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IR, XRD and SEM Studies to Elucidate the Mechanism of Azo Dye Sorption Interaction with Coal Based Adsorbents and Activated Carbon from Aqueous Phase

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Adsorption interaction of acid azo dye sorption onto coal based sorbent and activated carbon form aqueous phase was investigated using IR, X-ray diffraction, and SEM techniques. IR studies revealed the participation of some of the surface functional groups in the adsorption interaction. X-ray diffraction studies exhibited the increase in crystalline nature of the loaded sorbents compared to the unloaded sorbents. SE micrograms revealed the morphological observations of the unloaded sorbents and thereby changes in the loaded sorbents indicating the participation of the porous network of the sorbents in the sorption interaction.

Introduction

Among the physico-chemical processes, adsorption technology is considered to be the most effective and proven technology having wide potential applications in both water and wastewater treatment. Adsorption is a rapid phenomenon of passive sequestration separation of adsorbate from aqueous/gaseous phase on to solid phase. Adsorption occurs between two phases in transporting pollutant from one phase to another. It is considered to be complex phenomena and depends mostly on the nature of the adsorbent (surface chemistry), adsorbate, and the system conditions inbetween the two phases. In this process, various types of adsorbents ranging from activated carbon to waste materials have been studied for its applicability as adsorbents. Today more than 9000 types of dyes relating to various chemical and application classes have been incorporated in the colour Index. Among various industries, textile industry ranks first in usage of the dye. Textile sector consumes about 60 per cent of the total dyes production for colouration of various fabrics and out of it, about 10 to 15 per cent of the dyes used for colouration comes out through the effluents[1,2]. Adsorption technology has proven its application in treating various industrial effluents. Among them, treatment of textile effluents has been widely studied for removing both colour and organic constituents and in various types of adsorbents from activated carbon to waste materials were extensively studied [3-8]. Availability of various adsorbents, as well as varying chemical nature of the effluents further compound the intensity of the problem. To design an adsorption system, it is imperative to understand the process of adsorption mechanism so that optimization can be achieved. It is also important to understand adsorption mechanism for effective activation and regeneration of the adsorbents.

Understanding of the adsorption phenomena in the process of sorption with respect to its surface properties, gives better insight into the basic mechanism occurring inbetween the sorption surface and aqueous phase which further helps to design an effective adsorption system. An attempt has been made to investigate the mechanism of adsorption process using some techniques such as IR Spectroscopy, Scanning Electron Microscopy (SEM) and X-ray diffraction. Three coal based adsorbents were selected in addition to activated carbon (F-400) for the study.

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Materials and Methods

Charfines (a byproduct in the carbonization processes of the lignite coal) and lignite coal were acquired from the Neyveli Lignite Corporation. Bituminous coal was acquired from Talcheru mines. The coal acquired was cleaned and sieved to the geometric mean size of 106 lm using IS sieve and subsequently used as the adsorbent[5]. Activated carbon (F-400, Calgon Corporation, USA) was used as a reference adsorbent to assess the potential of the coal based sorbents as adsorbent in dye colour removal. C I Acid Red 88, a monoazo dye belonging to acid application class having a red hue when dissolved in aqueous phase was used as test dye in the adsorption experimental studies[5]. The C I Number of the dye is 15620.

Adsorption Studies

100 mg of dye was accurately weighed and dissolved in 1000 mL of distilled water to prepare the stock solution (1000 mg/L). Solutions of 50 mg/L dye concentrationwere prepared from successive dilution of the stock solution. The residual concentration of the dye in aqueous phase was estimated using a calibration curve prepared at the corresponding optimum wavelength (λ_{max}) of 515 nm using a spectrometer (Spectrochem MKII, Amil Pvt Ltd). Batch sorption tests were performed at 29±2°C, employing a Bottle-Point method. Many bottles containing reaction mixtures containing 50 mL of 50 mg/L dye solution and 200 mg of sorbent was taken in a 250 mL glass bottle and agitated on a horizontal shaker (100 r p m) to impart mixing for overcoming diffusive resistance to boundary layer during sorption process. Depending on the requirement, numbers of such identical bottles were employed for each sorption test. At the end of the desired contact time (0, 10, 20, 30, 45, 60, 120, 180 and 240 min), the bottles were withdrawn from the shaker, the contents filtered using Whatman No. 42 filter paper and analyzed for residual colour concentration[5]

