Removal of textile dyes from industrial effluents using burnt brick pieces: adsorption isotherms, kinetics and desorption

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Abstract

Textile dyes, namely Sumifix Blue Exf (Dye 1), Sumifix Rubine Exf (Dye 2) and Sumifix Yellow Exf (Dye 3), show their characteristic $\lambda_{\max}$ values at 605 nm, 545 nm and 415 nm, respectively. Gel electrophoresis of the three individual dyes investigated indicates that all of them are negatively charged. Among different adsorbents, brick clay shows the highest efficiency for the removal of dyes from aqueous solution. The optimum values of experimental parameters, namely treatment temperature, adsorbent dosage, shaking time, settling time and initial solution pH determined to be 200 °C, 4.0 g, 15.0 min, 15.0 min and pH < 10, respectively. The Langmuir model is the best-fitted one for the experimental adsorption data of the dyes leading to the highest removal ability under optimized conditions as 1667 mg kg⁻¹, 3333 mg kg⁻¹ and 2500 mg kg⁻¹ for Dye 1, Dye 2 and Dye 3, respectively. All three dyes follow pseudo-second-order kinetics for their adsorption describing initial rate of adsorption in the order, Dye 1 $\approx$ Dye 2 (10,000 mg kg⁻¹ min⁻¹) > Dye 3 (3333 mg kg⁻¹ min⁻¹), and further, real dye effluent containing each of the above dyes having calculated initial concentrations of 42 mg L⁻¹ (Dye 1), 106 mg L⁻¹ (Dye 2) and 39 mg L⁻¹ (Dye 3), shows, 87%, 86% and 45% removal efficiencies at their $\lambda_{\max}$ values with the treatment of burnt brick clay particles under optimized conditions. Desorption of the dyes from the dye-adsorbed adsorbent indicates that desorption prefers basic conditions.

Keywords Textile industry · Anionic dyes · Burnt brick clay · Isotherms · Kinetics · Desorption

1 Introduction

Dye pigments lead to selective reflection or transmission of incident light when applied to a substrate. Many industries, including textile, pulping, pharmaceutical, tanneries and bleaching, use dyes for their operations. In the dying process, 10–25% of dyes are typically lost, which would subsequently contaminate the effluent [1].

Thus, discharge of untreated dye effluents to the environment is undesirable due to its color, toxicity and carcinogenic nature. Most dyes are non-biodegradable, having carcinogenic action or cause allergies, dermatitis or skin irritation. Various dyes, mainly aromatic compounds, show

both acute and chronic toxicity. High potential health risk is caused by adsorption of azo dyes and their breakdown products through the gastrointestinal tract, skin, lungs and also formation of hemoglobin adducts and disturbance of blood formation. LD50 values reported for aromatic azo dyes range between 100 and 2000 mg kg⁻¹ body weight. Several azo dyes cause damage on DNA that can lead to the genesis of malignant tumors [1, 2].

Another problem associated with dyes in textiles industry is the excessive use of water, which would ultimately be discharged with dyes. As dyes and their degraded products show long-term stability, they could be accumulated in sediments, fish or other aquatic life forms [1].

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Dye removal techniques include physicochemical and biological treatment methods. Physicochemical wastewater treatment includes equalization and homogenization, floatation, ion exchange, coagulation-flocculation, chemical oxidation, irradiation and membrane separation process, while biological wastewater treatment includes aerobic treatment, anaerobic treatment or coupled aerobic anaerobic treatment [3, 4]. Although these techniques are effective, they suffer from many limitations, such as excessive chemical utilization, accumulation of sludge and cost. In view of these limitations, the focus on the removal of dyes using low-cost and environmentally friendly natural substances has been paid much attention. In this direction, the literature includes the use of adsorbents, such as rice husk, feldspar, bagasse fly ash, neem sawdust, chitosan, peat, corn cob activated carbon and cashew nutshell in their natural or modified forms [5–12]. Further, in order to improve the removal characteristics of the adsorbent, different complex modifications reported in the literature includes, sulfuric acid-treated orange peel, surface modified tamarind seeds, surface modified *Strychnos potatorum* seeds, ultrasonic modified corn pith, synthesized chitosan and microwave-assisted sawdust [13–18]. Further, much research has been conducted on dye removal by raw and modified clay varieties [19–21]. However, focus on dye removal by modified brick clay has not been paid much attention [22–25].

