

Original Research

Modified Clays as an Efficient Adsorbent for Brilliant Green, Ethyl Violet and Allura Red Dyes: Kinetic and Thermodynamic Studies

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Abstract

Clay minerals can effectively adsorb contaminants from aqueous effluents due to their good adsorption and high cation exchange capacity. However, naturally occurring clay materials possessing hydrophilic features are not especially effective for the removal of organic pollutants. Therefore, in the present work the issue of hydrophilicity is tackled by modification of the clay (Pakistan origin) to prepare organoclays. Hexadecylpyridinium chloride, cetyltrimethylammonium bromide, and sodium dodecyl sulfate were used as clay modifiers. Changes in the basal spacing of clay layers after modification with surfactants were determined through XRD analysis. Chemical compositions of the clay and organoclays were determined by FTIR spectroscopy. Surface morphology of the as-prepared organoclays was assessed from SEM analysis. The modified clays (organoclays) were tested for their ability as potential adsorbents for three dyes from water: brilliant green, ethyl violet and allura red. All three modified clays showed high adsorption characteristics by removing (>90 %) of all three dyes with an adsorption capacity ranging from 35 to 85 mg/g. The time-dependent adsorption experiments showed that the rates of adsorption of dyes on organoclays were fast, adsorbing maximum amounts of dyes ranging from 15 to 80 mins of contact time. The adsorption kinetic study revealed that the dye removal process is mainly governed by a pseudo-1st order mechanism. Thus, surfactant-modified clays are an excellent choice as cost-effective and efficient adsorbents for the purification of water from dye contaminants.

Keywords: organoclay, surfactant, dyes, adsorption, environmental remediation

Introduction

The demands of fresh water are increasing day by day due to high contamination of natural resources – especially in developing countries. Human beings are constantly jeopardizing the natural eco-system by releasing wastes into water bodies [1]. The environment is continuously degraded by anthropogenic activities, especially industries like textiles, pigments, and plastics using different chemicals/dyes and posing risks to people [2, 3]. Thus, it has been reported that dye-producing industries release a large portion of dyes directly into freshwater bodies. Although the nature and the amount of dye constituents in the effluent discharge depend on the nature of the operation in a particular industry, the textile industry is the biggest producer of disposing untreated dyes in industrial wastewater [3]. Dyes affect the diversity of the aquatic ecosystem by absorbing the sunlight entering into water bodies and thus hindering photosynthetic processes. Due to the presence of dyes in water, the wastewater characteristics also change because of high biological oxygen demand (BOD) and chemical oxygen demand (COD), leading to a polluted ecosystem. Therefore, treatment of dye-contaminated water is mandatory before their release into the sewerage system to ensure water quality standards.

Various physical, chemical and biological processes are used for the remediation of dyes from wastewater. These processes include flocculation, coagulation, adsorption, ozonation, electrochemical destruction, irradiation and aerobic or anaerobic treatment [4, 5]. However, the adsorption process for water purification is preferred because of its low cost and no extra sludge generation [6, 7]. Among the adsorbents, clay has been reported to act as an especially effective adsorbent for water pollutants [8]. Recent research in this area has focused on modification of clay with materials that could improve its properties being used as a catalyst or adsorption ability or hydrophobic nature for adsorbing organic contaminants [9, 10]. Efficiencies of these clay materials can be expanded remarkably by substituting exchangeable cations of clay with organic cations or grafting to yield hydrophobic organoclays [11-13]. This is like pillared interlayered clays (PILCs) and is based on a mechanism of cationic exchange in which robust inorganic molecules are introduced in the interlayer space of the clay minerals, forming oxides strongly bound to layers of the minerals [14]. However, PILCs remain hydrophilic, whereas organoclays make use of organic moieties for the intercalation process for making clay “hydrophobic”, which can be used for organic contaminant adsorption.

In one particular study the removal of acid red dye from an aqueous system by a bentonite organoclay intercalated with hexadecyltrimethylammonium chloride was examined, and a maximum adsorption efficiency was observed at pH 13 [15]. Another study claimed a composite clay adsorbent formed from

poly-methyl methacrylate grafted onto tragacanth gum and bentonite was used to remove a number of anionic azo dyes like methyl orange, acid blue 113 and Congo red with improved efficiencies [16]. Thus, modified clays hold great promise for wastewater treatment.