Instrumental Studies

For understanding the nature of the dye sorbent interaction, various instrumental studies were performed for both the unloaded and loaded adsorbents. IR studies were conducted to find the specific functional groups on the coal sorbents and the way adsorbed molecules are bound to the sorbent surface vis-a-vis participation of specific functional groups in the sorption reaction. IR studies were recorded on Nicolet 740 FT-IR Spectrometer at ambient conditions using KBr as diluent. Raw coal and loaded coal samples were subjected to powder X-ray diffraction studies to study the crystal nature and to understand the adsorption interaction. XRD studies were carried out using Philips PW 1051 diffractometer with nickel-filtered $C_u K_a$ (1.520!0.020 A^0) radiation. Loaded and unloaded coal sorbents were also scanned using SEM, in order to observe possible morphological changes and to know the shape, size, and surface structure of the sorbents on a Hitachi model S-520 SEM. The samples were mounted on a silver sample holder coated with gold metal at 10 mm Hg pressure and recorded at 10 kv accelerating voltage with different magnifications.

Results and Discussion

Adsorption Studies

From the batch sorption studies[5], it was noticed that the tested adsorbents showed sorption capacity of C I Acid Red 88 from aqueous phase. However the sorption capacity varied from coal to coal. Charfines showed highest adsorption capacity (71 per cent) compared to other two (lignite coal- 44 per cent and bituminous coal-41per cent). However, the activated carbon registered 81 per cent of adsorption of acid dye. From the sorption kinetics and desorption studies it was confirmed that the sorption interaction between coal based adsorbents is of chemisorption interaction, while in the case of activated carbon it is due to physisorption interaction. The kinetic data fit well with the Langmuir adsorption isotherm (lignite coal : Q^0–30.9 mg/g, b-0.0290 L/mg bituminous coal: Q^0–26.19 mg/g, b-0.0295 L/mg, Charfine: Q^0–333.33 mg/g, b-0.0225 L/mg, and activated carbon: Q^0–109 mg/g, b-0.0016 L/mg) indicating the single layer formation of dye over the homogeneous sorbent surface. Intra-particle diffusion studies suggest that diffusion was the rate-limiting step.

IR Spectroscopy Studies

Characterization of Unloaded Sorbents

IR analysis permits spectrophotometric observation of the solid surface in the IR range (4000 to 637 cm^{-1}), and serves as a direct means for the identification of the organic functional groups on the surface[9]. An examination of the sorbent surface before and after sorption reaction possibly provides information regarding

