



ADSORPTION CHARACTERISTICS OF VICTORIA BLUE ON LOW COST NATURAL SAND AND ITS REMOVAL FROM AQUEOUS MEDIA

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Triarylmethane dyes have been identified as one of the toxic dyes. The presence of triarylmethane dyes in water act as pollutant and cause hazardous effect on natural resources, aquatic life as well as to human being. Triarylmethane dyes are extensively used for wool, silk, cotton, leather and paper industries. In the present work, natural sand has been utilised as an adsorbent for developing methodology for the removal of these dyes, which does not easily biodegrades in aqueous medium. The adsorption efficiency of natural sand was tested by using Victoria Blue (VB) as model dye. The adsorption behaviour as a function of the pH of the aqueous dye solution, the contact time, initial concentration of the dye and the amount of adsorbent was studied. All studies were performed at room temperature (298 K). It was observed that under optimized conditions, 91 % of VB can be removed from aqueous media. The adsorption data was fitted well by the Langmuir and Freundlich adsorption isotherm; pseudo-second-order and intraparticle diffusion models were also applied.

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INTRODUCTION

The use of dyes in different industries (textile, paper and pulp, tannery, Kraft bleaching industries etc.) introduces a wide variety of organic pollutants into natural water resources, resulting in colored industrial effluents containing high concentration of organic chemicals.¹ The presence of dyes block sunlight, which is essential for many photo-initiated chemical reactions that are necessary for aquatic life.²⁻³ Worldwide More than 10,000 textile dyes are commercially available and their annual production is $\sim 7 \times 10^5$ metric tons.⁴ About 2% of the annual dye production is discharged in the effluent from manufacturing units.⁵ In textile industry, 10% of dyes are lost during textile coloration process.⁶ Color is one of the most obvious indicators of water pollution, and discharge of highly colored synthetic dyes in the effluent can be damaging to the receiving water bodies.⁷

Due to the low biodegradability of triarylmethane dyes, conventional biological wastewater treatment systems are not very effective. These methods include physicochemical flocculation with Fe(II)/Ca(OH)₂, membrane filtration, electrokinetic coagulation, electrochemical destruction, ion exchange, precipitation, ozonation, adsorption etc. However, apart from being costly, these technologies are not very effective for the removal of color.³ Amongst the numerous techniques available, adsorption is the procedure of choice due to its sludge free clean operation and capability to completely remove different types of coloring materials, even from dilute solutions.⁸⁻⁹ Of all the available adsorbents, activated carbon has been most widely used for the removal of pollutants from wastewater.¹⁰⁻¹¹ However, regeneration of the saturated carbon is expensive and is the main reason for the low economic efficiency in its application.

The objective of the work presented in this paper is to examine the adsorption characteristics of a non-biodegradable cationic dye from aqueous solution onto natural sand, which is porous crystalline solid. The structure of sand is given in Figure 1.¹²

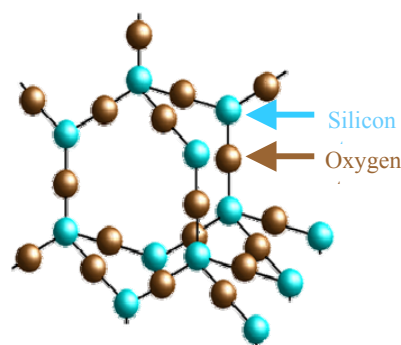


Figure 1. Structure of sand

EXPERIMENTAL

Materials

The sand sample was collected from Chandra Prabha Wildlife Sanctuary, Varanasi, UP, India. After removing stones and other bigger particles the sand was ground and sieved through a 230 mesh sieve.

The dye chosen for such study was the non-biodegradable Victoria Blue (Fig. 2), a basic blue 26 with the C.I. 44045 molecular weight 506.1 and molecular formula C₃₃H₃₂ClN₃ was procured from Thomas Baker Chemical Limited Mumbai.

A class of triarylmethane dye and extensively used for dyeing wool, silk and cotton.¹⁵ It is also used for staining in microscopic work.¹⁶ This dye is known to cause strong coloration and toxicity in the waste water and

can produce irritation to eyes and respiratory system.¹⁷ It may even promote tumour growth in some species of fish.¹⁸ Fe and Cu sulphates, analytical grade were procured from Qualigens fine chemicals, Mumbai.