Owing to low cost, high natural abundance, large specific surface area, excellent adsorption capacity, non-toxic nature and ease of modification, it is thus pertinent to replace costly and toxic adsorbents by organoclays for the treatment of wastewater [17]. With this consideration, we modified clay samples to organoclays by using hexadecylpyridinium chloride monohydrate (HDPCl.H₂O), cetyltrimethylammonium bromide (CTAB), and sodium dodecylsulfate (SDS) as modifiers. Under optimized conditions the as-prepared organoclays were tested for the removal of brilliant green, ethyl violet and allura red dyes from wastewater. This work underscores the importance of the use of Pakistan-origin clays and the diverse nature of the modifiers for the efficient adsorption of various dyes. To the best of our knowledge, this is the first time for reporting various clay-modified adsorbents for the removal of allura red, ethyl violet, and brilliant green with high-efficiency of adsorption.

Experimental

Materials and Methods

All of the materials used were analytical grade, surfactants (hexadecylpyridinium chloride monohydrate (HDPCl.H₂O), cetyltrimethylammonium bromide (CTAB), and sodium dodecylsulfate (SDS)) and dyes brilliant green (BG), (C₂₇H₃₄N₂O₄S, λ_{\max} 632nm) ethyl violet (EV) (C₃₁H₄₂N₃Cl, λ_{\max} 594nm) and Allura red (AR) (C₁₈H₁₄N₂O₈S₂.2Na, λ_{\max} 500nm). Commercially available bentonite clay is obtained from local market of Peshawar. For clay modification, 5 g of the clay was added to 100 mL of distilled water and stirred up to 6 hours for fine dispersion in water. Surfactant solution was formed by dissolving an appropriate amount (1.5x CEC) of each of the surfactants in 30 ml of water. Sonication was run for 30 minutes for all to get a homogeneous solution. The surfactant solution was added slowly in the clay-water mixture and previously stirred for 6 hours, which was then further sonicated for 24 hrs, resulting in the synthesis of organoclay modified with the specific surfactant. All of experiments were performed at room temperature. The resulting surfactant-modified clay was washed with distilled water to remove the dissolved unreacted surfactant. The presence/absence of halides was confirmed through the halide ion test, performed by using 0.5 molar aqueous solution of AgNO₃. The organoclays were dried at 110°C for 3 hours in an oven. The dried product was ground with the help of pestle and mortar and sieved through 200 mesh size and stored in a glass vial for further use. The organoclays obtained by modification with HDPCl.

H₂O, CTAB and SDS were named C3H1, C2CB1 and C2S1 respectively.

Characterization Techniques

The synthesized organoclays along with the pristine montmorillonite clay were then subjected to characterization by XRD, FTIR, and SEM. For XRD characterization, all the clay samples were dried before analysis. After drying, the samples were pressed separately in a stainless steel sample holder. A Philips PANalytical X'pert PRO diffractometer was used with CuK α radiation ($\lambda = 1.540598\text{\AA}$). The modified and unmodified clays were then subjected to FT-IR characterization and were recorded between 4000 and 400 cm⁻¹ (Nicolet Nexus 870).

Method of Dye Adsorption

To study the adsorption of different dyes on organoclay, a known volume of dye solution was mixed with organoclay, followed by stirring of the mixture. A small quantity of adsorption mixture was withdrawn from the supernatant and centrifuged (Centrifuge model 800) to remove the organoclay particles. The clear solution decanted from the centrifuging tube was then analyzed with a UV-visible spectrophotometer (Shimadzu 1700 spectrophotometer). The decrease in the absorbance indicated adsorption of the dye on the surface of the organoclay. Each study was repeated thrice in order to get data set for further experiments. The following formula was used to obtain adsorption percentage.

$$\% \text{ Adsorption} = \frac{c_i - c_e}{c_i} \times 100$$

The adsorption capacity (q) was determined through:

$$q = \frac{(c_i - c_e)V}{m}$$

...where c_i (mg/L) = initial concentration of the dye, c_e (mg/L) = dye concentration at equilibrium,

$v(L)$ = volume of the dye solution and m = adsorbent in grams.

