adsorption mechanism for the removal of dye can be explained by considering some the assumptions such as:

- Migrations of BCG dye from the solution phase to the surface of the adsorbent material.
- Diffusion of BCG through the boundary layer to the surface of the adsorbent.
- Adsorption of BCG dye at an active site on the surface of adsorbent and also
- Intra-particle diffusion of dye into the interior pores of the adsorbent particle.

The rate of adsorption process was mainly depends upon the resistance of boundary layer of the adsorbent molecule. With increase in the contact time the resistance of the boundary layer decreases which leads to increase the mobility of the dye molecules. Thus, the rate of uptake of dye on the active sites of adsorbent mainly governed by either liquid phase mass transfer or diffusion through the boundary layer or intra-particle mass transfer[16,32]. In addition, the above adsorption mechanism was supported by the change of characteristics pattern of spectra due to BCG before and after adsorption through UV-VIS study and FT-IR characterization results of APK, BCG and BCG loaded APK as discussed below.

Characterization study of typical samples in the adsorption of BCG on to APK

SEM analysis of PK, APK and BCG loaded APK

To confirm the phase transformation from *Phragmites karka* to activate *Phragmites karka* and to ascertain the adsorption mechanism, the surface morphological study for the adsorbent (before and after treatment/adsorption) was investigated. Characteristic behavior changes of raw adsorbent (PK) to the modified adsorbent (APK) phase was clearly evident as can be seen in the Fig. 4(a) and 4(b). The morphology of the PK showed regular, hard and shredded structure however, after its phase modification by chemical process there was a significant changes of its morphology was observed. The APK surface becomes more porous in nature leading to increase in surface area which substantially imparts high loading efficiency of dye (BCG) molecules on to the APK phases. As shown in the 4(b) and 4(c), the characteristic pattern of APK before and after adsorption ensuring about the transportation of BCG molecule on to APK phase and it was ensured due to the change in the surface morphological structures as the appearance of smooth regular pattern due to binding of BCG dye molecule over the APK sites after adsorption with BCG. Furthermore, FTIR and UV-VIS analysis of typical samples as provided in the following section strongly supports adsorption mechanism.

FT-IR and UV-VIS analysis study

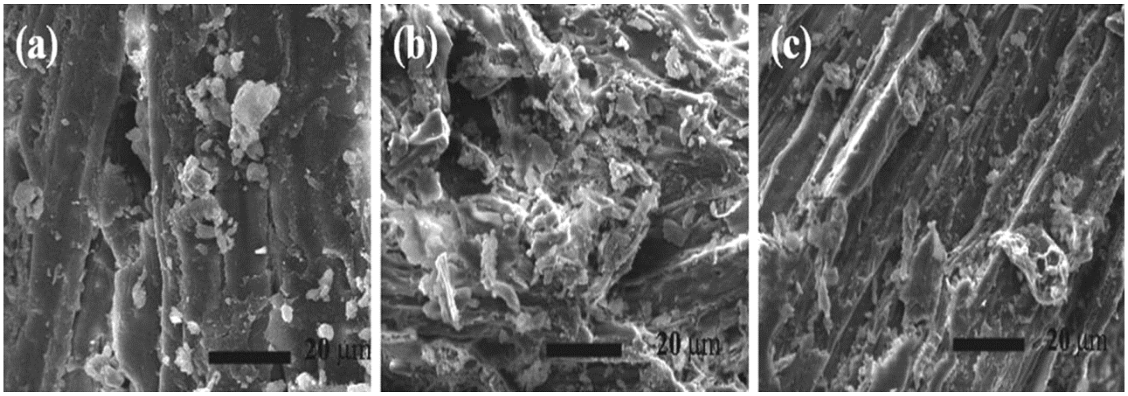

Fig. 4 — SEM analysis: (a) *Phragmites karka* (PK) (b) Activated *Phragmites karka* (APK) and (c) Bromocresol Green (BCG)-loaded APK.