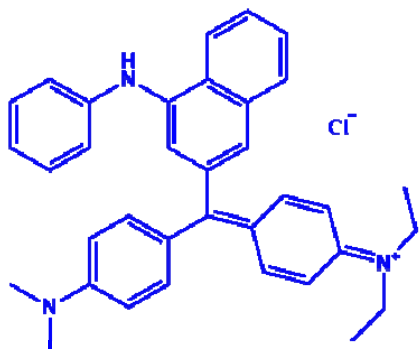


Figure 2. Molecular structure of Victoria blue

Instruments

Electronic absorption spectra were recorded on a Jena Analytik Specord 250 spectrophotometer, X-ray diffraction patterns were recorded on a Philips X' Pert-PRO PMRD (D8 Discover Bruker AXS) system using Cu K α radiation ($n = 1 \text{ \AA}$), FT-IR spectra were recorded using a Perkin-Elmer FT-IR (BxFTIR). TEM images were recorded using TECNAI G2T30 FEI Instrument operated with an accelerating voltage of 300 KV.

Effect of pH on the absorption behaviour of Victoria blue in aqueous media

The aqueous VB solution though the λ_{max} values remain same (617 nm) but the absolute value of absorbance appears to be influenced by the pH of the dye solution.

At higher pH (> 9), color of the dye solution was found to change from blue to wine red and at low pH (< 1), color of the dye solution changed to sky blue.

In case of pH 9 a very broad absorption band with λ_{max} at 555nm was observed. Maximum absorbance was observed between pH 3 to 5 therefore, quantitative estimation of the dye was performed at pH 5, pH of each solution was adjusted using an Elico India – Li120 pH meter with a combined pH electrode. pH meter was calibrated/standardized¹⁷ before every measurement.

Employing the batch extraction method, the adsorption behavior of VB onto natural sand was investigated as a function of (1) the pH of the aqueous dye solution, (2) the contact time of batch extraction method, (3) the initial concentration of the dye solution, and (4) adsorption as a function of metal ions.

Each experiment was performed using 50 mg of natural sand sample and 25 ml of dye solution at room temperature. Each batch experiment, the supernatant was separated by centrifugation at 8000 rpm for 15 minute using a REMI R24 centrifuge machine. The concentration of the dye in supernatant was estimated spectrophotometrically (Jena Analytik Specord 250 spectrophotometer).

The concentration of unadsorbed dye was determined from the corresponding Beer–Lambert plot. The percentage of the adsorbed VB (φ) onto the natural sand was calculated by using Eqn. (1).

$$\varphi = 100 \frac{C_i - C_e}{C_i} \quad (1)$$

where

C_i is the initial concentration (ppm) of the dye solution and

C_e is the concentration of the dye (ppm) in the supernatant at the equilibrium stage.

The amount of dye adsorbed, q_e (mg g^{-1}), was calculated via the mass-balance relationship shown in equation (2).

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

where

V is the volume of the dye solution (ml) and
 m is the mass of adsorbent employed (mg).

RESULTS AND DISCUSSION

Adsorption as a function of the pH of the dye solution

In the adsorption process pH of the dye solution plays an important role, particularly on adsorption capacity. This pH study was performed with 25 ml of 20 ppm dye solution. The uptake of VB onto natural sand sample at pH 7 and 7.5 exhibited 79.5 % and 79 % uptake respectively which decreased up to 74.5 at pH8. However, the percent uptake was much less at pH 2 showing only 58.5 % uptakes (Figure 3). Adsorption of VB at pH < 7 is low, may be because of the fact that the negative charge on sand tends to get saturated by protons¹⁸⁻¹⁹ in acidic media as making H^+ ions compete effectively with cationic dye causing a decrease in the adsorption of dye on the surface of the sand.

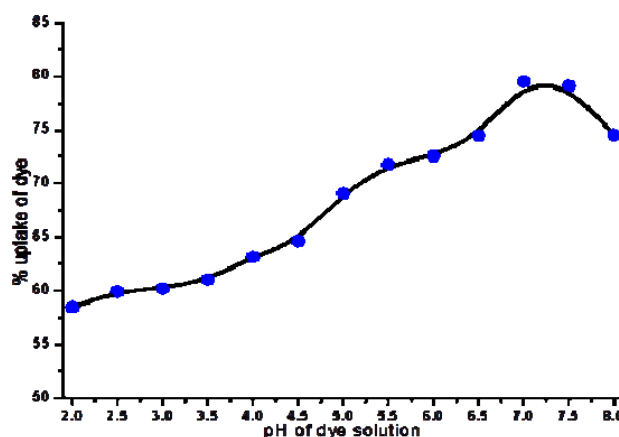


Figure 3. Effect of pH on the percentage uptake of VB by sand.