The present study is mainly based on the use of modified burnt brick clay particles for the removal of industrial dyes. Further, investigation of adsorption characteristics of dyes, determination of optimum conditions for the interaction under static conditions, adsorption equilibrium studies, kinetics of adsorption, and experiments on both synthetic and real effluents for their removal was studied. Finally, the mechanism of interaction of dyes with burnt brick clay particles and the efficiency of their removal was determined. Starting from experiments on laboratory-prepared synthetic dye solutions, the research was extended toward the treatment of real industrial effluent samples for the removal of selected dyes.

2 Materials and methods

2.1 Materials

Experiments were designed by focusing on treatment of real industrial effluent samples with some preliminary experiments. Real dye effluent samples were collected from different dyeing industries and were screened by UV–Visible spectroscopy to select a suitable dye effluent for experiments. The selected industrial effluent sample

contained a mixture of dyes and many other agents. To study the real effluent sample, three raw solid dyes (synthetic dye samples namely, Sumifix Blue Exf (Dye 1), Sumifix Rubine Exf (Dye 2), Sumifix Yellow Exf (Dye 3)) used in the selected industrial operation was collected simultaneously with the raw effluent. Real dye effluent released from the industry includes the above three dyes as major constituents and many others as minor ingredients. All experiments were conducted in triplicate, and the average results were reported. Rice husk, sawdust, coir dust, unfired brick clay, feldspar and dolomite were obtained from the Central Province, Sri Lanka. Rice husk used in its natural size, and sawdust and coir dust were sieved through 1.0 mm sieve without crushing, while unfired brick clay, feldspar and dolomite were crushed and particles of diameter (d) < 1.0 mm were used for all experiments. Solution pH was adjusted using HNO_3 and NaOH (both from Fluka).

2.2 Instrumentation

Representative samples of unfired brick clay were fired using Carbolite CTF 12/100/900 tube furnace, while UV–Vis spectrophotometer (Shimadzu-1800UV) was used to record the absorbance of solutions at different wavelengths. The charge of dye species was determined using CS Cleaver MP-250 V Electrophoresis instrument.

2.3 Experimental design

The extent of removal of each individual synthetic dye by the adsorbent was determined, followed by the treatment of synthetic dye mixtures and real dye effluent samples. Standard series of each dye was used to determine the linear dynamic range. For each dye, the relationship between absorbance and concentration within the range 2.0–50.0 mg L^{-1} was linear, within which all experiments were carried out. After the selection of best adsorbent among the selected adsorbent materials, all experiments were carried out with the selected material and extended toward real effluent treatment.

2.4 Characterization of dyes and the determination of the charge of dyes

The λ_{max} values of individual dyes were obtained using UV–Vis spectrophotometer. The charge of each dye was determined using individual synthetic dye samples prepared in the laboratory. First, 1% agarose gel was prepared by mixing agarose in TAE buffer, followed by boiling and cooling the mixture to room temperature. Sample slots were prepared by inserting comb at the gel setting stage.

Thereafter, 5 μL of dye samples were inserted to slots and an electric field of 150 V was applied for 10 min, and the traveling of bands was observed. Molecules were separated by applying an external electric field to the system to move the negatively charged molecules through a matrix of agarose gel and the buffer to the positively charged electrode and vice versa. As shown in Fig. 1, the application of an electric field in electrophoresis made the movement of all three dyes toward the positive electrode, indicating that they were negatively charged.

2.5 Selection of an adsorbent for dye removal

The most efficient adsorbent was obtained among the selected adsorbents without any heat treatment for all three individual dyes. For this purpose, 2.50 g each of rice husk, coir dust, sawdust and 5.00 g each of brick clay, feldspar and dolomite were shaken with 50.0 mL of 50.0 mg L^{-1} dye solution for 1.0 h, and solutions were allowed to stand for 1.0 h to reach equilibrium. Then, samples were filtered, and concentrations were determined with respect to the calibration curve at the predetermined wavelength.

2.6 Characterization of brick clay

Unfired brick clay collected from the kiln located at Gelioya, Central Province, Sri Lanka, and was fired at the laboratory for different temperatures using tube furnace and the best firing temperature, 200 $^{\circ}\text{C}$ was used for all experiments after optimization. As the same adsorbent was continued for different pollutants, the same material was characterized using the methods, X-ray diffraction (XRD), X-ray fluorescence (XRF) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM), and further, surface titrations

Fig. 1 Image of the gel electrophoresis unit with dyes used for the study

were also carried out. The results obtained were used to describe experimental findings [26, 27].