Results and Discussion

Clay Characterization

For the determination of the structural geometry and mineralogical composition of both unmodified and modified clays, X-ray diffraction analysis was performed. It was also used for the determination of both qualitative and quantitative phase analysis of multiphase mixtures. XRD offers information about the configuration of molecules and shows an increase in basal spacing between the layers of organoclay, which is caused by intercalated surfactant molecules. From the X-ray diffractograms shown in Fig. 1, a small increase (1.91 nm) can be observed in the basal spacing (d_{001}) for SDS-modified clay compared to the unmodified clay (1.41 nm). This small increase in the d-spacing can relate to the intercalation of a minute quantity of SDS into the clay layers, leading to a decrease in water of hydration, thus resulting in inducing some hydrophobic character in clay. However, in the case of CTAB and HDPCl, the d_{001} spacing increased to 2.26 nm and 2.63 nm respectively, indicating more effective intercalation in the layers of the clay. This stronger clay-surfactant interaction may be due to electrostatic interaction of the positively charged head groups of these surfactant molecules with negative surface sites of clay and orientation/intercalation of the hydrophobic tails into the clay layers. The XRD results also suggest that clay modification with organic cations changes the crystallinity of the clay materials as evidenced from the increase in peak intensity [18].

The intercalation of surfactant molecules in the clay was also studied by FTIR spectroscopy. The FT-IR spectra of pristine clay (with and without modifications) are shown in Fig. 2. Pristine clay shows a frequency of 3619-3612 cm⁻¹ corresponding to hydroxyl stretching band (hydroxyl sheet) in natural clay. In clay minerals the shape and position of the -OH stretching bands

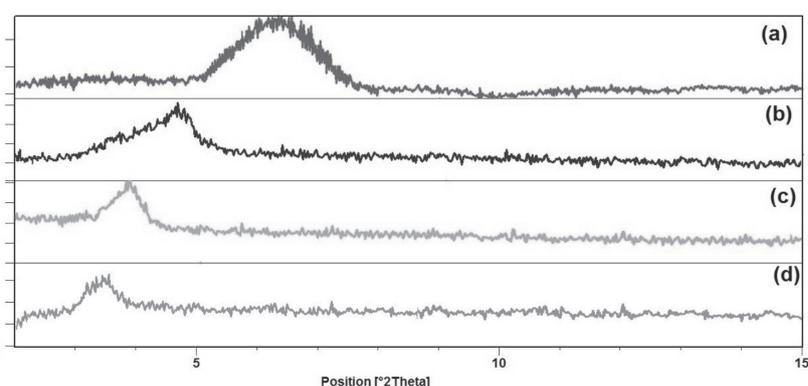


Fig. 1. XRD pattern of a) unmodified pristine clay and clay modified with SDS b), CTAB c) and HDPCl d).

are strongly influenced by the coordination of the hydroxyl group to the octahedral atom. The broad peak in 1000-1004 cm^{-1} region corresponds to Si-O planar stretching. The peak at 916 cm^{-1} corresponds to inner-surface Al-OH deformation. After the treatment of clay with different surfactants, the absorption band for -OH groups of the modified clay appear at lower wave numbers than the pristine clay. The bands between 2848-2964 cm^{-1} corresponding to the symmetric and antisymmetric stretching vibrations of the $-\text{CH}_2$, $-\text{CH}_3$ groups of surfactant's aliphatic chain ensure the formation of organoclay. The main peaks of the pure clay appearing in the modified clay suggest that the lattice of the clay remains intact even after modification [19, 20].

SEM images of unmodified clay (Fig. 3a, b) shows that the clay has large flakes/plates like structure, which has the capability to stick and stake on each other, making large lumps/particles that show the limited adsorption capacity of clay for dyes, etc. After modification of the clay it becomes more porous and fluffier (Fig. 3 c-f), and stabilized by the hydrophilic part of the surfactant, thus providing more room for the adsorption of dyes, etc., into the structure.