Every batch experiment was performed at pH 7 but after centrifugation the pH of supernatant was adjusted at pH 5, because maximum absorbance value of dye was observed at pH 5.

Adsorption as a function of contact time

81 % of the VB is extracted within 90 minutes at pH 7. This study was performed with 25 ml of 20 ppm dye solution. The maximum uptake was 91 % (Fig. 4) which was attained within 270 minutes and it remained constant up to 300 minutes.

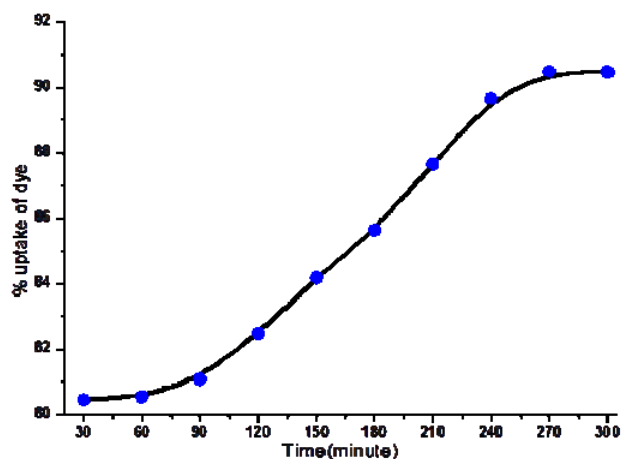


Figure 4. Effect of contact time on the percentage uptake of VB by sand

Adsorption as a function of initial concentration of the dye

Percentage uptake of VB on natural sand was found to decrease gradually at higher concentration. However, the uptake of dye (mg g⁻¹) with increasing concentration of dye (Fig. 5).

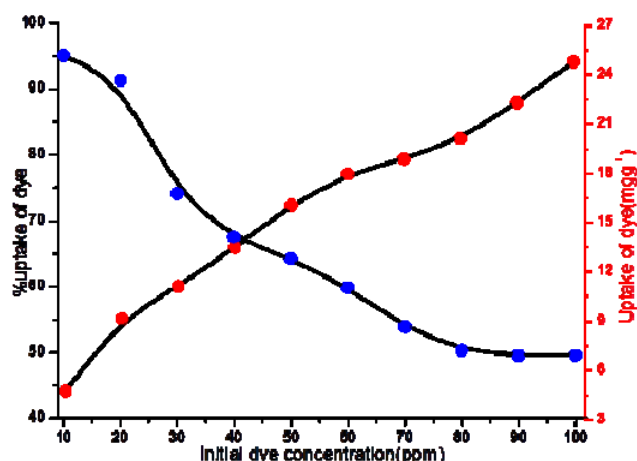


Figure 5. Effect of the initial dye concentration on the percentage uptake of VB by sand.

The percentage uptake of dye and efficiency of sand in mg g⁻¹ sand is given in Table 1.

Table 1. Adsorption of VB as a function of initial dye concentration

Adsorbent	Variation in concentration of VB		Amount of VB adsorbed on sand	
	S. No.	ppm (µg)	%	mg g ⁻¹
50 mg	01	10 (250)	95.07	4.75
	02	20 (500)	91.30	9.13
	03	30 (750)	74.12	11.12
	04	40 (1000)	67.46	13.49
	05	50 (1250)	64.26	16.07
	06	60 (1500)	59.80	17.94
	07	70 (1750)	53.91	18.87
	08	80 (2000)	50.33	20.13
	09	90 (2250)	49.55	22.29
	10	100 (2500)	49.57	24.79

Adsorption as a function of metal ions concentration

The percent uptake of dye without metal ion was found 91 %. In the presence of Cu²⁺ and Fe²⁺ the percent uptake of dye on sand decreases with increase in concentration of metal ions in solution (Fig. 6).

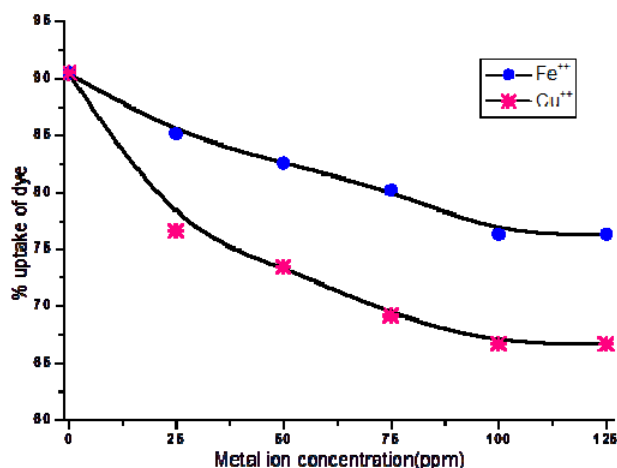


Figure 6. Effect of Fe²⁺ and Cu²⁺ ions on the percentage uptake of VB.