2.7 Optimization of experimental parameters for dye removal

Among different adsorbents, brick clay showed the highest removal ability for each of the dyes. Homogenized adsorbent materials of unfired brick clay and that heated at different temperatures (100 $^{\circ}\text{C}$, 200 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$) were treated with 50 mg L^{-1} dye solutions under static conditions at room temperature. The extent of removal of each sample was determined to identify the optimum adsorbent treatment temperature.

The effect of adsorbent dosage was investigated for brick clay samples, heated at the optimum treatment temperature. The experiment was conducted by varying the mass of brick clay from 1.00 to 5.00 g, keeping the other parameters unchanged. The extent of removal was calculated, and the optimum dosage was obtained for all three individual dyes, and used for further experiments.

The effect of contact time was investigated for brick clay samples by varying shaking time and settling time. For the optimization of shaking time, a 50.0 mL aliquot of 50.0 mg L^{-1} Dye 1 solution was shaken with the optimized mass of brick clay, which had been preheated at the optimum heating temperature, for different shaking times from 0 to 75 min, followed by a constant settling time of 1.0 h. After optimization of shaking time, similar experiments were carried out for different settling times from 0 to 60 min to optimize settling time (waiting time) at the predetermined optimum shaking time. These optimized shaking and settling times were employed for all further experiments for all three individual dyes.

Dye solutions of 50.0 mg L^{-1} were used to vary pH ranged from pH 1–12, prepared using HNO_3 and/or NaOH solutions. A 50.0 mL aliquot of each of the above solution was treated with brick clay at optimized conditions, and the extent of removal was determined and the optimized pH was obtained for the most efficient removal.

2.8 Adsorption isotherms

The amount of dye adsorbed on brick clay at the previously optimized contact time was studied using dye solutions of concentration varying from 2–2000 mg L^{-1} . The remaining concentrations of the dye in the supernatant solution were determined at the corresponding wavelength for each dye. Data obtained were then fitted to linearized forms of different adsorption isotherm models.

2.9 Kinetics modeling

To investigate the validity of kinetics models, 1000 mL of 50.0 mg L⁻¹ solutions of each dye solution was stirred with 80.0 g of brick clay. First, 12 samples were withdrawn in every 10 s interval, and thereafter, samples were withdrawn in every 1.0 min intervals for a period of 20 min. Samples were immediately filtered, and the remaining concentration of each dye was determined at the relevant $\lambda_{\max}$. The data obtained in these experiments were used for the investigation of the order of reaction by applying kinetics models.

2.10 Treatment of mixtures of synthetic dye solutions

After analyzing the real dye effluent sample collected from the industry for three wavelengths selected, synthetic dye solution was prepared at the laboratory by considering relevant absorbance values. Then, the mixture was treated with burnt brick clay (BBC) at the optimized conditions. The adsorbent dosage needed to treat the dye mixture was calculated by considering the maximum adsorption capacity results obtained under isotherm studies, and the selected dosage was confirmed by varying the mass of the adsorbent to investigate any difference in the extent of removal with the calculated dosage of the adsorbent.

2.11 Desorption of dyes from the adsorbent

Synthetic dye mixture prepared according to the real industrial dye was used for the desorption experiments. Dye-adsorbed BBC sample was allowed to air-dry until a constant mass was obtained and adsorbed dye amount was calculated using atomic absorption spectroscopy (AAS), by considering the remaining dye concentrations present in the solution after the treatment. Thereafter, 2.00 g of dried dye adsorbed BBC sample was shaken with 50.0 mL of pH-adjusted water for 1.0 h and allowed to stand for 1.0 h. The concentration of each dye leached out was determined and the extent of desorption was calculated. The same desorption experiment was repeated for different initial pH values in the range of pH 2–12.

3 Results and discussion

3.1 Characterization of dyes and the determination of the charge of dyes

The UV–Visible spectra of individual dyes indicate that $\lambda_{\max}$ values of Dye 1, Dye 2 and Dye 3 are 605 nm, 545 nm and 415 nm, respectively (Fig. 2).

