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Removal enhancement of basic blue 41 by brick waste from an aqueous solution

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KEYWORDS

Basic blue 41; Brick waste; Acid activation; Kinetics model; Langmuir isotherms **Abstract** A modification of brick waste by acid or base solutions was carried out to enhance its physicochemical properties. Treating brick waste with acid did not improve the removal capacity of basic blue 41. However, treating the brick waste with base increased its removal capacity two fold. The adsorption capacity (percentage of removal) decreased from 100% to 10% when the initial concentrations of basic blue and dose of the brick waste increased from 25 to 900 mg/L. The particle size of non treated brick waste affected also the removal capacity; more dye was removed with a smaller particle diameter, at the same initial dye concentrations. The resulting experimental equilibrium data were well-represented by the Langmuir isotherm, and the kinetic data fit a pseudo-second order model well. The maximum removal of basic blue 41 dye was 60–70 mg/g.

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1. Introduction

The scarcity of water sources is currently a difficult and ubiquitous problem. Therefore, recycling wastewater is a huge challenge worldwide to safeguard a sustainable future. The textile industry is a potential source of industrial wastewater contaminated with dyes, which can cause serious environmental problems. Because of their chemical structure, the dyes released into water streams might cause ecotoxicity and potentially dangerous bioaccumulation (Moawad et al., 2003; Vadivelan

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and Vasanth, 2005; Gomez et al., 2007). Various physicochemical methods have been proposed to eliminate the dyes from industrial textile-derived waste waters. Primary clarification methods, including sedimentation and flotation, do not remove colour effectively without simultaneous chemical treatment. Such processes as membrane separation, coagulation and ion exchange are also used to remove colour from dye wastewaters, but the cost of these processes is somewhat prohibitive (Mishra and Tripathy, 1993). The degradation of dyes in wastewater has been also employed, however, these techniques have not been effective due to the nonbiodegradability of most dyes, which are stable to light and oxidation. This has led to study other effective methods, the adsorption technique is proved to be an effective process for the treatment of colourised wastewater (Allen and Koumanova, 2005). This process has an edge over the other methods due to its sludge-free clean operation and complete removal of dyes from diluted solutions, simplicity of design and ease operation (Ozcan et al.,

1878-5352 © 2014 King Saud University. Production and hosting by Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.arabjc.2014.04.003 2004; Khan et al., 2013; Mittal and Gupta, 2013). Granular activated carbon adsorption is an effective method for removing various organic contaminants and different types of textile dyes, which are classified by their ionic character (Mckay, 1992; Kannan and Meenakshisundaram, 2002). However, the high volume of effluent produced by textile wet processes generates significant expense during the regeneration of the activated carbon (Walker and Weatherley, 1999). Substitutes for activated carbons billed as low-cost alternative adsorbents have been proposed based on their availability as either natural or industrial/agricultural waste or by-products. Several review articles discussing low-cost alternative adsorbents have already been published (Rai et al., 2005; Allen and Koumanova, 2005; Rafatullah et al., 2010).

Natural clays are gaining importance among low-cost adsorbents because their easy and abundant availability and high adsorption capabilities for cations and polar molecules. The presence of net negative charges on clay favours the adsorption of basic dyes (Jiuhui, 2008). There are a large number of clays which are widely used to remove dyes from wastewater, such as kaolinite (Hamdi-Karaoglu et al., 2009), montmorillonite (Almedia et al., 2009), bentonite (Eren and Afsin, 2009), clinoptiolite (Yener et al., 2006), speiolite (Alkan et al., 2004), palygorskite, (Al-Futaisi et al., 2007) and zeolite (Rytwo et al., 2002). Few studies have reported the use of clays calcined at high temperatures as adsorbents for metals or colourant dyes, and the limited examples used calcination temperatures limited to 700 °C (Gil et al., 2013; McKay et al., 1985). Comparison of the contaminant removal abilities of natural and thermally activated smectite clays demonstrates that their activation processes used did not significantly increase their adsorption capacity (Vimonses et al., 2009). The brick building materials were obtained from the calcination of a mixture of clay minerals, sand and other materials at temperatures above 900 °C (Bowler, 1999) any waste generated is reused in the production line of bricks (Demir and Mehmet, 2003), as aggregates in concrete production (Debieb and Kenai, 2008), or in road construction (Guo et al., 2012).