Condition Optimization for Dye Adsorption

For obtaining best conditions for dye removal, the effects of various variables were examined at room temperature (25°C). The modified clays were then

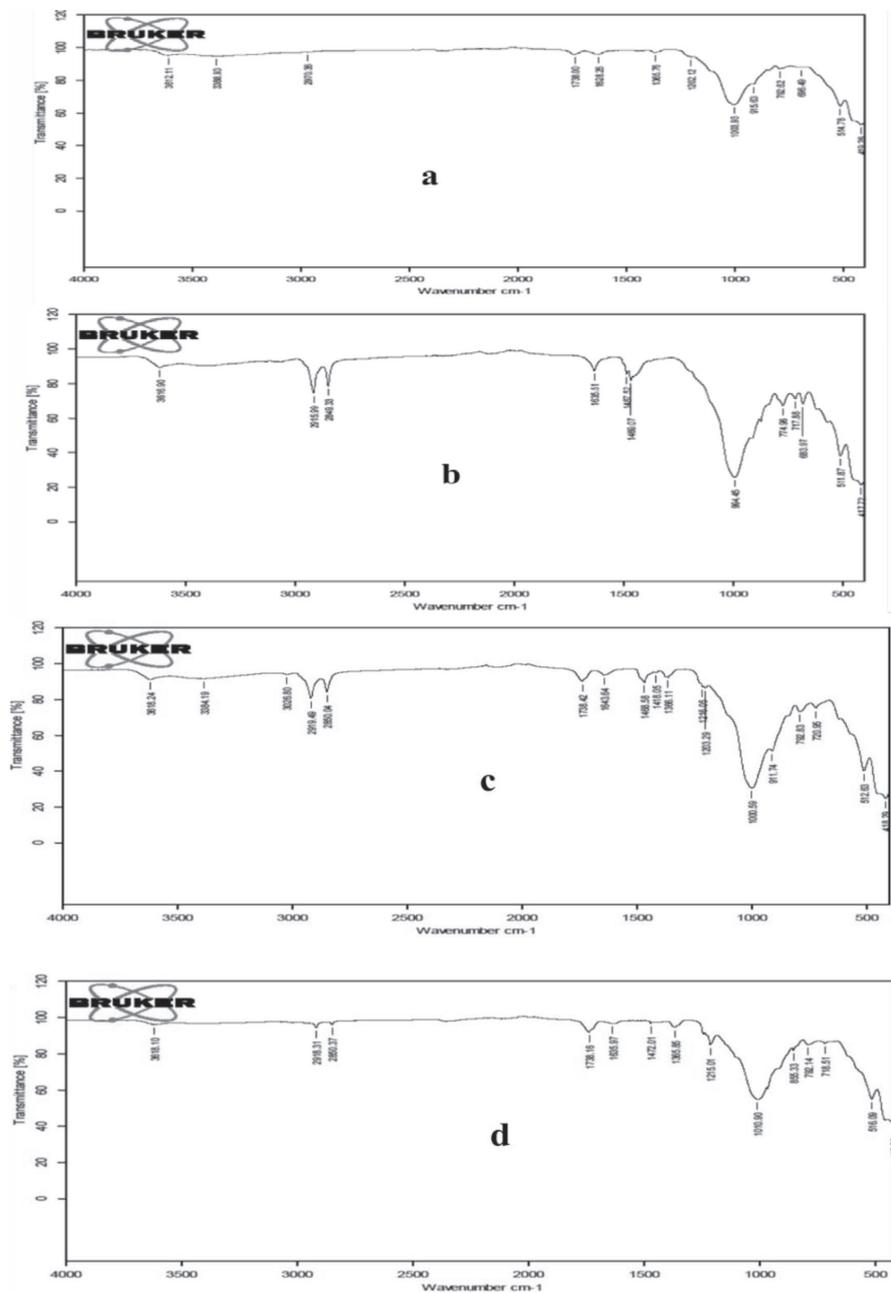


Fig. 2. FT-IR spectra of local bentonite a) without modification and modified with HDPCI b), CTAB c) and SDS d).