This is in agreement with the previous study mentioned in the literature (In the presence of trace metal ions i.e. Cd²⁺, Mn²⁺, Pb²⁺, Fe²⁺, Zn²⁺ and Ni²⁺ the adsorption capacity of dyes onto the sand surface decreases²⁰ because of the preferential adsorption of these metal ions onto the active site of the sand).

Freundlich adsorption isotherm

This is commonly used to describe the adsorption characteristics of the heterogeneous surface.²¹ These data often fit the empirical equation (3) proposed by Freundlich:

$$q_e = K_f C_e^{1/n} \tag{3}$$

where

K_f = Freundlich isotherm constant (mg g^{-1}),

n = adsorption intensity,

C_e = the equilibrium concentration of adsorbate (mg L^{-1}),

q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg g^{-1}).

Linearizing equation 3, gives Eqn. (4):

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

The plot of $\log q_e$ versus $\log C_e$ was linear (Fig. 8), with a slope equal to $1/n$ and an intercept equal to $\log K_f$. The correlation coefficient, R^2 , and the values of q_{\max} and K_L for sand is showed in Table 2.

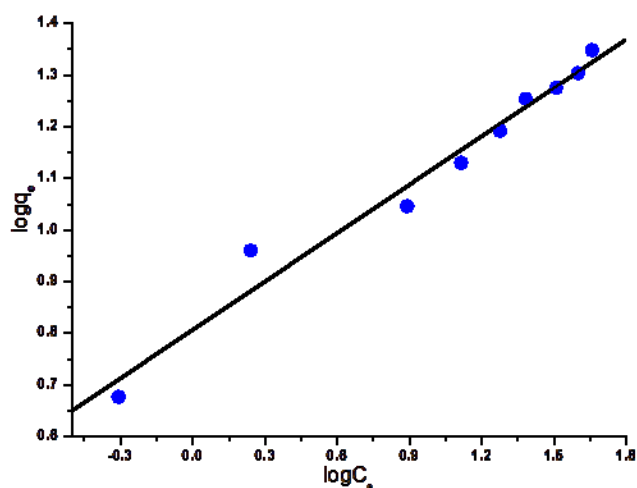


Figure 7. Freundlich adsorption isotherm

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process.²² If $n=1$ then the partition between the two phases is independent of the concentration. If a value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption.²³

This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between 1 to 10, this indicates a favorable adsorption process.²⁴ From the parameters obtained as in table 2, a value of $1/n = 0.3127$ while $n = 3.198$ indicates that the adsorption of VB onto the sand is favorable.

Langmuir adsorption isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of VB ions between the solid and liquid phases.²⁵ The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites.

The model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface.

Based upon these assumptions, the Langmuir isotherm equation may be expressed in a linearized form as shown in equation (5):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (5)$$

where

q_{\max} is the monolayer capacity of the adsorbent (mg g^{-1})

and K_L is the Langmuir adsorption constant ($\text{dm}^3 \text{mg}^{-1}$).

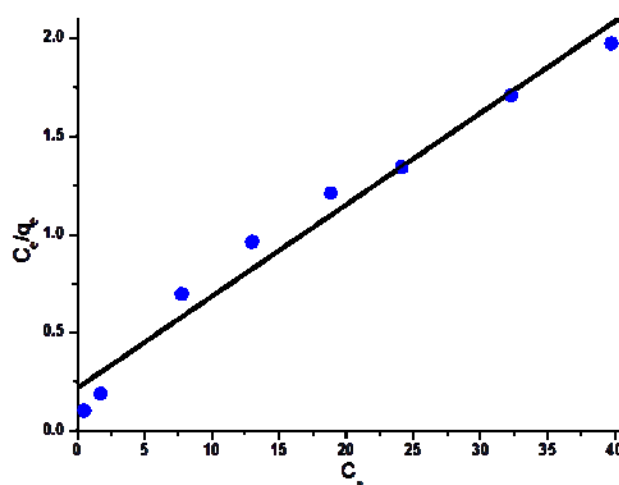


Figure 8. Langmuir adsorption isotherm

The plot of C_e/q_e versus C_e was linear (Fig. 8), with a slope equal to $1/q_{\max}$ and an intercept equal to $1/(q_{\max} K_L)$. The correlation coefficient, R^2 , and the values of q_{\max} and K_L for sand sample studied are listed in Table 2.