Fig. 2 UV–Visible spectra of individual dyes (Concentration of Dye 1—57 mg L⁻¹, Dye 2—53 mg L⁻¹ and Dye 3—53 mg L⁻¹)

Gel electrophoresis was used to determine the charge of three dye species. This technique is mainly used for the analysis of macromolecules and their fragments based on the size and the charge. Dye 1 (blue colored) travels the most, suggesting that it is the most negative followed by Dye 3 (yellow colored) and Dye 2 (red colored). Further, Dye 1 consists of two fragments separated by the electric field. From electrophoresis experiments, it can also be predicted that Dye 2 consists of the largest molecule while Dye 1 consists of the smallest molecule. Further experiments were carried out by considering the information on the surface charge.

3.2 Selection of an adsorbent for dye removal

The extent of removal of dyes from aqueous solution was tested at the relevant $\lambda_{\max}$ with all six adsorbents, brick clay is found to be the best adsorbent which removes each of the three dyes about 60% (Fig. 3). Rice husk, feldspar, sawdust and coir dust are mostly reported for the removal of acidic dyes, while information on the removal of reactive dye compounds using the above mentioned adsorbents is limited. The removal of dyes under investigation by brick clay and dolomite is probably due to the formation of strong attractive forces. By considering the highest removal ability, further experiments were conducted with brick clay.

3.3 Optimization of experimental parameters

3.3.1 Temperature of treatment

The extent of removal of each dye was determined using brick clay particles treated at three different temperatures

Fig. 3 Extent of removal of three dyes with different adsorbents: Dye 1 (■), Dye 2 (□), Dye 3 (▨) (50.0 mL of 50.0 mg L⁻¹ dye solution treated with 2.50 g each of rice husk, coir dust, sawdust and 5.00 g each of brick clay, feldspar and dolomite, 1.0 h shaking time, 1.0 h settling time)

by keeping all other parameters constant (ESM 1). The treatment temperature of 200 °C, being the most efficient temperature, was thus selected for further experiments.

3.3.2 Adsorbent dosage

The extent of removal was found to increase with the increase in the adsorbent dosage in a similar manner for all three dyes (ESM 2). Therefore, 4.00 g of brick clay particles heated at 200 °C [BBC], for which the extent of removal reaches the maximum, was used to treat 50.0 mL of dye solution in subsequent experiments.

3.3.3 Contact time and pH

Since the three dyes under consideration behave similarly based on previous experiments, optimization of parameters, such as shaking time, settling time and solution pH, was carried out under static conditions only for Dye 1, representing all three dyes (ESM 3).

Dye 1, representing all three dyes (ESM 3). According to the variation of the percentage removal of Dye 1 with different variables, both shaking and settling times were selected as 15 min each for subsequent experiments. The adsorption process is critically related to pH, due to changes in surface functional groups and chemical composition with solution pH [28]. The decrease in the extent of removal at high pH values is probably due to competition of OH⁻ ions for the same adsorption sites for dye adsorption [7]. However, no such competitive effect was encountered in acidic medium. Therefore, the optimum initial pH of the solution is kept below pH 10, which gives the maximum percentage removal. The same optimized

Fig. 4 Amount of dyes adsorbed on brick clay, Dye 1 (♦), Dye 2 (■), Dye 3 (▲) (50.0 mL solutions of different concentrations of dye solution shaken with 4.0 g of BBC)

parameters were used for adsorption isotherm and kinetics studies for all three dyes.

3.4 Isotherm studies

Variation of the amount of dye adsorbed on BBC with the initial concentration of all three dyes indicates that the BBC reaches the saturation limit at concentrations beyond 700 mg L⁻¹ (Fig. 4), qualifying Type I(b) isotherm according to the IUPAC isotherm classification [29].

Type I(b) model describes adsorbents having pore size distribution with microporous solid surface which has relatively small external surfaces. Although there are some differences depending on the type of the dye, it is evident that BBC shows microporous characteristics for the adsorption of all three dyes on it. The model represents a reversible process, and the limiting uptake is governed by the accessible micropore volume rather than by the internal surface area.