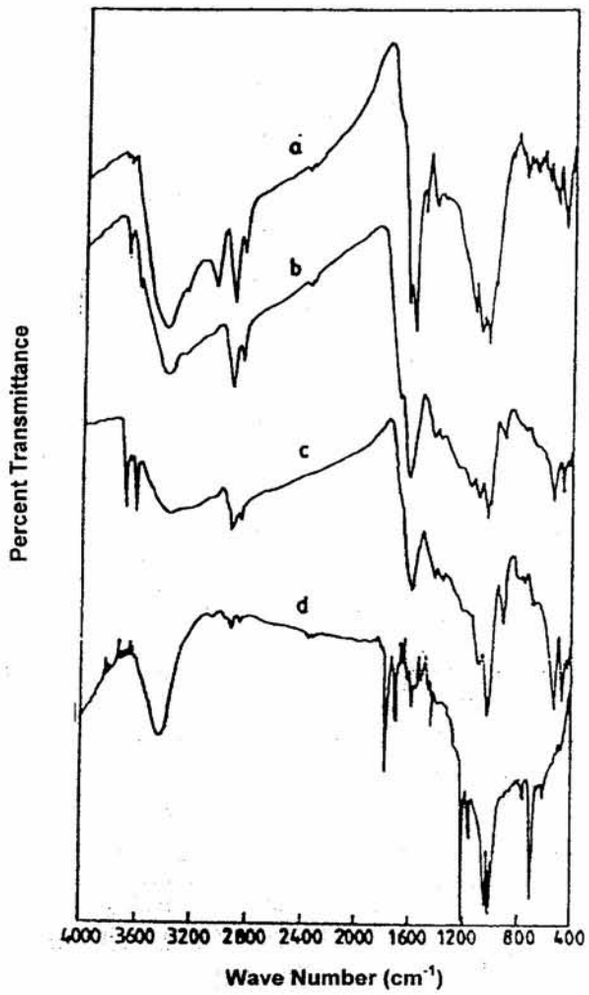


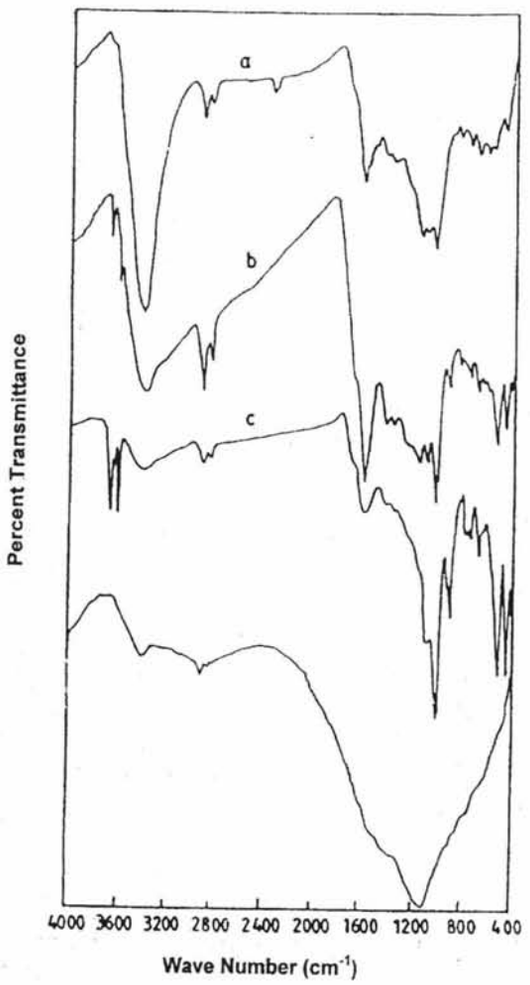
Figure1 — IR Spectra of unloaded sorbents:[(a)Lignite coal; (b) Charfines ; (c) Bituminous coal; (d) Activated carbon]

the surface groups that might have participated in the adsorption reaction and also indicates the surface site(s) at which sorption might have taken place. Interpretations of the spectra was based on the information and reference[9-17]. IR spectra of lignite coal, charfines, bituminous coal and activated carbon are presented in Figure 1. Perusal of the spectras of lignite coal, charfines, bituminous coal and activated carbon indicates more or less similar trends; however the intensities of the bands varied for each sorbent. All coal based adsorbents exhibited predominant and well-defined bands. The intensity of various bands increased from lignite coal to bituminous coal, which may be due to conversion of peripheral hydroxyl and carboxyl groups, as a result of coalification process. IR spectras of the lignite coal showed peaks in the range of 3450-3350 cm^{-1} which may be ascribed to the phenolic end groups (OH stretching) and carboxylic acid groups, whereas the bands in the region of 300-2900 cm^{-1} may be due to the presence of aromatic C-H stretching. The presence of the bands around 2400 cm^{-1} denotes the presence of C=O stretching. Bands around 1720-1600 cm^{-1} are associated with C=O stretching of lactonic and carboxylic groups and bands around 1775-1675 cm^{-1} are due to lactonic groups. The bands in the region of 1700-1670 cm^{-1} may be attributed to aromatic carboxylic groups. The overlapping bands in the region 1600-1500 cm^{-1} may be related to C=C vibration and around 1660-1550 cm^{-1} is attributed to the presence of highly conjugated C-O in a quinone/carbonyl structure. Quinone type oxygen accounts for about 25 per cent of the total oxygen present on the surface of the carbon[18]. The bands between 1480-1300 cm^{-1} may be due to the presence of the OH bending vibration and indicates the presence of phenolic group. The bands in the region of 1300-1230 cm^{-1} and 1100-1000 cm^{-1} is due to C-O stretching (lactonic and phenolic groups). The bands in the region of 1200-1059 cm^{-1} are attributed due to C-O stretching frequency of COOH group. The bands around 900-800 cm^{-1} region may be attributed to symmetric CO_3 stretch and is associated with the deformation of the carbonate group. The overlapping bands in the region of 800-600 cm^{-1} may be due to out of plane ring deformation (750 cm^{-1}) and out of plane CH deformation (700 cm^{-1}).