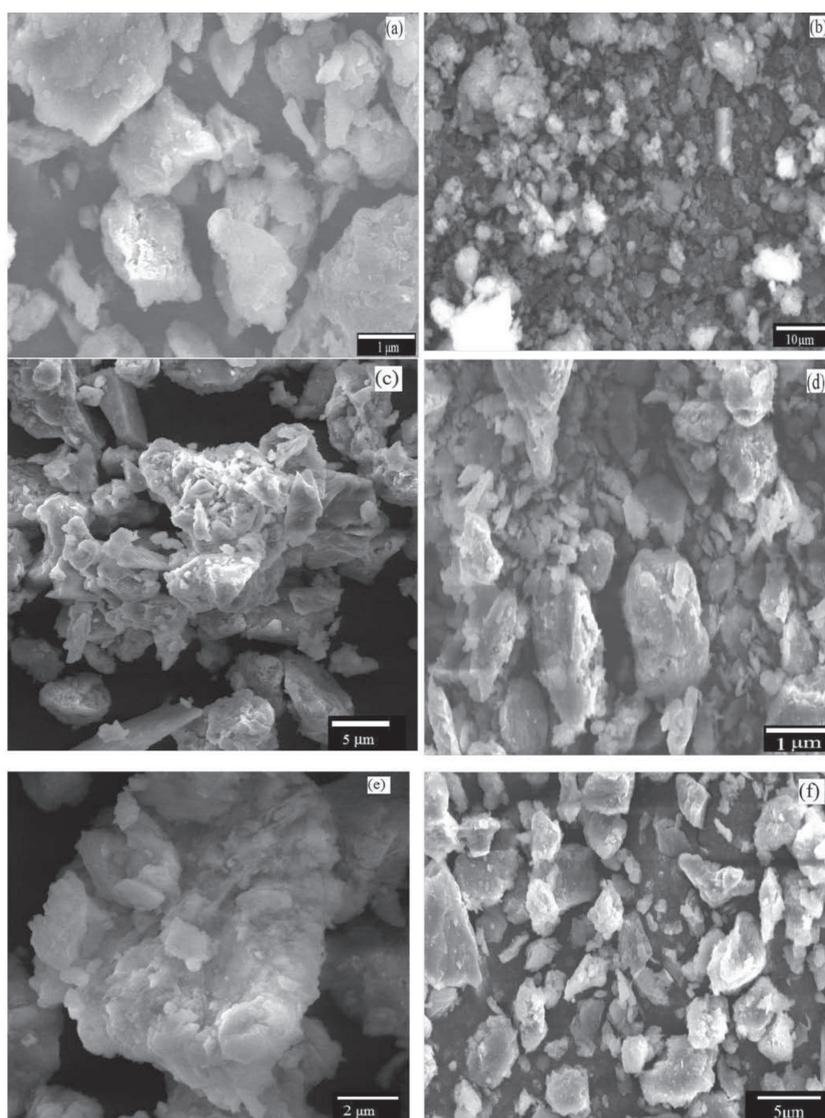


Fig. 3. SEM images of unmodified clay (a, b) and modified (c-f) at various magnifications.

tested for their sorption efficiency under optimized conditions. First the influence of pH was studied as this parameter disturbed the surface charge of the adsorbents, further affecting the degree of ionization of dyes in solution. Table 1 shows the influence of pH of the solution on the dye adsorption efficiency of organoclays in the pH range 3 to 10. To figure out optimized pH, a 0.1g initial amount of adsorbent was used for a 70 mg/L (50 mL) of allura red, 0.05 g of adsorbent for 50 mg/L (50 mL) of brilliant green and 0.1 g of adsorbent for 50 mg/L (50 mL) ethyl violet to analyze its absorption. Table 1 shows that the uptake profiles of all three dyes in organoclays (all type) with respect to change in pH are similar. A slightly acidic value of pH 5 or 6 is required with little variation in sorption efficiency. The decrease in adsorption at pH above 5 may be related to competition of hydroxyl ions with dye anions for the active sites in the organoclay, as the overall surface of the organoclay (C3H1) is positive due to pyridinium sites of the surfactant. Under such

conditions with regards to adsorption, only hydrophobic interactions are expected as protonation of the dye molecular ions exclude the possibility of electrostatic interactions.

The effect of contact time on dye adsorption ability of organoclays was also investigated. Table 1 shows the dependency of the percentage adsorption of all three dyes onto organoclays by varying the contact time. The obtained data show that the adsorption percentage increases by increasing time of contact between the dye and the organoclay. Although BG and EV show quick adsorption and reach the maximum within 15 minutes, the AR shows slow kinetics of adsorption and requires 60-80 mins to achieve maximum adsorption capacity, and no observable effect occurred with further increase in contact time.

After both pH and contact time effects, optimization of experiments was carried out to see the effect of dosage of adsorbents on the property of the as-synthesized clay. The amount of the adsorbents (C3H1, C2S1 and C2CB1)

Table 1. Optimization parameters for the removal of selected dyes.