The R^2 value of 0.988 for sand sample indicates that the adsorption of VB onto sand sample is well fitted by the Langmuir isotherm.

Table 2. Freundlich constants for the adsorption of VB onto the sand sample.

Adsorbent	Freundlich isotherm constants			
	$1/n$	n	K_f (mg g^{-1})	R^2
Sand	0.313	3.198	6.408	0.971

Table 3. Langmuir constants for the adsorption of VB onto the sand sample.

Adsorbent	Langmuir isotherm constants		
	q_{\max} (mg g^{-1})	K_L ($\text{dm}^3 \text{mg}^{-1}$)	R^2
Sand	2.371	2.719	0.988

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless constant which is called equilibrium parameter defined as:

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

where

K_L is the Langmuir constant was found, which is used to determine the enthalpy of adsorption, and

C_i is the highest initial dye concentration employed.

The value of R_L was found 0.00368 it indicates whether the type of isotherm observed is unfavorable ($R_L > 1$), linear ($R_L = 1$) or favorable ($R_L < 1$).²⁶ The R_L values are listed in Table 3 along with the other Langmuir constants. For all the adsorption studies of Victoria blue dye onto sand, the R_L values were in the range $0 < R_L < 1$, indicating that the adsorption process was favourable.

Adsorption kinetics

Several kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism of the adsorption process and to test the experimental data. In the present investigation, the adsorption data were analyzed using three kinetic models, the pseudo-first-order, pseudo-second-order kinetic and the intraparticle diffusion models.

The pseudo-first-order model was presented by Lagergren.²⁷ The Lagergren's first-order reaction model is expressed in linear form as Eqn. (7):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (7)$$

where

q_e and q_t are the amounts of VB dye (mg g^{-1}) adsorbed on the sand at equilibrium, and at time t , respectively and

K_1 is the rate constant (min^{-1}) of the pseudo-first-order adsorption process.

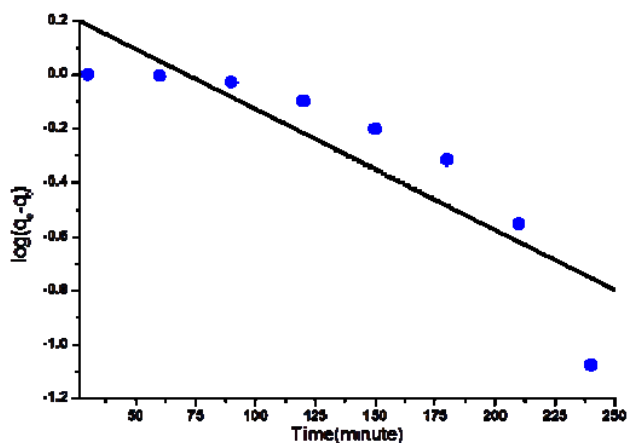


Figure 9. Pseudo-first-order kinetic model for the adsorption of VB onto sand sample.

The plot of $\log(q_e - q_t)$ versus t would be linear with a slope of $-K_1/2.303$ and an intercept of $\log q_e$ (Fig. 9).

The adsorption data was also analysed in terms of pseudo-second-order mechanism, described by Ho and McKay.²⁸ The linear form of the Eqn. (8) as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where K_2 is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), $K_2 q_e^2$ is the initial rate of adsorption ($\text{mg g}^{-1} \text{min}^{-1}$). The plot of t/q_t against t of Eqn. (8) should give a linear relationship with a slope of $1/q_e$ and an intercept of $1/K_2 q_e^2$ (Fig. 11).

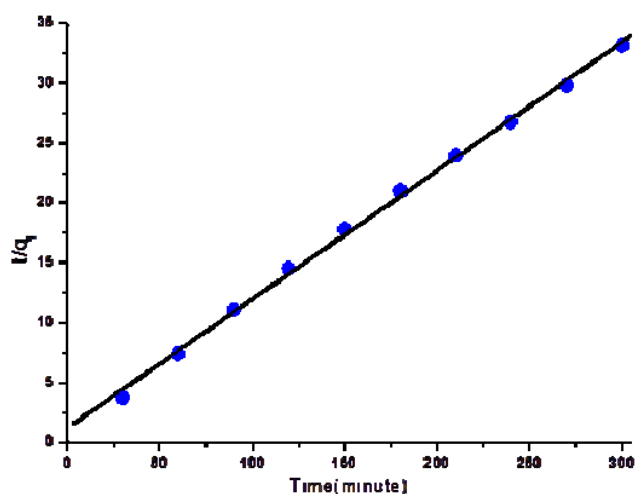


Figure 10. Pseudo-second-order kinetic model for the adsorption of VB onto sand sample.

