

Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study

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Abstract

This communication presents the results pertaining to the investigation conducted on color removal of trisazo direct dye, C.I. Direct Brown 1:1 by adsorption onto coal based sorbents viz. charfines, lignite coal, bituminous coal and comparing results with activated carbon (Filtrisorb-400). The kinetic sorption data indicated the sorption capacity of the different coal based sorbents. The sorption interaction of direct dye on to coal based sorbents obeys first-order irreversible rate equation and activated carbon fits with the first-order reversible rate equation. Intraparticle diffusion studies revealed the dye sorption interaction was complex and intraparticle diffusion was not only the rate limiting step. Isothermal data fit well with the rearranged Langmuir adsorption model. R_L factor revealed the favorable nature of the isotherm of the dye–coal system. Neutral solution pH yielded maximum dye color removal. Desorption and interruption studies further indicated that the coal based sorbents facilitated chemisorption in the process of dye sorption while, activated carbon resulted in physisorption interaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Direct azo dye; Coal based sorbents; Kinetics study; First-order rate reaction; Intraparticle diffusion; Langmuir isotherm; Chemisorption and physisorption

1. Introduction

The synthetic fiber industry ranks first in consuming the dye (about half of the total dye production) in the dyeing process and out of this around 10–20% of the dye comes

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back through the effluents and enter into different environment segments [1,2]. Dyes are generally synthetic organic aromatic compounds, which is embodied with various functional groups and heavy metals. The colored dye effluents are considered to be highly toxic to the aquatic biota and affect the symbiotic process by disturbing the natural equilibrium through reducing photosynthetic activity and primary production due to the coloration of the water in streams. Also, the persisting nature of color, non-biodegradable, toxic and inhibitory nature of the spent dye bath has considerable deleterious effect on the total environmental matrix (water and soil). The complex framework of dye with the presence of heavy metals induces chronic toxicity particularly; they are mutagenic, teratogenic and carcinogenic.

Fung and Muller [3] in their study on 42 different types of dyes on bacteria species reported the toxic nature of the dye. Rao and Reddy [4] reported that dye has altered considerable physical and engineering properties of the soil. Rao et al. [5] observed that the toxic nature of dye effluents cause death of soil microorganisms which may effect agriculture productivity. Some of the rare species of flora and fauna in the catchment area where dye effluents are discharged in Rajasthan state (India) was eliminated and also the vegetative cover of the catchment area is considerably reduced [6].

Azo group of dyes (monoazo, diazo, triazo and polyazo) are considered to be the largest chemical groups of dyes presently in existence (around 26,000 dyes). Various experiments conducted on animals revealed the potential of azo compounds to cause cancer and reported to be carcinogens for human being also [7,8]. Among all types of dyes investigated, the toxicity of azo dyes on the *Bacillus cereus* and *Escherichia coli* cultures was found to be prominent [9]. Azo dyes, which on reductive cleavage of one or more azo groups will form a carcinogenic aromatic amine, which are generally, acknowledge being an animal carcinogen. Azo dyes were banned by several countries due to its potential toxic nature.

Hence, it become imperative that dye is to be removed from the effluents before it is disposed off. Among various treatment technologies, adsorption onto activated carbon proved to be one of the effective and reliable physicochemical treatment methodology [10–15]. However, the overlying cost of activated carbon and its regeneration problems associated with ever changing dye bath characteristic with newer dyes invention for a stable hue, compounds the problem further. In this realm, various adsorbents derived from natural materials (silica, coal, soil, minerals, chitosan, etc.) and waste materials (fly ash, rice husk, biogas slurry, silica fumes, saw dust, etc.) have been studied in place of activated carbon [11,14,16–23]. However, the potential application accounts for amount of availability and economic considerations.

The prime objective of the present study is to find the potential of different coal based sorbents which are available in large quantities as adsorbents in wastewater treatment. Lignite coal, charfines and bituminous coal are widely available in huge quantities and have all physical and chemical requirements of an adsorbent. The present investigation reports results pertaining to direct trisazo dye color removal by adsorption onto various abundantly available coal-based sorbents. The kinetic data and equilibrium data of sorption studies were processed to understand the sorption mechanism of the dye molecule onto the coal based sorbents.

2. Materials

Coal based materials, namely, Lignite coal (Neyveli Lignite Corporation, Neyveli, India), charfines and bituminous coal (Talcheru Mines, Talcheru, India) were obtained from mines and ground to a geometric mean (GM) size of 106 μm , cleaned and used in this study to determine their potential as adsorbents. Charfines is a by-product produced during the carbonization of lignite coal. The results were compared with Filtrasorb-400 activated carbon (Calgon Corporation, USA) of the same size was employed as a standard adsorbent for comparison of the test result to know the relative efficacy of the studied adsorbents.

To assess the potential of the selected adsorbent potential, C.I.Direct Brown 1:1 (Atul Products, Atul) bearing C.I.No. 30110, belonging to direct application class and trisazo chemical class was employed as the test dye.

Synthetic test dye solution was prepared by dissolving accurately weighed amount of dye (1 g/l) in distilled water and subsequently diluted to required concentration by distilled water. Synthetic test dye solution of a concentration of 50 mg/l, having an aqueous phase pH of 7.0–7.2 and conductivity of 0.89–0.94 $\mu\text{M h/cm}$ was used in all the experiments. All the glassware used in this study was of 'pyrex' quality and wherever required, analytical grade (AR) chemicals were used in the study.