Few studies have reported using brick waste products to remove metals and colourant dyes from polluted solutions (Hamdaoui, 2006; Djeribi and Hamdaoui, 2008; Cheng et al., 2011; El-Shahat and Shehata, 2013). According to our knowledge, the treatment of brick waste by base solution was not performed, while, acidic treatment was proposed by Dehou et al., 2012 to remove metal cations. In this study, we explore the use of a local brick waste as a removal agent for colourant dyes, such as basic blue 41, from artificially polluted water, and we propose its treatment with sulphuric acid or sodium hydroxide solutions at room temperature to modulate its chemical properties, and therefore optimise the removal of basic blue 41. The brick waste and its acid- or base-treated counterparts were characterised before being used in the removal process. Batch experiments were conducted to study the effects of the initial concentration, dose volume, particle size of the crushed brick waste, contact time and pH on the dye elimination. Kinetic studies indicated that more than 95% of the dye was removed in 2 h. Brick waste has a removal capacity of 50 mg g^{-1} , which can be achieved at a low adsorbent dose and volume, and exceeded this value for the base treated brick waste.

2. Experimental

2.1. Materials

The brick waste (WB) was obtained from Al-Maimani Red Bricks, which is a local brick manufacturer in Al-Madinah Al-Munawwarah, Saudi Arabia. The samples were crushed using a hammer and ground with a householder grinder before being screened with mechanical sieves to obtain six different particle sizes: 2 ± 1 mm, 1 ± 0.5 mm, 0.5 ± 0.225 mm, 0.225 ± 0.125 mm, 0.125 ± 0.062 mm, and 0.065 ± 0.0044 mm. The above fractions were used without any further treatment. The chemical treatment and the study of the different material parameters on the removal of BB-41 were performed using WB 0.225 ± 0.125 mm in diameter, unless otherwise noted.

In some cases, brick waste with 0.220 mm \pm 0.125 mm particles was treated with an inorganic acid ((H₂SO₄) or alkali (NaOH) solution. The modification was performed as follows: five grams of brick waste were mixed with 50 mL of sulphuric acid (at different concentrations 2 M, 4 M and 6 M) or 50 mL of NaOH (4 M) solution at room temperature overnight. The choice of the NaOH solution of 4 M was based on our preliminary adsorption experiments. The solid was collected by filtration, washed with distilled water several times, and dried at room temperature. The samples were designated as follows: A2-BW, A4-WB and A6-WB correspond to WB treated with 2M, 4M, and 6M acid solutions, respectively. B4-WB corresponds to WB treated with a 4M basic solution.

2.2. Batch mode adsorption studies

Basic blue 41 (BB-41) of analytical grade was purchased from Sigma–Aldrich, and used without further purification. It has the molecular formula C20H26N4O6S2 (mol. weight. 482.57 g/mol) with a colour index Number 11105. The structure of the basic blue 41 is shown in Fig. 1.

Batch mode adsorption studies with basic blue (BB-41) were carried out to investigate the effect of different parameters, such as the initial BB-41 concentration, sorbent dose, the volume of added BB-41 and the pH of the solution before adsorption. Known amounts of sorbent (0.1 g) were placed in 12 mL centrifuge glass tubes containing 10 mL of BB-41 solution. The tubes were shaken at 120 rpm at 30 °C for 18 h to reach equilibrium before being centrifuged for 10 min at 5000 rpm. The collected solution was diluted before analysis. The adsorption behaviour of the samples was studied by evaluating the percentage removal efficiency and the amount of adsorbed BB-41.

2.3. Characterisation

Mineralogical analysis of the brick waste was carried out using powder X-ray diffraction (PXRD) with advance 8 (Ni-filtered



Figure 1 Structure of the dye basic blue 41.