The plot of q_t against $t^{1/2}$ of Equation (9) should give a linear relationship with a slope of K_d and an intercept of C (Fig. 10). where q_t is the amount of dye adsorbed (mg g^{-1}) at time t , K_d ($\text{mg g}^{-1} \text{min}^{0.5}$) is the rate constant for intraparticle diffusion.

The intraparticle diffusion plots for the effect of temperature on the adsorption of VB onto sand sample. In adsorption systems where there is the possibility of intraparticle diffusion being the rate-limiting step, the intraparticle diffusion approach described by Weber and Morris is used.²⁹

$$q_t = K_d t^{1/2} + C \quad (9)$$

The R^2 value was 0.9998 for sand indicates that the adsorption of VB onto these adsorbents was well fitted by the intraparticle diffusion (Table 4c). The K_d for sand is 0.13423 and intercept of C is 7.8099 was calculated by using Eqn. 9.

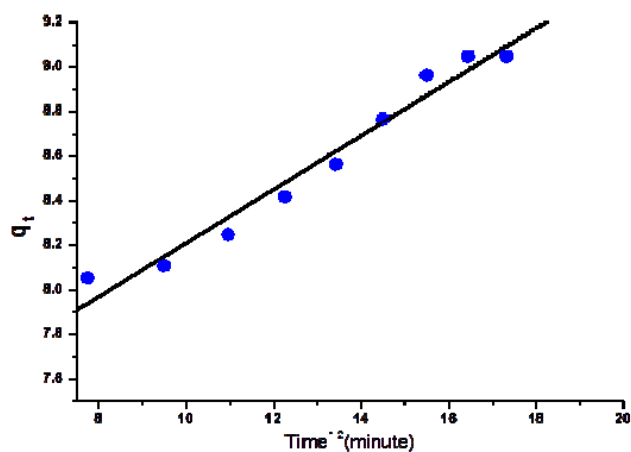


Figure 11. Intraparticle Diffusion model for the adsorption of VB onto sand sample.

Table 4a. Parameters of the fitted kinetic of Pseudo-first-order mode for the sand.

Adsorbent	Pseudo-first-order model		
	K_1 (min^{-1})	q_e (mg g^{-1})	R^2
Sand	0.010364	2.084	0.7781

Table 4b. Parameters of the fitted kinetic of Pseudo-second-order model for the sand.

Adsorbent	Pseudo-second-order model		
	K_2 [$\text{g mg}^{-1} \text{min}^{-1}$]	q_e (mg g^{-1})	R^2
Sand	0.00939	9.3197	0.9982

Table 4c. Parameters of the fitted kinetic of Intraparticle diffusion model for the sand

Adsorbent	Intraparticle diffusion		
	K_d	C	R^2
Sand	0.13423	7.8099	0.9998

Table 4a, 4b and 4c represents the equilibrium sorption capacity (q_e), the correlation coefficient, R^2 , and the rate constants for the pseudo-first-order (K_1) and pseudo-second-order (K_2) models. The data demonstrate good compliance with pseudo-second-order rate law rather than the pseudo-first-order rate law. This shows that the pseudo-second-order kinetic model show a better explanation of the kinetic adsorption data obtained in the present study. This was probably true in the present case sand is negatively in nature which attracts the positively charged dye charged. This would allow electrostatic interaction between the positively VB dye and the sand surface.

XRD analysis

Before recording XRD patterns sand sample was kept in double distilled water for 24 hours and was washed with double distilled water followed by centrifugation at ~ 8000 rpm for 10 minutes. The supernatant was rejected and the residue was dried in the oven at 100°C , for 24 h. XRD pattern of the sand sample shows sharp peaks indicating its crystalline nature as the presence of silica as its constituents.