In order to get more details on the adsorption process, dye adsorption data were fitted to linearized forms of six different adsorption isotherm models, namely Langmuir, Freundlich, Temkin, D-R, R-P and Sips, and results are given in Table 1 with the regression coefficient values of the linear fits of each model; where, q_m and q_e are maximum adsorption capacity and equilibrium adsorption capacity; C_e is the equilibrium concentration of dye; K_L , K_F , K_T , K_{RP} , K_S are Langmuir, Freundlich, Temkin, Redlich-Peterson and Sips isotherm constants, respectively; n , B , b_{RP} , b_S are constants, and E is the mean free energy of adsorption. Comparison of regression coefficients of all isotherms leads to the acceptance of the Langmuir model as the most suitable model.

Five different error functions were determined for each six isotherm models, given in Table 2. According to results (ESM 4), the R-P and Sips isotherm models are rejected

due to its much higher error values than those of other adsorption isotherm models. The Langmuir isotherm shows the smallest error values, in general, and hence, the selection of the Langmuir isotherm as the best fitted model is further convinced.

The Langmuir adsorption model results in monolayer coverage, which is acceptable for large organic molecules, such as dyes. Adsorption of the dyes on the adsorbent is favorable according to the values of the equilibrium parameter (R_L), given in Table 3. Further, the maximum adsorption capacity represented by q_{max} in the Langmuir isotherm provides the highest value for Dye 2, while it is the lowest for Dye 1. These results are supported by the size and surface charge of dyes analyzed using gel electrophoresis, and surface charge of brick clay determined using surface titrations [26]. Surface titrations results show that brick clay has a negative surface charge, and the dye molecules investigated also have negative surface charges in the order of Dye 1 (blue colored) > Dye 3 (yellow colored) > Dye 2 (red colored). From electrophoresis experiments, it can also be predicted that Dye 2 consists of the largest molecule while Dye 1 consists of the smallest molecule. According to the above results, the highest adsorption by Dye 2 is supported by the adsorption of the least negative dye on the negatively charged brick clay surface. The largest size of Dye 2 molecules may lead to the increase in the mass adsorbed on the adsorbent. Further, the adsorption capacity of the dyes determined from the Langmuir model demonstrates a stronger ability of BBC for sorption of dyes when compared to some adsorbents reported [31].

Table 3 lists constants of two other isotherms, Temkin and Dubinin Radushkevich (D-R), both of which show lower error function values, as compared to Freundlich, R-P and Sips. The heterogeneity of the BBC surface is further

Table 1 Standard equations of isotherm models with regression coefficient values (R^2) for three different dyes [30]

Isotherm Model	Standard equations	R^2		
		Dye 1	Dye 2	Dye 3
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}}$	0.985	0.987	0.997
Freundlich	$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$	0.784	0.812	0.886
Temkin	$q_e = B \ln K_T + B \ln C_e$	0.981	0.865	0.951
Dubinin-Radushkevich	$\ln q_e = \ln q_s - B\epsilon^2$ $\epsilon = RT \ln[1 + \frac{1}{C_e}]$ $E = \frac{1}{\sqrt{2\beta}}$	0.905	0.948	0.907
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}}$	0.969	0.982	0.896
Sips	$q_e = \frac{K_S C_e^{1/b_S}}{1 + a_S C_e^{1/b_S}}$	0.959	0.981	0.880

Table 2 Error functions used in isotherm analysis [7, 30]

Type of errors	Equations
Average relative error (ARE)	$\frac{100}{n} \sum_{i=1}^n \left \frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right _i$
Sum square error (SSE)	$\sum_{i=1}^n (q_{e,meas} - q_{e,calc})_i^2$
Hybrid fractional error function (HYBRID)	$\frac{100}{n-p} \sum_{i=1}^n \left \frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right _i$
Sum of absolute error (EABS)	$\sum_{i=1}^n q_{e,meas} - q_{e,calc} $
Nonlinear chi-square test (χ^2)	$\sum_{i=1}^n \frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}}$

supported by the validity of the D-R isotherm [26]. The saturation capacity determined by this model shows the lowest for Dye 1 as 844 mg g⁻¹, as compared to other dye adsorbent systems. The mean free energy values obtained from the D-R model indicate physical adsorption as they are less than 8 kJ mol⁻¹ for all dye—BBC systems (Table 3), which is the maximum limit reported to be qualified [32]. According to the constants of the Temkin adsorption isotherm, the parameter B is related to the heat of adsorption for the reaction to occur. This also varies in the same order as the variation of adsorption capacity.