Characterization of Dye Sorbed Sorbents

Adsorption interaction/reaction of dye, over sorbents studied has resulted in some spectral changes in the spectrogram like disappearance of some bands, broadening of some bands, and spectral shifts. Spectral changes in the spectra of the unloaded and loaded sorbents are on the basis of the changes in the nature of the surface like participation of specific functional groups in sorption interaction and the ensuing chemical changes thereon. The spectrograms of the loaded and unloaded coal samples are further compared in terms of the resultant changes in the bands like appearance/disappearance of the bands, broadening/sharpening of the bands, and shifting of the bands (spectral shifts). An attempt was made to correlate these changes with the sorption interaction.

The IR spectra of C I Acid Red 88 loaded sorbents is shown in Figure 2 Sorption of Acid Red 88 a monoazo acid dye onto lignite coal has resulted in considerable changes in the spectrogram in the wave num-



gure 2 — IR Spectra of C I acid red 88 loaded sorbents:[(a) Lignite coal ; (b)Charfines; (c)Bitminous coal;(d) Activated carbon]

er 3300-1650 cm^{-1}. The bands in the region 3300 cm^{-1}, 000 cm^{-1} , and 1650 cm^{-1} respectively disappeared indicating participation of phenolic, carboxylic, and carbonyl groups in sorption reaction and it is most likely at the hydrogen in OH group involved in the formation of surface complex with Intra-molecular hydrogen onding[11], in which case the OH stretching vibration will most diminish, broaden or even disappear altogether. he disappearance of the quinone band around 1600 n^{-1} suggests the participation of C=O in the quinone or arboxyl ion in the sorption reaction.

Batch sorption studies suggest uptake of dye probly due to the chemical reaction leading to chemisorption and indicate participation of surface (acidic) functional groups in the sorption reaction[5].The adsorbed dye olecule may be retained in the diffuse layer by the talytic reaction with molecular oxygen as an anchor as the hydration type reaction[14]. The oxygen ion adsorbed on the coal surface is neutralized in an aqueous solution and further reduces in the subsequent steps to perhydroxyl anion and surface charge become positive and the charged anion of the dye are nonspecifically adsorbed in the diffusion layer. Alternatively, the adsorbed oxygen complex (surface complex) on the surface of the coal in neutral solution may cause the oxidation of water molecule. The resultant solution after adsorption interaction exhibits an increase in pH and the positive charge remains on the surface of the sorbent[19] which facilitates the adsorption of dye on the surface with a concomitant release of H_2O_2.

In the case of activated carbon, adsorption resulted in significant changes in the spectrogram. Several well defined bands in the range 2400 cm^{-1}, 1800-1000 cm^{-1} disappeared and a broad band around 1100 cm^{-1} was observed. Disappearance of bands in 1800-1000 cm^{-1} range probably indicates participation of lactonic, carboxylic, and phenolic OH groups in the sorption interaction.

From the above discussion, it seems that the surface functional groups present on coal and activated carbon surface participated in the sorption reaction of dye. The presence of carbonyl groups and quinone structure enhances adsorption of aromatic compounds due to formation of a donor-acceptor complex involving the benzene ring with partial positive charge on the carbonyl groups[13]. Surface functional groups impart polar characteristics to the sorbents, which may results in preferential adsorption of more polar compounds like dyes[20]. Surface acidic groups present on the sorbent surface enhance sorptive removal of acid dyes. As a result of hydrolysis of surface oxide on the surface of the sorbent the chemisorbed water molecule leads to decrease in the intensity of adsorption bands in the range of 1800-700 cm^{-1}. OH stretching vibration in the range of 3600-2000 cm^{-1} due to adsorption of water indicates the OH group linked by hydrogen bonding, which facilitates sorption of dye molecules.