Cu K α radiation) from Bruker. The chemical analysis was carried out with an X-ray fluorescence (XRF) Bruker S4 explorer. The nitrogen adsorption isotherms were performed with an Autosorb 4204. The samples were degassed at 120 °C overnight before the measurements. The total surface areas (S_{BET}) were estimated using the BET equation over a range of 0.05 to 0.3. The pore volumes were determined at a p/p_o value of 0.95. FT-IR spectra of the WB and modified materials were carried out with a Shimadzu spectrometer and the use of KBr pellets. The changes in morphology of the brick waste grains before and after chemical treatment were observed with a scanning electron microscope (SEM) Jeol model. UV spectrophotometer (Cary/100 conc) from Varian was employed to measure the concentration of the BB-41 dye after treatment with the brick waste at a λ_{max} of 610 nm.

3. Results and discussion

3.1. Characterisation of Brick waste

The PXRD of a WB sample indicated that the material was mainly composed of a silica phase of quartz JCPDS card Number 30444) with other minor phases, such as albite (JCPDS card Number 90466). Treating WB with a concentration of acid (A2-WB sample), did not alter the mineralogical composition, and PXRD patterns similar to untreated WB were obtained (not shown). However, some variation within the range of 27–30 (2 theta) was observed because minor phases dissolved in acidic or basic media.

The chemical analysis indicated that the main constituent of WB was silica (54.60%), in addition to smaller amounts of other oxides, such as alumina (17.57%), iron oxide (9.42%), CaO (7.40%), and MgO (4.48%) (Table 1). After treatment with low concentrations of sulphuric acid (A2-WB), slight variations in the oxide content were observed. However, when treated with sulphuric acid concentrations above 4 M (A4-WB and A6-WB), the percentage of SiO₂ increased from 54% to 61.27% and the percentage of MgO, Al₂O₃ and CaO oxides decreased because these materials leached during the acid treatment. The decrease in the CaO content could be attributed to the dissolution of a Ca-containing phase (Table 1). The extent of the oxide leaching depended on the origin and type of clay minerals (Kooli and Yan, 2013). Similarly, the dissolution of Mg, Al and Ca in the brick waste also depended on the origin of the brick, as well as the activation temperature. Dehou et al. (2012) have reported an important decrease of Al₂O₃ and Fe₂O₃ contents (above 50%) in their brick waste. This difference might be caused by the mineralogical phases present in their sample and the acid treatment temperature. However, for B4-WB, a slight

 Table 1
 Chemical analysis (weight%) of brick waste and their modified counterparts.

	F				
Samples	SiO_2	MgO	Al_2O_3	Fe_2O_3	CaO
WB	54.60	4.48	17.57	9.42	7.40
A2-WB	54.88	4.70	17.14	9.72	7.42
A4-WB	60.60	4.63	15.59	9.36	3.62
A6-WB	61.27	4.12	14.86	8.94	3.69
B4-WB	54.88	4.7.	17.24	9.70	7.31

variation in the chemical composition was observed. Generally, the basic treatment of clay minerals results in the dissolution of amorphous silica phase (Kooli et al., 2014. In our case, the silica phase was strongly attached to the brick grains because our materials were subjected to firing temperatures above 950 °C.

The microtextural properties of the WB treated with different concentrations of acid are presented in Table 2. The WB sample exhibited a low BET surface area of 1 m²/g and a 0.001 cm³/g pore volume. After acidic activation, an improvement in the surface area was obtained; the surface area increased by an average of 20 m²/g. Surprisingly, these changes did not depend on the acid concentration. The increased BET surface area generated acid activation is caused by the acidmediated cleaning of the WB grains' surface and the greater accessibility of pores towards nitrogen molecules. The pore volume and sizes increased depending on the concentration of the acid. The increase in the average pore volume could be attributed to the dissolution of some of the phases, which created large pores in the materials. Similar observations were reported for brick waste treated with HCl (Dehou et al. 2012). The treatment of WB with a basic solution did not alter significantly the values of the S_{BET} or pore volume. Similar data were reported for non-calcined clay minerals (Kooli et al., 2014).

The SEM micrographs indicated that the WB has a compact appearance, which is free of pores and has plate-shaped grains. After acid treatment, the A4-WB exhibited a different morphology, the plate-shaped grains disappeared, and small aggregates were formed with detectable pores. The formation of these pores might cause an increase in the surface area and pore volumes of the activated WB. However, treatment with NaOH did not alter the morphology of the obtained material, and stacked platelets with a compact appearance were observed. This type of arrangement limits the accessibility of nitrogen molecules and generates a lower surface area and pore volume.