Table 4 gives previous results reported for the amount of adsorbates adsorbed at equilibrium on different adsorbents for different dye substances at specific pHs and different contact times. According to the results obtained, brick clay-dye system shows much lower adsorption capacity as compared to some other values reported. However, it is clear that contact time of the system is much less and also the results are valid within the whole range of pH, unlike the other systems reported.

Further, the adsorbent modified only with heat treatment can be further enhanced through surface modifications. Therefore, the adsorbent material shows

Table 3 Values of isotherm constants determined for different adsorption isotherms

Isotherm model	Parameter	Dye 1	Dye 2	Dye 3
Langmuir	$q_{max}/\text{mg kg}^{-1}$	1,667	3,333	2,500
	K_L	0.074	0.021	0.036
	R_L	0.208	0.407	0.197
Temkin	B	235.1	460.3	336.1
	K_T	3.23	1.35	1.15
D-R	$q_{max}/\text{mg g}^{-1}$	844	1433	2286
	$B/\times 10^{-6} \text{ mol}^2 \text{ kJ}^{-2}$	0.4	0.6	4.0
	$E/\text{J mol}^{-1}$	1,118	913	353

considerable achievement in order to apply in real scale treatment without using any chemicals for the modification.

3.5 Kinetics modeling

The variation of the extent of adsorption with contact time for different dye solutions was studied to check the kinetics of the reaction mixture. An aqueous solution of each dye sample was individually treated with BBC which had been preheated at the optimum temperature. According to the results (ESM 5), the rate at which BBC—dye solution reaches equilibrium is different for each dye. Since none of the dye solution reaches equilibrium instantly, investigation of kinetics is possible to determine relevant parameters.

The data were then fitted to three different kinetics models and four different diffusion models to predict the mechanism of the reaction process occurs within the system. The standard equations with respective regression

coefficient (R^2) values are given in Table 5, where k' is the apparent rate constant, t is contact time; q_e and q_t are the masses of dyes sorbed by unit mass of sorbent at equilibrium and at time t , C_t and C_0 are dye concentrations in solution at time t and at $t=0$, β_L is the liquid–solid mass transfer coefficient, S is the specific surface area for mass transfer, X_i is the thickness of the boundary layer, k' is the rate constant, R is the percentage adsorption of dye, n is the gradient of linear plots and k_{id} is the intra-particle diffusion rate constant.

Among three different kinetics models; pseudo-first-order, pseudo-second-order and Elovich model, the R^2 values obtained for pseudo-second-order kinetics plots are very close to 1 while it is not for other models.

Adsorption capacity at equilibrium (q_e), pseudo-second-order rate constant (k'), initial adsorption rate ($h_0 = k'q_e^2$) obtained from the pseudo-second-order kinetics model are given in Table 6. The data reported in the table indicate that the initial rate of adsorption (h_0) follows the order,

Table 4 Comparison of adsorption capacity at equilibrium with different adsorbents

Dye	Adsorbent	pH	Contact time/ min	$q_{\max}$ / mg g ⁻¹	Reference
Methylene blue	Marine alga	> 8	10	107.5	[33]
	Wood apple shell	10.0	360	95	[34]
	Palm kernel fiber	> 7	20	95.4	[35]
	Coffee husks	> 6	240	90	[36]
	Raw Enteromorpha intestinalis (REI)	> 7	90	76.3	[37]
	Sulphuric acid modified E. intestinalis (SMEI)	> 7	60	95.3	
Acid fuchsin dye	De-oiled biomass	–	50	9.9	[38]
Rhodamine B	Acacia nilotica leaves	> 6	120	37	[39]
Sumifix Blue Exf	Brick clay fired at 200 °C	< 10	15	1.7	This study
Sumifix Rubine Exf		< 10	15	3.3	
Sumifix Yellow Exf		< 10	15	2.5	

Table 5 Standard equations of kinetics and diffusion models with R^2 values [40–44]

Kinetic model	Standard equations	R^2		
		Dye 1	Dye 2	Dye 3
Pseudo-first order	$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t$	0.649	0.847	0.895
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{(k' q_e^2)}$	0.999	1.000	0.999
Elovich model	$q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t$	0.874	0.862	0.944
External mass transfer diffusion	$\frac{C_t}{C_0} = -L St$	0.539	0.534	0.795
McKay and Poots intra-particle diffusion model	$q_t = X_i + k' t^{0.5}$	0.702	0.691	0.898
Weber and Morris intra-particle diffusion model	$\log R = \log k_{id} + n \log (t)$	0.813	0.933	0.933
Boyd model	$B_t = -0.4977 - \ln \left(1 - \left[\frac{q_t}{q_e} \right] \right)$ versus t	0.649	0.847	0.895

Dye 1 $\approx$ Dye 2 > Dye 3, which is a measure of how fast the reaction proceeds.