FT-IR analysis was performed using Shimazdu, IRAffinity-1S FTIR Spectrophotometer in the region of 400-4000 cm^{-1}. FT-IR spectrum of both *Phragmites karka* and activated *Phragmites karka* was shown in Fig. 5(a). This APK was used for adsorption of BCG and showed various absorption bands for corresponding various functional group which is responsible for binding of dye molecule. The peak observed at 1743 cm^{-1} is due to ν(C=O), and the peak at 1605 cm^{-1} is due to the ν(C=C) stretching that can be attributed to the aromatic ν(C-C) bond which was observed both for BCG as well as BCG adsorbed APK. The peak found at 1424 cm^{-1} is due to the symmetric bending of CH_3, and band appears at 2854 cm^{-1} and 2924 cm^{-1} may be due to the CHO groups for APK. There is a shift of absorption peak observed from 1200 (for BCG) to 1150 cm^{-1} for BCG loaded APK correspond to ν(S=O) of the $–SO_3^-$ group. The absorption peak found at 3450 cm^{-1} due to ν(O-Hstr) of BCG was shifted to a broad band at 3270 cm^{-1} showed the conjugation of BCG on surface of the APK. The UV-VIS spectra analysis of the BCG sample resulted at different time (while adsorbing with APK) was shown in Fig. 5(b) and the major colour change of BCG before and after adsorption can be seen from Fig. 5(c). The significant change of the peak intensity at different time of the adsorption was well pronounced from the UV-VIS results which evident on the adsorption process.

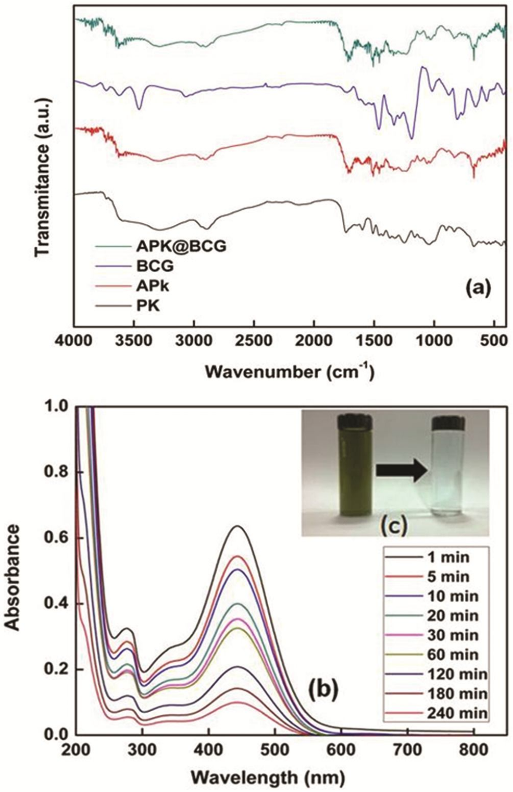

Fig. 5 — (a) FTIR spectroscopy of PK, APK, BCG and BCG loaded APK, (b) UV-vis spectroscopy for significant changes in absorbance w.r.t. time and (c) significant colour changes of dye solution resin beads before and after adsorption.

Adsorption Isotherms

The adsorption equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. The isotherm studies were performed by varying the initial BCG concentration from (50 to 500) mg.L^{-1} at *p*H = 0.5 and the other parameters were: mass of adsorbent 0.1gm, agitation speed 250 rpm, temp 303K and solution volume of 100ml kept constant. As shown in Fig. 1(a), it was seen that the amount of BCG dye adsorbed per unit mass of APK increased with time and reached the plateau value when the active sites of the adsorbent were saturated. The equilibrium adsorption data of different initial dye concentrations listed in Table 3 were analyzed according to Langmuir, Freundlich and Tempkin adsorption isotherm models [6,16,28,33].