3. Experimentation

Agitated batch sorption experiments were performed at the room temperature ($27 \pm 2^\circ\text{C}$) using a bottle point method [14]. A 100 mg of the adsorbent was taken in a 250 ml glass bottle containing 100 ml of the test dye solution of required concentration (50 mg/l) and the mixture was agitated for a predetermined time period using a horizontal shaker operated at 100 rpm. Kinetics of sorption were determined by analyzing adsorptive uptake of the dye color from aqueous solution at different time intervals of 5, 10, 20, 40, 60, 90, 120, 240, 360 and 480 min. In order to get accurate results for each point on the graph, represent independent bottle containing adsorbent and dye mixture. Isothermal studies to determine the sorption capacity and intensity were conducted by adding various doses of sorbent and agitating the reaction mixture for the equilibrium time. Influence of the pH on the dye sorptive uptake was studied by adjusting the reaction mixture to different initial pH values (3.0–11.0) and analyzed for residual color after equilibrium contact time. Interruption studies were carried out by interrupting the sorption process for a period of 30 min and again restarting the sorption and analyzing for any increase in uptake of sorbate after interruption. Desorption studies were conducted by suspending the adsorbent loaded with adsorbate in distilled water or organic solvents or inorganic solvents and agitated for equilibrium time and analyzed for color desorbed into the aqueous phase. The residual dye color in the aqueous phase was analyzed colorimetrically using a spectrophotometer (Spectrochem MKII, Aimil Pvt. Ltd., India) by measuring OD/%T at maximum wavelength ($\lambda_{\text{max}} = 435 \text{ nm}$) and computing concentration from the calibration curve. To evaluate dye color removal, color concentrations were measured before and after the experiment by measuring OD/%T.

4. Results and discussion

4.1. Sorption kinetic studies

The influence of contact time on dye color removal by coal based sorbents and activated carbon is presented in Fig. 1. All the adsorbents showed their ability to adsorb the dye with various efficiencies. Among coal based sorbents, charfines showed around 30% of dye color removal at equilibrium and lignite coal and bituminous coal are comparable in terms of their equilibrium sorption capacity (22–24%). However, activated carbon possesses the highest sorption capacity (84%). Ranking of the sorbents in terms of color removal capacity is of the following order.

activated carbon > charfines > lignite coal > bituminous coal

A steep sloped curves of coal based sorbents (Fig. 1) indicates instantaneous sorption capacity. The plots visualized three distinct phases in which the first phase (initial steep slope) indicates the instantaneous (overshoot phenomena) sorption of the dye molecules within 5 min of the contact time; may be due to chemisorption interaction of the dye molecules with the surface of the sorbents. The second phase of the plot shows a gradually attainment of the equilibrium where only about 4–6% of sorption is encountered indicates the utilization of the all active sites on the sorbent surface. The third phase of the plots indicates attainment of equilibrium of the dye molecules with the sorbent (sorption is relatively negligible). From the above discussion, the sorption of the dye over the coal based sorbents is mainly due to a chemisorption type of interaction. The initial high uptake of the dye at relatively less contact time enumerated the above statement. In case of activated carbon, the nature of the plot is different. The initial dye uptake was not so rapid and it attained equilibrium gradually. This may be due to the fact that the activated carbon is composed of macro and micro pores. In the process of dye sorption, initially dye has to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto sorbent surface and then finally it has to diffuse into the porous structure of the adsorbent. The sorption of dye here is mainly due to physisorption even though chemisorption may not be written off. This phenomenon will take relatively long contact time and this is a classic example for an idealized adsorption. From the kinetic sorption data, contact time required to attain equilibrium was 60 min for coal based sorbents and 400 min for activated carbon. The rapid initial uptake of sorbents on different sorbents were reported earlier [13,14,20,24–26].

Differential sorption capacity of coal based sorbents may perhaps be due to the grade of the coal samples, i.e. progression of the coalification process that the coal may have undergone, and may even be related to their inherent ion-exchange capacity. The inherent ion-exchange capacity decreases with the progression in the coalification process from lignite to bituminous coal. With the coalification process, there is a marked increase in the hydroxyl and carboxyl group content of coal accompanied by a corresponding loss of water which converts gradually the peripheral carbon structure originally existing as carboxyl and hydroxyl groups into methyl groups. The presence of hydroxyl and carboxyl groups imparts ion-exchange properties.