In order to obtain mechanistic information on binding of dyes on the adsorbent, intra-particle diffusion models and the external mass transfer diffusion model were employed to find the rate-determining step, but external mass transfer diffusion model was rejected by considering its R^2 value.

Variation of the amount of dye adsorbed with $t^{1/2}$, which describes the validity of the McKay and Poots intra-particle diffusion model, results in poor R^2 with a nonzero intercept indicating that the rate-limiting step has another contribution in addition to what is proposed. Therefore, Weber and Morris intra-particle diffusion model applied for further interpretation results in satisfactory R^2 giving evidence that the above model is in good agreement for adsorption of dyes on the adsorbent. The gradient of plots (n) and intra-particle diffusion rate constant (k_{id}) determined are given in Table 6. The value k_{id} is taken as a rate factor, which is correlated to the rate of adsorption, while larger n values show strong adsorption indicating strong bonding between the dye and the adsorbent. The value of k_{id} increases in the order of Dye 2 > Dye 1 > Dye 3 for the adsorbent, which describes the difference in rate of adsorption for different dyes.

The Boyd model provides information on the actual slow step involved in adsorption. The straight line of B_t versus time does not pass through the origin, indicating that the adsorption process is mainly governed by film diffusion and not intra-particle diffusion [45].

3.6 Adsorption mechanism

Adsorption of the three dyes on microporous BBC explains that all adsorption systems lead to favorable adsorption. The differences among adsorption capacities can be attributed to structural differences of dyes. The excessive species

either form additional layers or transfer in to pores of the brick clay matrix through diffusion. Further, Boyd model indicates that the rate-limiting step has another contribution in addition to what is proposed; indicating that the adsorption process is mainly governed by film diffusion, and not intra-particle diffusion. The extent of adsorption may thus depend on the following factors:

1. Molecular sizes of dye molecules.
2. Layered structure of brick clay (SEM images of brick clay samples fired at 200 °C show the presence of different particle sizes and layers) [26]
3. Type of dispersive interaction between the delocalized π electrons in adsorbent planes and the free electrons in the aromatic ring of dye molecules.

Therefore, the mass transfer of the dyes to the adsorbent surface involve,

1. Migration of the dye from the bulk of the solution to the surface of the adsorbent;
2. Diffusion of the dye to the film of the adsorbent through boundary layer of the surface of the adsorbent;
3. Adsorption of dyes at active sites on the adsorbent (Presence of carbonyl and hydroxyl groups in brick clay fired at 200 °C is evident according to FTIR spectroscopic peaks) [26].

3.7 Adsorption characteristics of mixtures of dyes

According to the absorption spectrum obtained for the real dye effluent sample, the concentrations of each individual dyes present were approximately calculated as 42 mg L⁻¹ (Dye 1), 106 mg L⁻¹ (Dye 2) and 39 mg L⁻¹ (Dye 3), by considering individual dye characterization results. Further, by comparing the spectrum of the real dye mixture, synthetic dye mixture was prepared in the laboratory. Experiments were carried out with the mixture prepared which would be important to extend the methodology developed for real applications.

By considering adsorption capacities obtained from isotherm analysis for three individual dyes, the amount of the adsorbent needed to treat the synthetic dye mixture was calculated to be 15.0 g of BBC for 50.0 mL of the dye mixture having concentrations of each dye given above. The purple color of the synthetic dye mixture was completely disappeared after the treatment with the calculated amount of the adsorbent. The extent of removal of each dye was calculated at the respective λ_{max} values are 95% (Dye 1), 98% (Dye 2) and 86% (Dye 3).