Langmuir Isotherm

It is known that the Langmuir equation is valid for monolayer adsorption process. In this process the adsorption is completely taking place on the homogeneous surface with negligible interaction between adsorbed molecules, is represented in the linear form based on equation (11).

$$\frac{c_e}{q_e}=\frac{1}{b_{qm}}+C_e\left(\frac{1}{q_m}\right) \qquad ...(11)$$

where, b is the Langmuir adsorption constant (L.mg^{-1}) and q_m is the maximum adsorption capacity (mg.g^{-1}). Langmuir isotherm model for the adsorption of BCG was plotted as c_e/q_e vs c_e and shown in Fig. 6(a). The value of q_m, b and R_L for the Langmuir isotherm are presented in Table 3. The essential characteristics of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L, defined by equation (12).

Table 3 — Langmuir, Freundlich and Tempkin isotherm results BCG adsorption by APK

Langmuir isotherm			Freundlich isotherm			Tempkin isotherm		
$q_{m,}$ mmol.g^{-1}	b, mmol^{-1}	R^2	n	k_F	R^2	k_1	k_2	R^2
25	0.0039	0.81	1.0034	0.1023	0.99	16.025	45.49	0.93

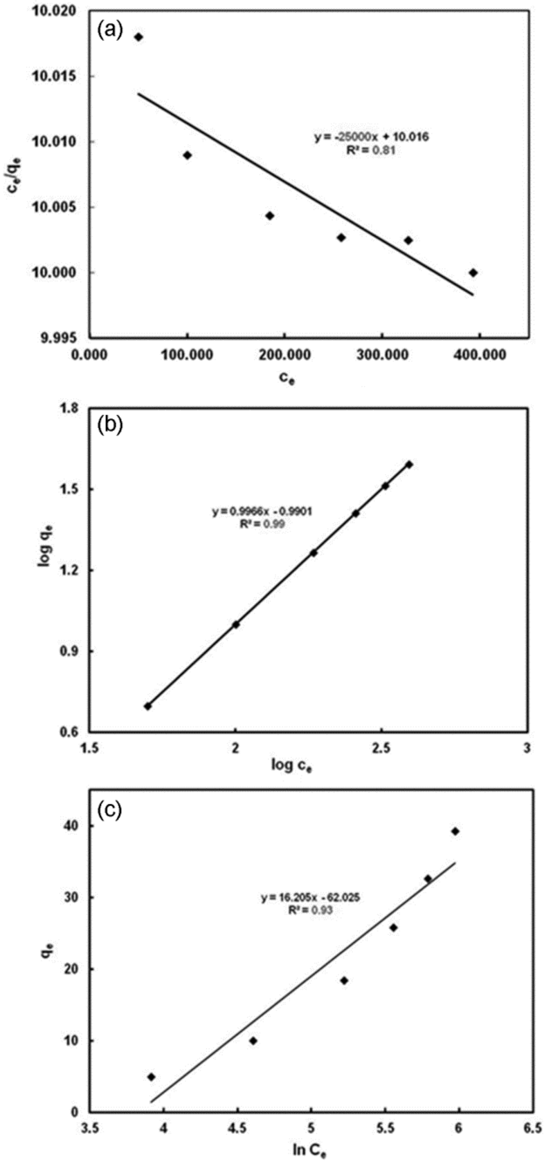

Fig. 6 — Plot of (a) Langmuir isotherm (b) Freundlich isotherm and (c) Tempkin isotherm for adsorption of BCG by APK, conditions: Mass of APK 100mg., temperature 303 K, solution 100mL.

$$R_L = 1/(1 + bC_0) \qquad \ldots(12)$$

where, b is the Langmuir constant and C_0 is the highest initial dye concentration. From this R_L value the process of adsorption isotherm could be determined. The adsorption isotherm is irreversible if R_L=0, the isotherm is favourable if $0 < R_L < 1$, linear if $R_L = 1$ or unfavourable if $R_L > 1$. From this study, the R_L values for the adsorption of BCG dye on the APK sample were calculated and were found to be 0.0739, 0.0383, 0.0259, 0.0195, 0.0098, 0.0066, 0.0049 and 0.0039 for the BCG dye conc. of 25, 50, 75, 100, 200, 300, 400 and 500 mg/L, respectively at temperature 303 K, indicating that the adsorption of BCG on APK is favourable[17,20,28].