Parameter	Adsorbent	Dyes	Range studied	Selected parameter
pH	Allura red	C3H1	3-10	5
		C2CB1		5
		C2S1		6
	Brilliant green	C3H1	3-10	6
		C2CB1		6
		C2S1		5
	Ethyl violet	C3H1	3-10	5
		C2CB1		5
		C2S1		5
Time (mins)	Allura red	C3H1	05-90	60
		C2CB1		60
		C2S1		80
	Brilliant green	C3H1	05-90	15
		C2CB1		15
		C2S1		15
	Ethyl violet	C3H1	05-90	15
		C2CB1		15
		C2S1		15
Adsorbent dose (mg)	Allura red	C3H1	10-150	100
		C2CB1		100
		C2S1		100
	Brilliant green	C3H1	10-150	50
		C2CB1		50
		C2S1		50
	Ethyl violet	C3H1	10-150	100
		C2CB1		100
		C2S1		100

varied from 0.01 to 0.15 g for 50 mL of each dye. The results are presented in Table 1, which illustrate that 0.05 g of organoclay is enough for the complete uptake of BG dye from the aqueous solution used, whereas 0.1 g is necessary for complete sorption of the other two dyes AR & EV. Maximum uptake of the dyes occurred with a slight or no increase in the adsorption of the dye upon further increase in the amount of organoclays. The fast-initial uptake of the dyes is manifested as enhanced adsorption on the exposed surface and boundary layers of the organoclay as the majority of the binding sites on organoclay are expected to be available at the initial stage. The slow adsorption of dye after a certain time period may be related to the saturation of surface of organoclay with the respective dye and existence of repulsive forces among the dye molecules. Furthermore,

the slow adsorption at equilibrium could be due to the low concentration of dyes at that saturation point.

Study of Adsorption Kinetics

To understand the kinetics of adsorption, two empirical kinetic models, i.e., pseudo first-order and pseudo second-order models were used. The experimentally observed adsorption capacity was correlated with that calculated from kinetic models. Matching of experimentally observed adsorption capacity with that calculated from kinetic models is judged from the value of linear regression coefficient represented by R^2 . The pseudo first-order model can be expressed as [21]:

Table 2. Kinetic parameters for the adsorption of selected dyes on organoclays.

Dye	Adsorbent	Pseudo-1 st order				Pseudo-2 nd order		
		q _{exp} (mg/g)	q _e calc. (mg/g)	K ₁ (min ⁻¹)	R ²	q _e calc. (mg/g)	R ²	K ₂ (x10 ⁻³ g/mg.min)
Allura Red	C3H1	35	32.35	0.0191	0.9534	29.4	0.9797	3.1
	C2CB1	32	34.67	0.0201	0.9792	25.3	0.9977	8.9
	C2S1	25	25.7	0.0124	0.9944	20.3	0.9816	2.5
Brilliant Green	C3H1	50	48.9	0.0134	0.9897	37.4	0.9762	5.5
	C2CB1	45	47.8	0.0113	0.9978	39.9	0.9714	6.2
	C2S1	50	45.9	0.0092	0.9989	41.9	0.9817	1.5
Ethyl Violet	C3H1	25	21.87	0.046	0.9879	21.5	0.9778	4.5
	C2CB1	25	26.3	0.0352	0.9983	19.7	0.9589	6.5
	C2S1	30	26.9	0.044	0.9896	18.9	0.9698	7.5

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

The pseudo second-order kinetic model considers the chemical reaction important for controlling the rate of the reaction [22]. The empirical equation for this model is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Both models were used, and their outcomes are presented in Table 2. It is clear from the study that the pseudo first-order kinetic model is better in terms of q_e (calculated), which is found to be similar to that of the q_e (experimental) for all three types of dye onto the organoclays. In addition, the k₁ and R² were also found to be suitable for the pseudo first-order kinetic model.

Adsorption Isotherm Models

Various types of models (for isotherm data fittings) have been put forward to analyze the equilibrium adsorption data over the last three decades with different levels of acceptance. However, Langmuir and Freundlich isotherm models are still being used and have been found extensively in the literature and can be represented as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

The Freundlich adsorption isotherm equation in linear form can be represented as:

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e$$

Table 3. Adsorption isotherm parameters.