X-Ray Diffraction Studies

XRD Pattern of Unloaded Sorbents

Adsorption reaction may lead to changes in molecular and crystalline structure of the sorbent and hence an understanding of the molecular structure and crystalline structure of the adsorbent and the resulting changes thereof would provide valuable information regarding

adsorption reaction. Examination of the diffraction patterns of the adsorbents indicates wide variations (Table 1).

XRD data in Table 1 shows that sorbents contain traces of compounds such as quartzite, tridynite and kaolinite (lignite coal and charfines), quartzite and kalonite (bituminous coal) and quartzite and graphite (activated carbon) which remained unchanged even after sorption of dye. It appears from the XRD pattern that the lignite coal, charfines, and bituminous coal are crystalline in nature of the sorbents which increases with the increasing coalification process.

XRD Pattern of Dye Loaded Sorbents

The XRD pattern of the dye-laden sorbents showed significant changes. Lignite coal and charfines indicates significant change in the crystalline nature of the coal. In the case of bituminous coal also some change in crystalline nature was observed. Improvement in the crystalline nature of the sorbent is perhaps due to the formation of mixed stages leading to the growth of the sorbent crystal result of the dye sorption reaction. The XRD data of the loaded charfines have an evidence of slight modification from the original crystallinity with a variation in the size of crystalline from $3.3x10^{-6}$ cm to $3.0x10^{-6}$ cm. The XRD pattern of loaded activated carbon exhibits no variation and this suggests that the dye molecules might diffuse into micropores and macropores and sorb mostly by physisorption without altering the structure of the adsorbents, as a result of the sorption reaction. The above observation corroborated well with batch sorption experiments.

Table 1— XRD details of unloaded adsorbents

Sorbents	Observations
Charfines	Monoclinic Crystalline (size $3.3x10^{-6}$ cm)
Lignite coal	Orthorhombic Not crystalline (size $3.5x10^{-6}$ cm)
Bituminous coal	Highly crystalline (size $2.5x10^{-6}$ cm)
Activated carbon (F 400)	Microcrystalline (fused hexagonal rings)

Scanning Electron Microscope (SEM) Studies

Morphology of Unloaded Sorbents

SEM is widely used to study the morphological features and surface characteristics of the sorbent materials[21-22]. In the present study, SEM is used to assess morphological changes in the coal based sorbent surfaces following adsorption of the dye molecule. Perusal of the SE micrographs of unloaded adsorbents, indicates morphological features given in Table 2.

Table 2 — Morphology observations of the unloaded adsorbents

Sorbent		Morphological observation
Charfines	Surface	Smooth
	Pores	Irregular, unevenly distributed, less dense; Transitional pores:20-40 μm; Internal network of pores observed
	Structure	Skeleton structure –not observed
Lignite coal	Surface	Not smooth
	Pores	Irregular, evenly distributed, more or less dense; Transitional pores: 65-25 μm; Internal network of pores apparent
	Structure	Skeleton structure observed
Bituminous coal	Surface	Not smooth
	Pores	Well defined, place at regular intervals and denser; Transitional pores:80-24 μm; Internal network of pores is noticeable
	Structure	Skeleton structure
Activated carbon (F 4000)	Surface	Uneven
	Pores	Irregular intervals and uneven; Transitional pores:120-28 μm; Good internal network of pores
	Structure	Skeleton structure

It follows from the morphological observations of the sorbent surface that surface porosity, pore size, pore density, and distribution, skeletal structure and internal network of pores appear to increase with the increase in the rank of coal.

Morphology of Dye Loaded Sorbents

The morphology of the loaded adsorbents showed some important observations. Coverage of the surface of the adsorbents due to adsorption of the sorbent molecule presumably leading to formation of a monolayer of the sorbent molecule over the sorbate surface is evident from the formation of a white layer (molecular cloud) of uniform thickness and coverage (spread). The above observation was further confirmed by variation in the pore structure on the surface of the adsorbents. The above observations augment well with the batch sorption studies.

Conclusions

The results of the present investigation reveal some important observations of azo dye sorption mechanism. The batch-studied results are correlated with the instrumental observations. IR studies indicate the participation of the specific functional groups in adsorption interaction, while XRD studies shows change in the crystallinity of the sorbents due to adsorption reaction. SEM studies visualized the formation of the molecular cloud of the dye over the surface. Further studies may be carried out for proper interpretation of data which may explain further the adsorption mechanism.

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