Freundlich Model

Freundlich model is valid for the adsorption of heterogeneous surface sites having different energies of adsorption. The linear form of Freundlich isotherm model can be described by equation (13) as given below.

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \qquad \ldots(13)$$

where, q_e is the amount of adsorbate ($mg.g^{-1}$), c_e is the equilibrium concentration of BCG. The Freundlich adsorption isotherm model as a plot of $\log q_e$ vs $\log c_e$ was shown in Fig. 6(b). From this isothermal, the correlation coefficient (R^2) was found to be well fitted to the experimental data of Freundlich isotherm's model. The values of k_f and 1/n obtained from the slope and intercept of the straight line are also listed in Table 3. where k_f can be defined as the adsorption or distribution coefficient and q_e represents the quantity of dye adsorbed onto adsorbent at unit equilibrium concentration and 1/n represents the favourability of adsorption. In this investigation, the value of 1/n for the Freundlich isotherm was found falls in between zero and one, indicating that BCG is favorably adsorbed by APK. This result was strongly supported by the reported literatutures[20,31] while removing the dyes using activated carbon[16,20].

Tempkin Isotherm

The derivation of Tempkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic form as implied in the Freundlich equation. The heat of adsorption of all of the molecules in the layer would decrease linearly with coverage due to adsorbate / adsorbate interaction. The linear form of the Tempkin isotherm can be expressed as equation (14).

$$qe = k_1 \mathrm{In}\, k_2 + k_1\, Inc_e \qquad \ldots(14)$$

where c_e = concentration of the dye at equilibrium ($mg.L^{-1}$), q_e = amount of dye adsorbed at equilibrium ($mg.g^{-1}$), k_1 (RT/b) is related to the heat of adsorption, and k_2 is the equilibrium binding constant ($L.mg^{-1}$). A plot of q_e versus $\ln c_e$ was shown in Fig. 6(c) and the values of constants k_1 and k_2 and the correlation coefficients for Tempkin was calculated and presented in Table 3. From the results it was observed that the correlation coefficient (R^2) did not fit well with the experimental data. Therefore, the adsorption process is depending upon the chemical structures of the dye and also the absorbents. While comparing the results with Langmuir and tempkin isotherm model, it was also seen that the R^2 value is close to unity in case of Freundlich isotherm's model indicating about the adsorption mechanism which is governed by chemisorptions process[20,31].

Conclusion

Removal of BCG from the aqueous solution bearing 100 mg/L of APK has been investigated. The adsorption studies have been carried out as a function of contact time, temperature, resin dose, initial dye concentration and *p*H of the solution. The resulted data of the above adsorption parameters is rigorously interpreted by kinetics, thermodynamics and isotherm study to establish the mechanism of adsorption process of BCG onto APK. The adsorption of BCG with APK is critical with the influence due to contact time, temperature and *p*H. Removal of the BCG decreased with increase in initial dye concentration and temperature, but increased with increase time. The adsorption equilibrium has been achieved in 300 min contact time while attaining maximum loading capacity as 392.3 mg/g which seems significantly larger than the reported literatures. As it is well known that the solution *p*H affects the surface charge of the adsorbent and the degree of ionization of adsorbate and therefore, overall BCG adsorption is found to be efficient at higher acidic *p*H range (*p*H-0.5). The adsorption of BCG is also enhanced while increasing APK dose as well as initial BCG concentration. Experimental equilibrium data show best fit with Freundlich isotherm (R^2=0.99). Thermodynamic parameters such as change in Gibbs free energy (ΔG^o), adsorption enthalpy (ΔH^o) and adsorption entropy (ΔS^o) were determined show the relevance on favouring the adsorption process. The positive value of ΔS^o suggesting an increase in degrees of freedom of adsorbed species and positive value of ΔH^o indicate that the process is of endothermic in nature. The present investigation ensured on effective usage of APK for purification of water bearing contaminated dye.

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