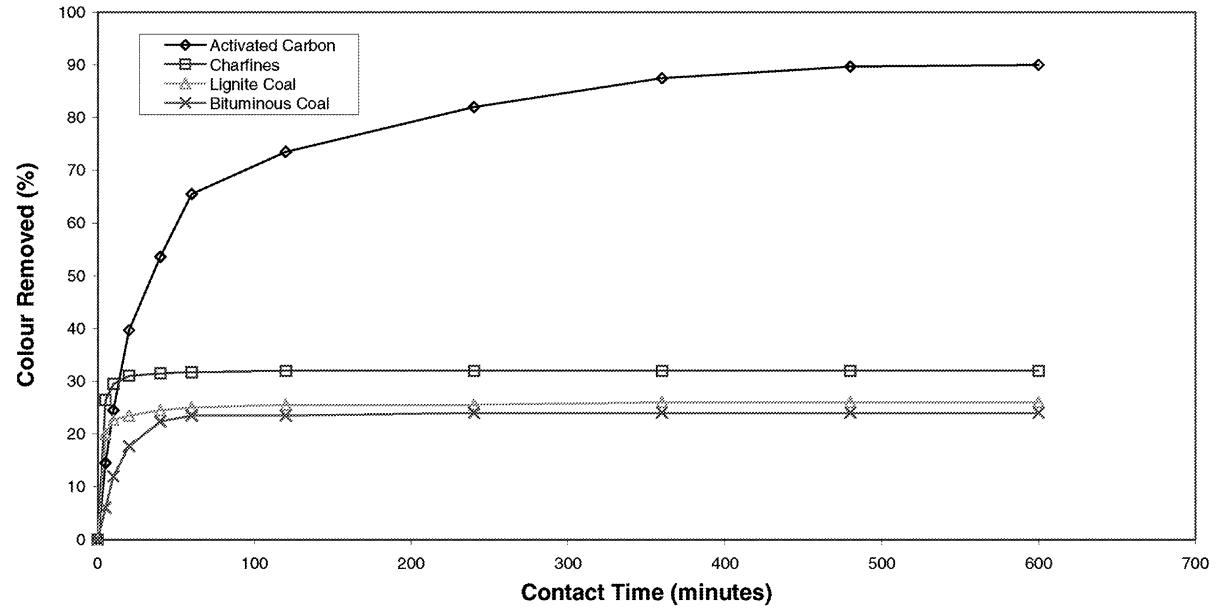


Fig. 1. Effect of contact time on dye color sorption (mass of the sorbent = 1000 mg; initial dye concentration = 50 mg/l; temperature = 27 ± 2 °C).

The increasing sorption capacity also corroborates well with decreasing carbon content and increasing ash content of the coal sorbents (aging of coal enhance carbon content and vice versa for ash). The overshoot phenomenon, i.e. instantaneous adsorption is probably due to involvement of surface acidic functional groups leading to chemisorption of dye molecules whereas slow uptake by activated carbon presumably denote predominant physisorption possibly due to diffusion, migration and intraparticle transport of dye molecules.

4.2. Sorption kinetics rate constant

The kinetic sorption data was processed to understand the dynamics of the sorption reaction in terms of the order of the rate constant. The process of dye color removal from aqueous phase by coal based sorbents may be assumed to be of a first-order irreversible reaction in the form

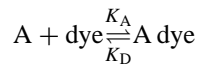


Accordance with the rate equation it can written as

$$\log \left(\frac{C}{C_e} \right) = \left(\frac{K}{2.303} \right) \times t \quad (1)$$

where C is the initial dye concentration (mg/l), C_e the equilibrium dye concentration (mg/l), t the time (min) and K the first-order reaction rate constant (min^{-1}) (Fig. 2). It follows from the straight line plots of the figure that the dye sorption reaction is of first-order irreversible type and the values of rate constant “ K ” was calculated from the slope of the plots as 0.00106, 0.0018 and 0.1123 min^{-1} for lignite coal, charfines and bituminous coal, respectively. Venkata Mohan and Karthikeyan [13,14], Mansi and Fouad [23] and Pandey and Chaudhuri [27] reported similar findings.

In case of the activated carbon, the kinetic data did not fit in the first-order reversible equation. However, the nature of the sorption from the aqueous phase onto the sorbent can be considered as a reversible reaction with an existence of the equilibrium between two phases [28–30].



The rate constants of adsorption, desorption and overall reaction rate were determined using the following equation [28].

$$\ln [1 - u(t)] = -K_T \quad (2)$$

$$K_C = \frac{K_A}{K_D} = \frac{C_{De}}{C_{Ae}} \quad (3)$$

$$K_T = K_A + K_D \quad (4)$$

where $u(t)$ is the fractional attainment of the equilibrium, K_T the overall rate constant (min^{-1}), K_C the equilibrium constant (min^{-1}), K_A and K_D are the rate of adsorption and desorption, respectively, (min^{-1}) and C_{Ae} and C_{De} are the equilibrium concentrations of