In order to confirm the performance of the calculated mass of BBC (15.0 g), experiments were conducted by

Table 6 Kinetic parameters for the pseudo-second-order model and Weber and Morris intra-particle diffusion model for adsorption of dyes on BBC

Dye	Pseudo-second order model			Weber and Morris intra-particle diffusion model	
	q_e /mg kg ⁻¹	k' /kg mg ⁻¹ min ⁻¹	h_0 /mg kg ⁻¹ min ⁻¹	n	k_{id}
Dye 1	588	0.029	10,000	0.027	89.60
Dye 2	588	0.029	10,000	0.021	92.34
Dye 3	588	0.010	3333	0.038	84.45

varying the adsorbent mass from 10.0–15.0 g under the same experimental conditions. According to the spectra obtained, 15.0 g of the adsorbent is determined to be the optimum dosage for treatment of synthetic effluent samples (Fig. 5).

3.7.1 Color removal of real effluent sample

Similar volumes of the real dye effluent were subsequently treated with BBC under similar conditions show the effectiveness of the adsorbent for the removal of dyes from real effluent samples (ESM 6). The extent of removal of the real dye effluent sample and the synthetic dye mixture was then compared under similar experimental conditions (Table 7).

The decreased extent of removal of real effluents may probably be due to the interference effects of chemicals added, such as enzymes, bath chemicals, wash off agents, fixing agents, softeners, to improve the quality of the dyeing process, which would compete with the dyes for adsorption.

3.8 Desorption of dyes from the adsorbent

In order to investigate the leaching ability of adsorbed dyes into the environment under different conditions, desorption experiments were carried out by varying the initial solution pH. Figure 6 shows the spectra obtained for samples desorbed with distilled water at different medium pH after pre-adsorption of a synthetic dye effluent mixture having about similar concentrations as real effluent (Dye 1–39 mg L⁻¹, Dye 2–103 mg L⁻¹, Dye 3–36 mg L⁻¹).

According to the results obtained, percentage desorption significantly increases with increase in the pH of the medium, and it is much higher at the pH > 10.0 (ESM 7). As

Table 7 Comparison of the extent of removal at each wavelength for real dye effluent sample and synthetic dye mixture prepared at the laboratory

Wavelength/nm	Extent of removal/%	
	Real effluent	Synthetic dye mixture
605	87	95
545	86	98
415	45	86

explained in the adsorption of dyes with varying pH of the medium, the dyes adsorbed on BBC have surface negative charge [26] supporting the findings of the research. According to the previous results, at much higher pHs, solution OH⁻ groups would compete with negatively charged dye molecules, replacing dye molecule, which would subsequently come to the solution phase. Therefore, desorption mainly prefers much basic conditions. More importantly, desorption experiments confirm that the dyes adsorbed on the adsorbent would not leach to the environment under normal conditions.

4 Conclusion

Three industrial dyes, namely Sumifix Blue Exf (dye 1), Sumifix Rubine Exf (Dye 2) and Sumifix Yellow Exf (Dye 3), show their maximum removal ability with BBC under optimized shaking and settling times (15 min each) and at the optimized pH (< 10) as 1667 mg kg⁻¹, 3333 mg kg⁻¹ and 2500 mg kg⁻¹, respectively, according to the Langmuir adsorption isotherm. This order follows the charge of the dyes determined using gel electrophoresis. The initial rate of adsorption of the dyes follows the order, Dye 1 ≈ Dye 2

Fig. 5 Spectra obtained for the treatment of synthetic dye solution with different brick clay masses. **a** Comparable initial spectrum; **b** Spectra after treatment with different masses of the adsorbent. Enlarged spectra obtained for treated samples are shown inside the circle (50.0 mL dye mixture solution treated with BBC, 15 min shaking and settling time)

Fig. 6 Spectra obtained for desorbed sample at different initial solution pH values

> Dye 3, according to the pseudo-second-order kinetics. The extents of removal at the wavelengths of 605 nm, 545 nm and 415 nm for the synthetic dye mixture were 95%, 98% and 86%, while the corresponding values for the real dye effluent samples were 87%, 86% and 45%. Such decreased values indicate the interferences due to chemicals added during the industrial dyeing process. Further, desorption of dyes from the adsorbent indicates that the extent of desorption increases with increase in pH of dye mixtures. The experimental results on real effluents conclusively demonstrate that BBC would be used as an effective option for the removal of dyes present in real industrial effluents, which is an important finding of this research. Further, parameters obtained would be helpful in designing treatment systems for the treatment of dyes in real scale.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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