Dye	Adsorbent	Langmuir					Freundlich		
		q _m exp (mg/g)	q _m calc. (mg/g)	K _L L/mg	R ²	R _L	n _F	K _F (mg/g)	R ²
Allura Red	C3H1	60	60.4	0.77	0.9834	0.0082	4.67	28.8	0.9797
	C2CB1	60	56.7	0.76	0.9892	0.0081	3.45	32.6	0.9977
	C2S1	55	55.8	0.79	0.9944	0.0078	3.89	36.7	0.9816
Brilliant Green	C3H1	80	76.9	1.29	0.9897	0.0071	4.61	67.8	0.9762
	C2CB1	85	75.1	1.12	0.9978	0.0069	4.21	69.7	0.9914
	C2S1	75	78.9	1.07	0.9989	0.0073	4.01	70.7	0.9817
Ethyl Violet	C3H1	40	38.7	1.18	0.9879	0.0064	3.57	27.6	0.9778
	C2CB1	40	37.8	1.08	0.9983	0.0061	3.81	25.8	0.9589
	C2S1	35	35.9	1.12	0.9896	0.0068	4.12	26.6	0.9698

Table 4. Comparison of various reported adsorbents with organoclays for the removal of dyes.

Adsorbate	Adsorbent (g)	Adsorption capacity (mg/g)	Adsorption (%)	Reference
Allura red	Heated pine wood at 1.0 g	4.8	-	[23]
Allura red	Chitosan- tripolyphosphate	-	98	[24]
Brilliant green	Lignin from Guava/Stearate/Al ₂ O ₃ at 0.1g	227	94.3	[25]
Brilliant green	Tannin gel at 0.6 g	8.55	88.38	[26]
Brilliant green	Amine functionalized Tannin gel at 0.6 g	20.41	94.05	[26]
Brilliant green	Solanum tuberosum Peels (Potato) at 0.6g	-	99.07	[27]
Brilliant green	activated carbon from acorn at 2 g/100 ml	2.11	>90	[28]
Allura Red	C3H1	60	>90	This work
	C2CB1	60	>90	This work
	C2S1	55	>90	This work
Brilliant Green	C3H1	80	>90	This work
	C2CB1	85	>90	This work
	C2S1	75	>90	This work
Ethyl Violet	C3H1	40	>90	This work
	C2CB1	40	>90	This work
	C2S1	35	>90	This work

Table 3 reveals that both models are suitable for explaining the adsorption behavior of synthesized organoclays. The experimental maximum adsorption capacity $q_{e (exp)}$ is nearly the same as that of $q_{m (calc)}$ from the Langmuir model, and the match is better than the Freundlich calculations (K_F). However, the regression coefficient (R^2) values of both models are similar for all three types of dyes. The results in Table 3 also show that the heterogeneity factor “nF” is larger than 1, which indicates the favorable adsorption.

A dimensionless separation factor, R_L (from Langmuir equation), is also being used for adsorption favorability and can be calculated using equation:

$$R_L = \frac{1}{(1 + K_L C_0)}$$

The numerical value of R_L can be used to show favorable (R_L values lies between 0 & 1), unfavorable (R_L value > 1), linear (R_L value = 1) or irreversible (R_L value = 0) values. Based on our calculations, results in Table 3 show the favorable Langmuir adsorption process.

A comparison of these organoclays with various reported adsorbents [23-28] is given in Table 4. The results reveal promising candidature of our surfactant-modified clays for dye removal from water bodies.

Conclusions

The advent of the industrial revolution brought a boom in economics but also led to a devastating

implication on the ecosystem by contaminating it from the effluents released from industries. Hence, in order to backtrack the devastating repercussions of the industrial discharge, especially on water bodies, organoclays seem a plausible, economical and viable option. To contribute in this area, we prepared three organoclays using clay of Pakistani origin modified with surfactants (HDPCI, H₂O, CTAB and SDS). The modification of clay was confirmed by XRD and FT-IR. Modification of clay by intercalating surfactant ions resulted in the development of the hydrophobic character and an increase in the interlayer spacing. All three modified clays showed high adsorption characteristics by removing 99.99% of all three dyes with an adsorption capacity ranging from 35 to 85 mg/g. The time-dependent adsorption experiments showed that the rates of adsorption of dyes on organoclays were fast, adsorbing maximum amounts of dyes ranging from 15 to 80 mins contact time. The adsorption kinetic study revealed that the dye removal process is governed by a pseudo first-order mechanism. Thus, surfactant-modified clays are an excellent choice as cost-effective and efficient adsorbents for the purification of water from dye contaminants.

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Conflict of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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