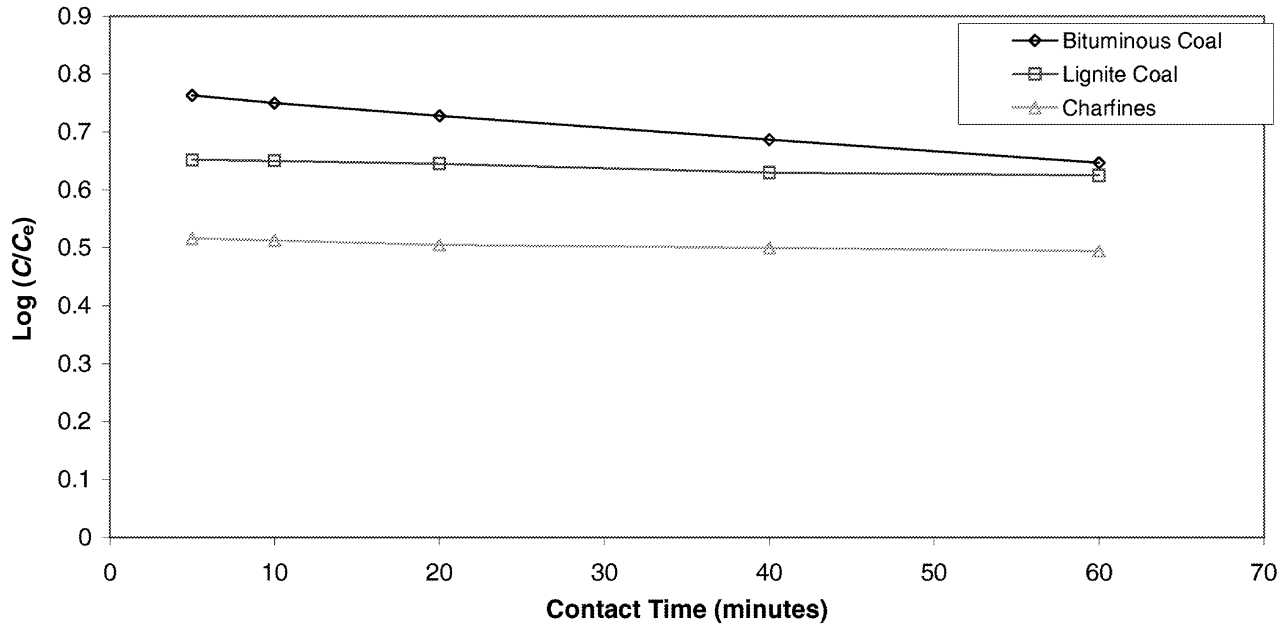


Fig. 2. First-order irreversible sorption kinetic plot for coal–dye system (mass of the sorbent = 1000 mg; initial dye concentration = 50 mg/l; temperature = $27 \pm 2^\circ\text{C}$).

the sorbent and aqueous phase, respectively. The kinetic data obtained was plotted relating $\ln[1 - u(t)]$ with the contact time and the K_T was computed from the slope of the straight line plot (Fig. 3). The plot presents a straight line indicating the validity of the equation with K_T value of $1.2 \times 10^{-2} \text{ min}^{-1}$. The constants K_A ($1.01 \times 10^{-2} \text{ min}^{-1}$) and K_D ($1.90 \times 10^{-2} \text{ min}^{-1}$) were computed using the Eqs. (2)–(4). Furthermore, linear plot of the activated carbon passes very near to the origin and this further suggests that the adsorption of dye molecule by activated carbon be predominantly due to physisorption reaction.

4.3. Intraparticle diffusion studies

Sorption kinetic data was further processed to determine whether intraparticle diffusion is rate limiting and also to find rate parameter for intraparticle diffusion (K_p) [10,30]. Fraction of dye uptake against square root of contact time ($t^{0.5}$) is shown in Fig. 4 and the plots are of general type, i.e. initial curved and final linear portion. The initial curved portions may be attributed to the boundary layer diffusion effect [31], while the final linear portions may be due to intraparticle diffusion effects [10,31]. The slope of the linear portion has been defined as a rate parameter (K_p) and characteristic of the rate of adsorption in this region where intraparticle diffusion is rate limiting and were obtained as 0.2694, 0.2977, 0.2531 and 0.7566 mg/(g/min) for lignite coal, charfines, bituminous coal and activated carbon, respectively. From the figure, it may be observed that the straight line did not pass through the origin and this further indicates that the intraparticle diffusion is not only the rate controlling step [10,13–15,24,29,30]. However, in case of activated carbon, the straight line drawn should intercept the axis very near to origin. The sorption data indicate that the adsorption removal of the dye from aqueous solution is rather complex process, involving both boundary layer diffusion and intraparticle diffusion; however, intraparticle diffusion appears to be the rate limiting step in case of the activated carbon in direct azo dye uptake.

4.4. Sorption equilibrium studies

Langmuir [32] developed a quantitative model that has been widely applied to describe experimental sorption data based on the assumption that maximum adsorption corresponds to a saturated monolayer of the solute molecule on the adsorbent surface with a constant adsorption energy and there is no transmigration of the adsorbate in the plane of the surface. The isothermal equilibrium sorption data was processed employing the modified/rearranged Langmuir adsorption isothermal model, which may be expressed as

$$\frac{1}{(x/m)} = \frac{1}{Q^0} + \frac{1}{bC_e} \quad (5)$$

where x is the amount of dye adsorbed (mg), m the mass of the adsorbent (mg), C_e the concentration of the dye remaining in the solution (mg/l), Q^0 the maximum surface coverage (formation of the monolayer) of the sorbent (mg/g) and b the adsorption energy constant of Langmuir adsorption isotherm (l/mg). It may be observed from the plot (Fig. 5a and b) is linear and this suggests the applicability of the Langmuir sorption isothermal model. Conformation of the experimental data into langmuir isotherm model indicates the homogeneous nature of the sorbent surfaces and depicts the formation of the monolayer coverage