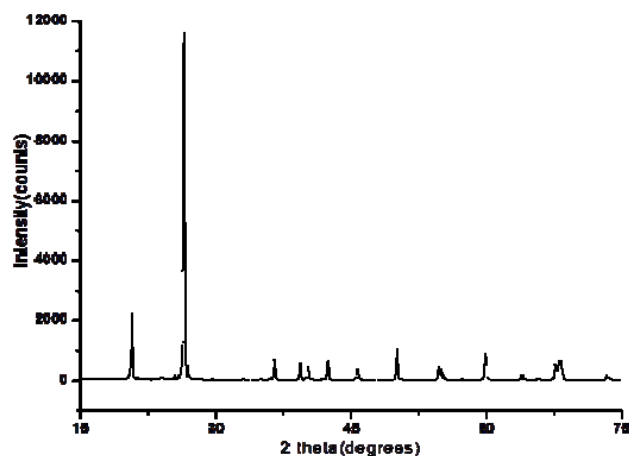


Figure 12a. XRD patterns of sand

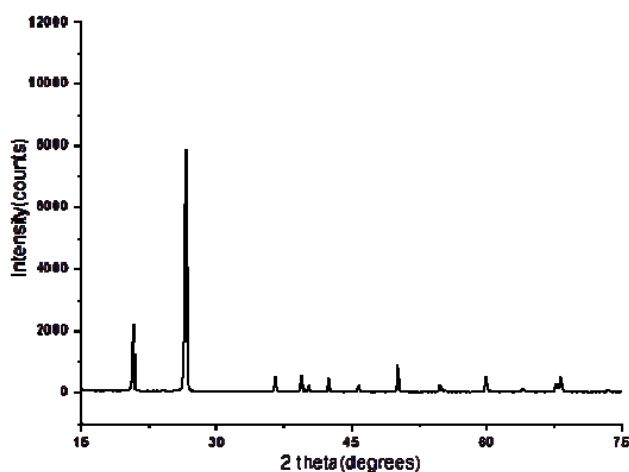


Figure 12b. XRD patterns of VB adsorbed sand

In the XRD analysis of sand sample and VB adsorbed sand sample (Figs. 12a and 12b), a slightly different in intensity (counts) curves. This is because of the dye adsorb on sand surface and made a layer around the sand surface.

FT-IR spectroscopic studies

FT-IR spectra of sand, washed sand, VB adsorbed sand and VB was recorded over the $500\text{--}4000\text{ cm}^{-1}$ wavenumber region and represented it in two parts (Figs. 13a and 13b). In the FT-IR spectrum of VB, secondary amines (Ar_2NH) show only a single weak band in the $3300\text{--}3000\text{ cm}^{-1}$ region, since they have only one N-H bond. Tertiary amines (Ar_3N) do not show any band in this region since they do not have N-H bond and the bands in the region $3100\text{--}3040\text{ cm}^{-1}$ exhibit aromatic C-H stretching vibrations. The C-N stretching frequency³⁰ appears at 1289 cm^{-1} due to the aromatic nature of the VB dye. While the C-C stretching band of the aromatic ring was observed at 1584 cm^{-1} . There is no any substantial difference in the FTIR spectrum of natural sand and washed sand. The absorption band at 1105 cm^{-1} indicate silicon sulfide (Si-S stretching), the one at 1010 cm^{-1} correspond to Si-O, 1049 cm^{-1} has been assigned to Si-O stretching peak³¹, The characteristics IR absorption band in both case sand and VB adsorbed sand the presence of 3442 cm^{-1} , 1584 cm^{-1} and 1289 cm^{-1} indicates VB dye adsorbed on the sand surface.

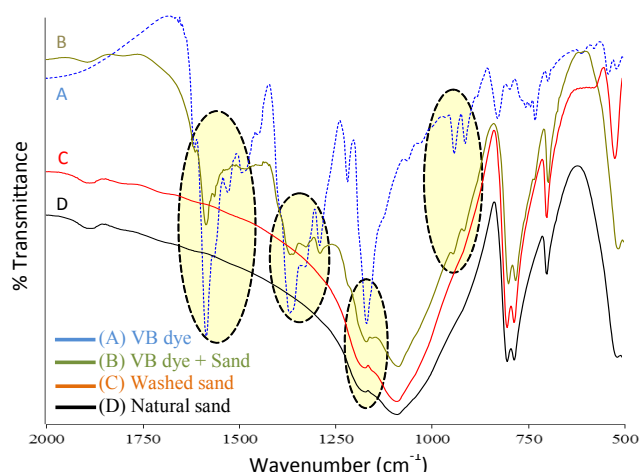


Figure 13a. FT-IR spectra of VB + sand (B), VB (A), washed sand (C) and sand (D).