The FTIR spectra of the WB exhibited two major bands at 1044 cm⁻¹ and 460 cm⁻¹, which were assigned to the asymmetric stretch of the Al–O and Si–O bonds within the aluminosilicate structure (Calyden et al., 1991). The band at 778 cm⁻¹ indicated the presence of mineral quartz (Barilaro et al., 2005). Our materials did not exhibit a band between 540 and 580 cm⁻¹, which is assigned to highly crystalline iron oxide (Dhanapandiana et al., 2010). The XRF data indicated the presence of Fe₂O₃ oxide, but it might be dispersed within the silica phase. The treated WB exhibited similar spectra, although the Si-O bond was shifted to a higher wavenumber (1080 cm⁻¹). A similar spectrum was obtained for the B4-WB sample, indicating that the overall structure of WB was not modified; this result is in good agreement with the XRD data.

 Table 2
 Textural properties of brick waste and their modified counterparts.

Samples	$S_{BET} \ (m^2\!/g)$	Pore volume (cc/g)	APD (nm)
WB	1.00	0.001	7.81
A2-WB	21.0	0.017	3.43
A4-WB	22.80	0.022	4.07
A6-WB	21.55	0.022	4.22
B4-WB	3.77	0.003	4.6

APD corresponds to average pore diameter.

3.2. Removal properties of BB41

3.2.1. Effect of pH

The pH values of the solution are an important parameter during the adsorption processes, and the initial pH value of the solution has greater influence than the final pH (Hem et al., 2007; Monash and Pugazhenthi, 2008). Generally, the initial pH value might enhance or depress the uptake. Fig. 2 demonstrates the relationship between the pH value and the percentage removal of BB-41 across a wide range of pH's (2-9), when using WB, and initial concentration of 200 mg/L. The percentage removal increased when changing from pH 2 to pH 4; further increases in the pH did not affect any significant changes. The slight decrease in the amount of dye adsorbed that correlated with the decreasing pH may be caused by the species with the same charge, which are the dye molecule and the surface of WB, repulsing one another. At pH values above 10, the BB-41 reacted with the hydroxyl groups of the basic solution to generate a brown precipitate that formed at the bottom of the beaker; we could not carry out the removal of BB-41 dye with this material. (Reyad et al., 2003). The lower adsorption at acidic pH was most likely caused by the competition between the excess proton ions and the cationic dye groups for the adsorption sites (Aravindhan et al., 2007). For the case of the acid treated A4-WB, the removal percentage increased as the pH of the BB-41 solution increased until it reached the maximum, which was 80% at pH 9.

3.2.2. Effect of the initial concentrations

The effect of initial dye concentration on the removal of BB-41 by brick waste (untreated) is summarised in Fig. 3. The percentage removal (R%) of BB-41 increased with a decreasing initial dye concentration, where the highest percentage



Figure 2 Effect of the initial pH of the basic blue solution on the removal capacity of the brick waste ($C_i = 200 \text{ mg/L}$).



Figure 3 Effect of the initial solution (C_i) of the basic blue 41 solution, on the removal capacity of the brick waste.

removal was achieved within the range of 25–150 mg/L before decreasing gradually with further increases in the initial concentration. However, the removed amount of BB-41 per unit mass of brick waste increased with an increase in the dye solution concentrations added between 25 and 600 mg/L. For lower concentrations, the total removal was caused by the large number of vacant sites available for the lower number of BB41 molecules; therefore, the driving force of the concentration gradient between adsorbate in solution and adsorbate in the adsorbent increased (Mane et al., 2007).

3.2.3. Effect of adsorption temperature

Fig. 4 illustrates the effect of the temperature on the removal of BB41 dye at different temperatures within the range of 30-60 °C, and at natural pH value. When the temperature increased from 30 to 60 °C, the percentage removal of BB41 reached 98% and remained unchanged between 25 and 300 mg/L. At concentrations of 600 mg/L, the percentage removal improved with increases in temperature to reach a maximum of 95% at 60 °C. The amount adsorbed increased with when the initial concentrations and the adsorption temperature increased to reach a maximum of 60 mg/g of WB at 60 °C. The increase observed in the adsorbed amount at a fixed temperature indicated that the adsorption of the dye involves an endothermic process.