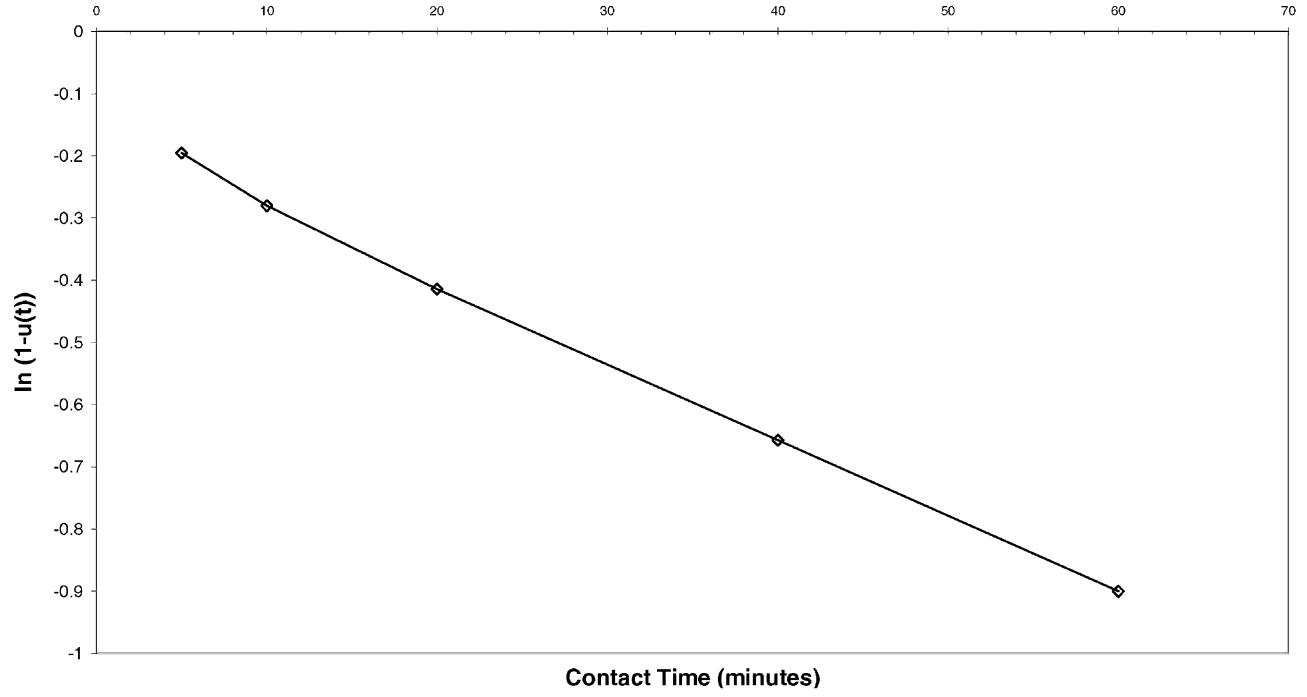


Fig. 3. First-order reversible sorption kinetic plot for activated carbon–dye system (mass of the sorbent = 1000 mg; initial dye concentration = 50 mg/l; temperature = $27 \pm 2^\circ\text{C}$).