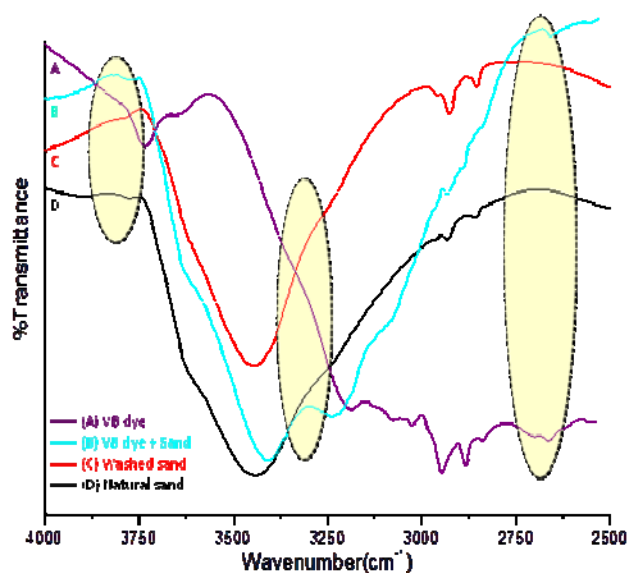


Figure 13b. FT-IR spectra of VB (A), VB + sand (B), washed sand (C) and sand (D).

Transmission electron microscopic studies

The samples were prepared by depositing the aqueous suspensions of the sand samples on a carbon film attached to a 400 mesh Cu grid.

The high resolution transmission electron microscopic images of sand sample (Fig. 14) show the layerand pellets like structure and particles of 100 nm in size (A) which is vanished due to deposition of VB around the sand surfaces and change into rough granular smoke like structure and particles of 100 nm in size (C).

The diffraction pattern of sand (B) shows white granular spotted circling in a continuous way of the TEM image; it indicates sand is crystalline in nature.

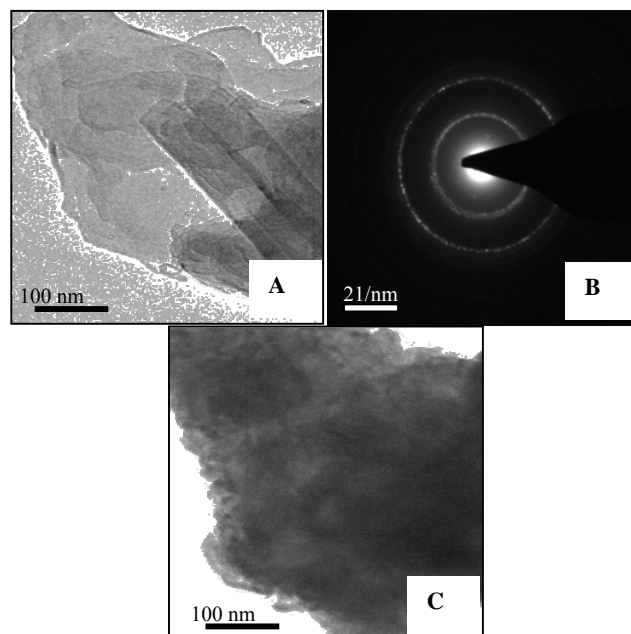


Figure 14. TEM images of sand (A), diffraction pattern of TEM image of the sand (B) TEM image of VB adsorbed sand (C).

The adsorption mechanism

The mechanism of adsorptive removal of VB dye by sand sampl is shown in Fig. 15. The sand molecule composed of oxygen atoms carries a partial negative charge while Victoria Blue dye beaing cationic in nature carries a partial positive charge on nitrogen atom. Thus there occur an electrostatic interaction³² between the negatively charged sand and positively charged charged dye.

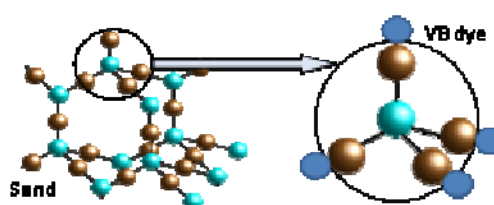


Figure 15. Electrostatic interaction between sand surface and VB dye

CONCLUSION

Sand has negatively charged surface and imparts electrostatic attraction towards cationic dye. Maximum 91% of Victoria Blue dye was removed. For the present sand sample, which was collected from Chandra Prabha Wildlife Sanctuary, Varanasi, UP, India, the active component was related to tridymite, cristobalite, a negatively charged mineral that imparts electrostatic attraction towards cationic dye. The adsorption data for VB investigated in this work fitted well to Langmuir adsorption isotherm equation and pseudo-second-order kinetic model.

The present study indicates that natural sand sample is a good low cost adsorbent moreover which can be used for the removal of VB dye from aqueous solution. Beautifully colored dye adsorbed sand thus recovered may be further used as a colorant in various application.

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