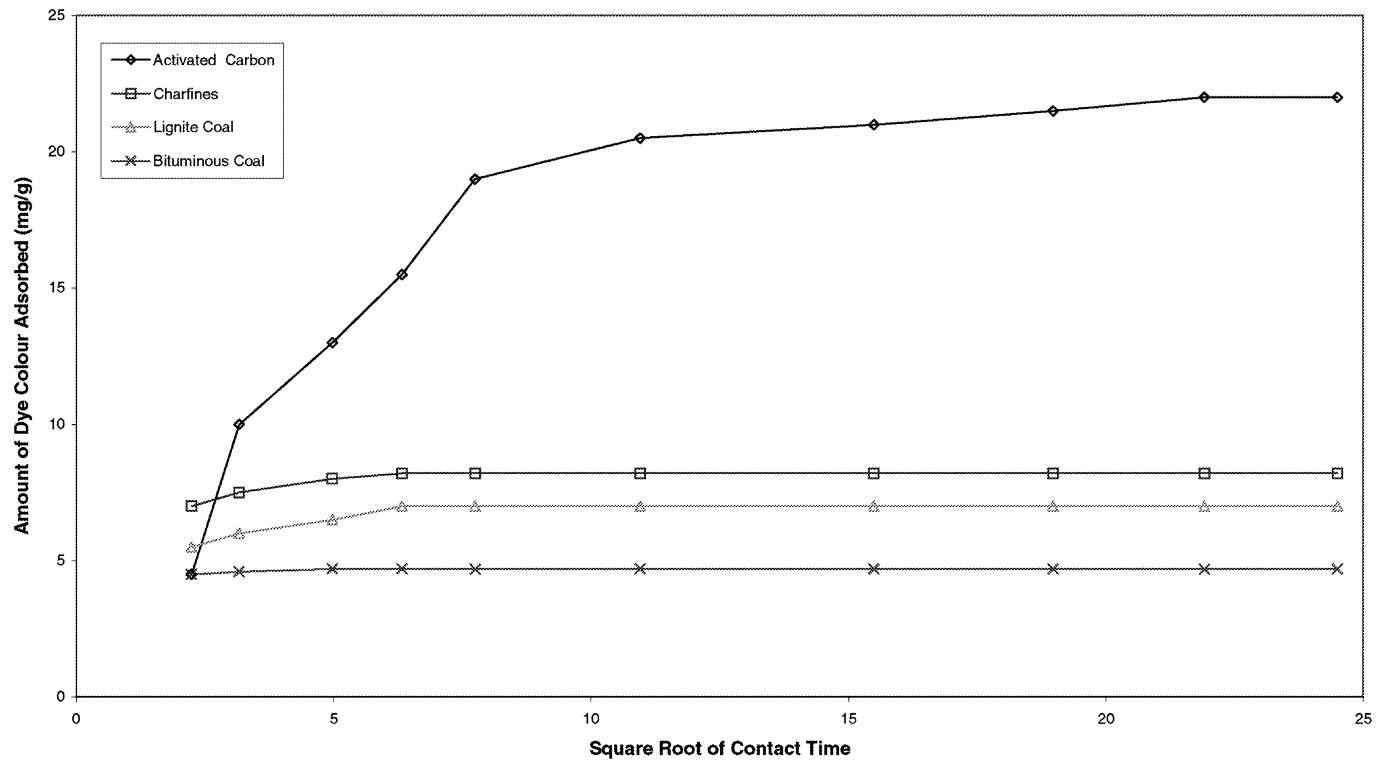


Fig. 4. Intraparticle diffusion plot for dye-sorbent system (mass of the sorbent = 1000 mg; initial dye concentration = 50 mg/l; temperature = $27 \pm 2^\circ\text{C}$).

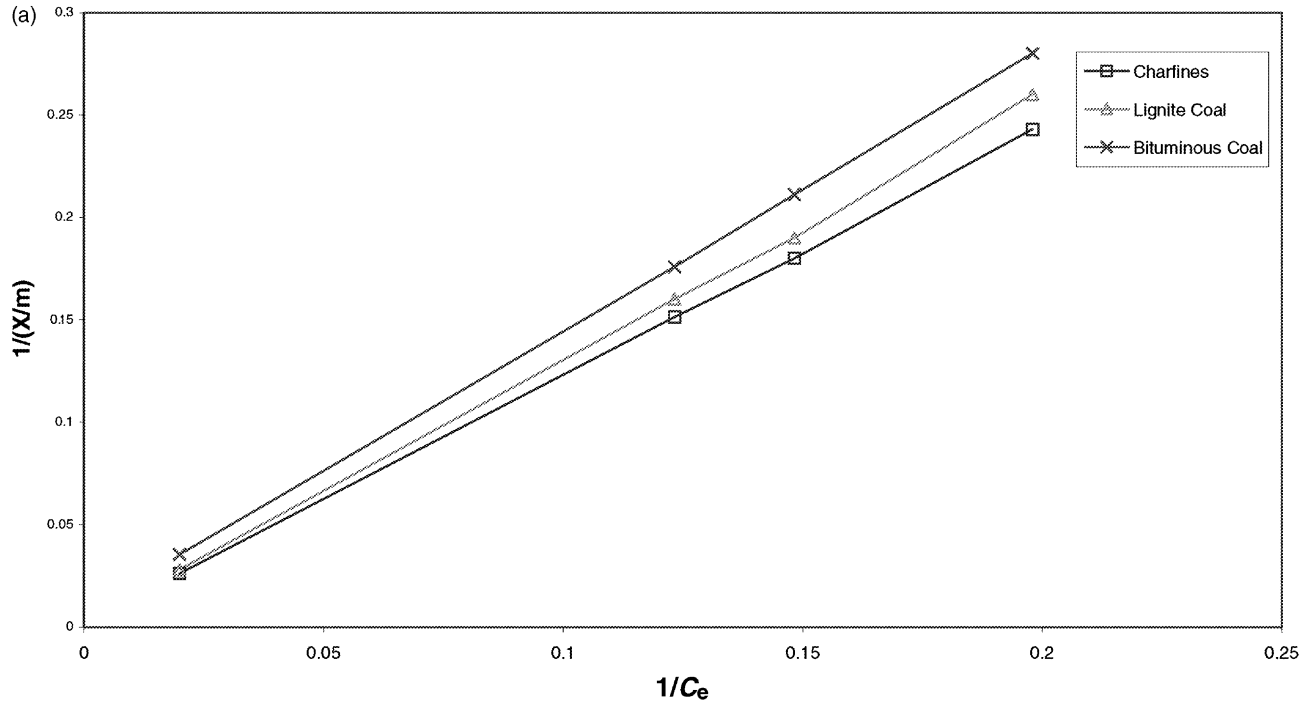


Fig. 5. Linearised Langmuir adsorption isotherm plot for dye-sorbent sorption: (a) lignite coal, charfines and bituminous coal; (b) activated carbon (mass of the sorbent = 1000 mg; initial dye concentration = 50 mg/l; temperature = $27 \pm 2^\circ\text{C}$).

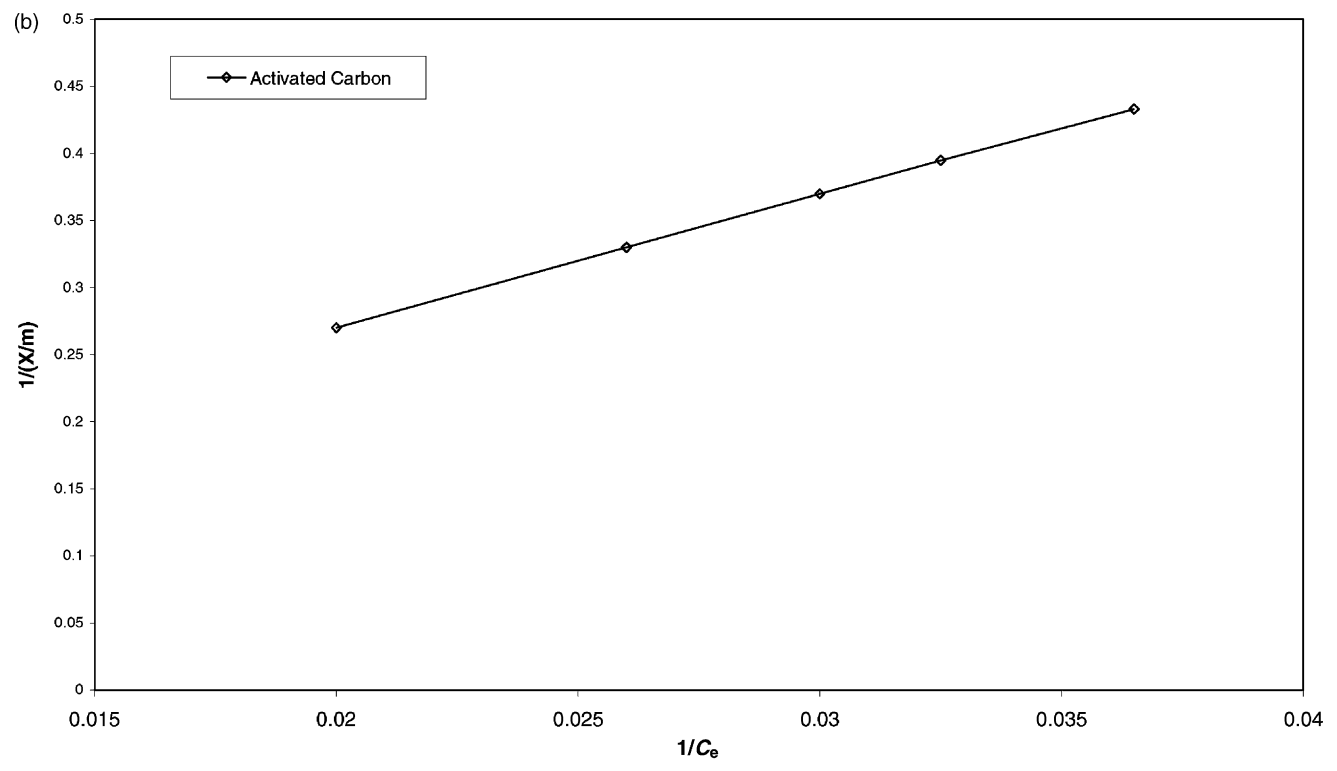


Fig. 5. (Continued)

Table 1
Langmuir adsorption isotherm constant for coal dye sorption reaction

Isotherm constants	Charfines	Lignite coal	Bituminous coal	Activated carbon
Adsorption capacity Q^0 (mg/g)	6.4	4.1	2.04	7.69
Adsorption energy b (l/mg)	0.127	0.080	0.087	0.255

of the dye molecule over the coal based sorbent surface. Similar observations were reported for dye sorption onto different sorbents [13,14,20,26]. Formation of the monolayer of the dye molecule over the adsorbent surface further indicates the chemical nature of the sorption reaction (chemisorption interaction of dye molecule over adsorbents).

Adsorption capacity (surface monolayer coverage) Q^0 and adsorption energy constant b were computed from the slope and intercepts of the isothermal plots, respectively, and are presented in the Table 1. Steep slope of the Langmuir plots is indicative of the usefulness of the adsorbent at high concentration and also of the efficiency in column operations. In this study, charfines exhibited a steeper slope compared to bituminous coal and lignite coal indicating its potential at even higher concentrations for column operations.

The essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant separation or equilibrium parameter (R_L), which is expressed by the following equation [33].

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where C_0 is the initial dye color concentration (mg/l) and b the Langmuir's adsorption constant (l/mg). By processing the above equation, the R_L values for investigated dye-sorbents system was; charfines (0.136), lignite coal (0.20), bituminous coal (0.189) and activated carbon (0.072). From the separation factor (R_L) values, it is conformed that the dye-coal adsorption system was of 'favorable isotherm shape' indicating favorable sorption of dye over coal based sorbents and activated carbon (since R_L values fall in the range of 0 to 1) [15,26,34].

4.5. Influence of pH of the dye solution on sorptive uptake

The pH of the aqueous medium exert profound influence on the sorptive uptake of the dye color presumably due its influence on the surface of the sorbent and ionization/dissociation of the sorbent molecule. The variations of the dye color removal at various solution pH values were depicted in Fig. 6 for all the sorbents. From the figure, the maximum dye color removal for all the sorbents was observed at the neutral pH ranges. At neutral pH ranges, there is a possibility of oxidation of the surface oxygen complexes present on the surface which may impart positive charge to the coal surface and the dissociated charged dye molecules presumably attracted on to the coal surface leading maximum dye removal [15]. Inhibition of the dye sorption onto coal surface at acidic and basic pH ranges may be attributed to the increase of hydroxyl and hydrogen ions leading to formation of aqua complexes thereby retarding the dye sorption.

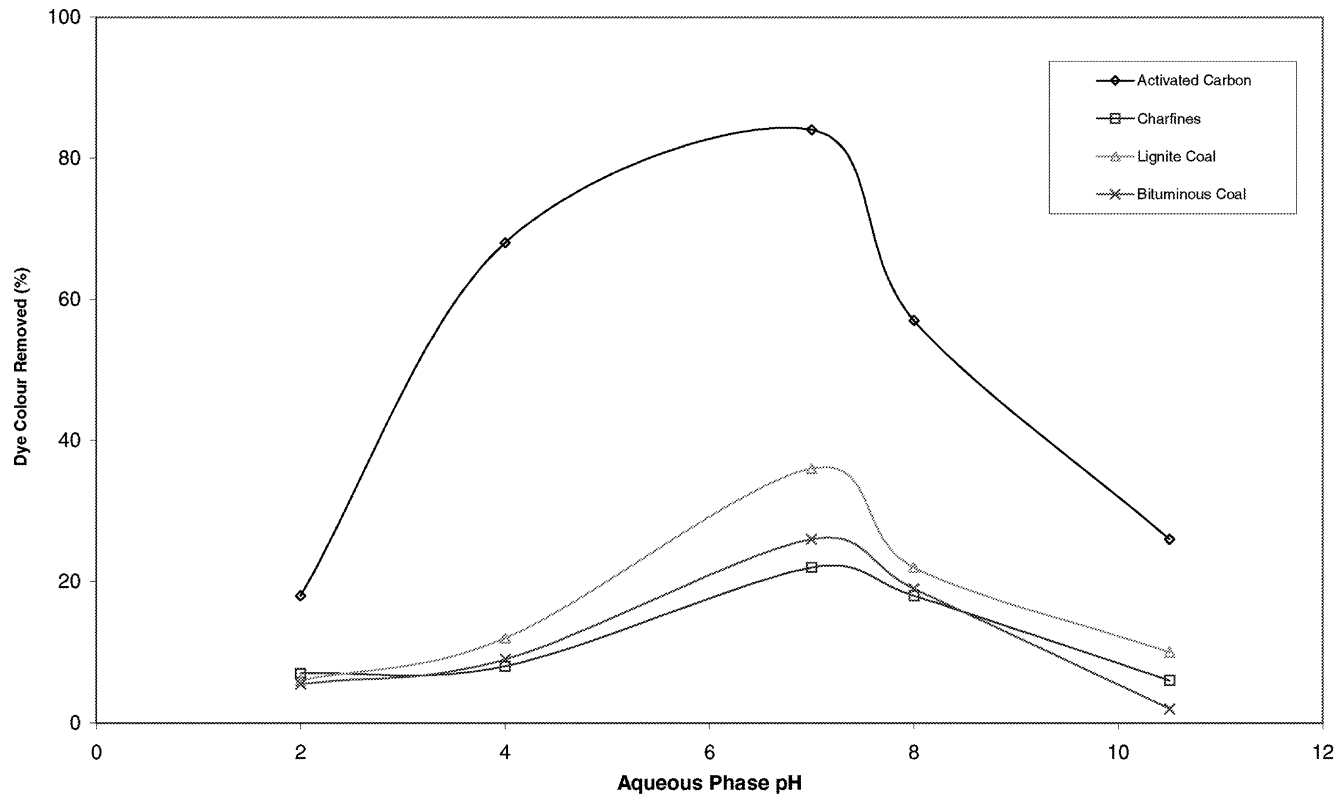


Fig. 6. Effect of solution pH on dye sorption (mass of the sorbent = 1000 mg; initial dye concentration = 50 mg/l; temperature = $27 \pm 2^\circ\text{C}$).

4.6. Desorption and interruption studies

In order to probe further into the mechanistic aspects of the dye sorption onto coal based sorption, desorption and interruption studies were conducted. For coal based sorption, after interrupting (the ongoing sorption process for a period of 30 min and continuing) does not affect the rate of uptake and hence it may be inferred that the film diffusion may be the rate limiting [35] in dye color sorption. However, in case of activated carbon the rate of uptake after interruption was affected (>5%) and this indicates the possibility of pore diffusion to be the rate controlling step in the sorption process.

Coal based sorbents yielded no desorption (<2%) with distilled water, 0.1N NaOH and 0.1N HCl and it may be inferred from the desorption studies that the most of the dye sorbate molecules binds to the sorbent surface through a strong chemisorption interaction and established a strong bond [14,15] precluding the possibility of physisorption. Lignite coal and charfines disintegrated and dissociated in 0.1N NaOH [36]. Organic solvents also desorbed negligible amount of dye. In case of activated carbon, 10% desorption resulted in organic solvents and distilled water (ion-exchange sorption is not occurring) and 32–40% desorption yielded in organic solvents indicating physisorption interaction nature of sorption [15]. The above stated observations were well corroborated with the sorption kinetic data discussed earlier.

5. Conclusion

Adsorption studies performed on the coal based direct azo dye system revealed the varying adsorption capacity of sorbents. Batch kinetic studies performed on the coal–dye system indicated the varied sorption capacity of dye over the tested adsorbents. The initial high uptake of dye on coal may be reasoned due to chemisorption interaction while gradual uptake by activated carbon may be indicative of physisorption interaction. Coal–dye interaction accounts to first-order rate irreversible equation and intraparticle diffusion study indicating that intraparticle diffusion is not only the rate limiting step. Isothermal data fit well with langmuir adsorption isotherm. Desorption and interruption studies further revealed the chemisorption interaction of dye on coal based sorbents and physisorption interaction of dye over the activated carbon.

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