3.2.4. Effect of WB mass

A study of the amount of WB used during the removal of the dye was carried out for different masses of brick waste from 50 to 1000 mg using two initial concentrations (25 and 200 mg/L) of BB-41 solution (Fig. 5). When the initial concentration was 25 mg/L, increasing the mass of WB from 10 to 100 mg increased the percentage removal from 20% and 98%. This



Figure 4 Effect of the temperature on the removal of basic blue 41 at different initial concentrations with brick waste: (a) $40 \text{ }^{\circ}\text{C}$, (b) $50 \text{ }^{\circ}\text{C}$, and (c) $60 \text{ }^{\circ}\text{C}$.



Figure 5 Effect of the dose of brick waste on the removal of basic blue 41 ($C_i = 200 \text{ mg/L}$).

value remained unchanged when the mass of WB was higher than 100 mg. At the initial concentration of 200 mg/L, the removal of BB-41 increased initially as the dose was increased from 10 to 700 mg. However, beyond 700 mg, there was no longer a significant increase in the removal percentage



Figure 6 Effect of the chemical treatment of brick waste on the removal of basic blue at different initial concentrations. (a) A4-BW, (b) BW and (c) B4-BW.

(Fig. 6). A maximum of 98% removal was achieved. The amount of adsorbed BB-41 varied when the WB mass was changed; it decreased with an increase in the WB mass. The decrease in the adsorbed dye when the mass of the adsorbant increased is due to the split in the flux or concentration gradient between the solute concentration in the solution and the solute concentration on the surface of the adsorbent (Sulak et al., 2007).

3.2.5. Effect of volume to brick waste ratio

The ratio of adsorbent/adsorbate could be controlled by keeping the mass of the adsorbent unchanged and varying the volume of the adsorbate solution. The effect of volume used during the removal process has not been studied extensively nor has it been reported frequently in the literature. Different volumes of 200 mg/L BB-41 solution were added to 0.1 g of BW with a diameter of 0.22 ± 0.125 mm. The removal of the BB-41 decreased when the volume added to the WB increased, and a maximum of 98% removal was achieved using volumes from 5 to 10 mL, which corresponded to a higher ratio of adsorbent/adsorbate. At higher added volumes, a removal value of 25% was obtained. This result could be attributed to the smaller amount of surface area available to adsorb the BB-41 molecules; when the number of adsorbate molecules was high, less BB-41 was removed.

3.2.6. Comparison of treated and untreated brick waste

The chemically treated WB material was studied at a fixed 100 mg adsorbent dose with different initial concentrations of BB-41 at a temperature of 25 °C. It is evident from the data in Fig. 6 that the percentage removal of the BB-41 effected by the acid treatment. The treated A4-WB had lower percentage

removal than the untreated BW. However, the alkaline treated B4-BW exhibited a higher removal capacity than the acid and untreated BW. We noted also that the percentage removal decreased with the increase of the used sulphuric acid concentrations. These observations could be related to the increase of protons on the surface of the brick waste that computed with the cationic basic blue. These data indicated that the removal of BB-41 was not related to the available surface area; the A4-WB exhibited a higher surface area (Table 2), but it had a lower adsorption capacity. For the WB treated with NaOH, the high pH of NaOH solution caused an increase in the number of hydroxyl groups in the WB and therefore increased the number of negatively charge sites, enhancing the attraction between the dye and the WB surface.

3.2.7. Effect of the particle size

The experimental results obtained from a series comprised of different particle sizes indicated that the dye uptake of WB increased when the particle size decreased from +1 nm to +0.044 nm. The removal percentage of BB-41 decreased from 100% at lower initial concentrations (25–100 mg/L) to 20% at higher concentrations approximately 1000 mg/L. This suggests that the surface activity of the sorbent plays an important role in the removal of dye molecules. Furthermore, smaller particle sizes move faster in the dye solution compared to larger particles and therefore resulting in a faster rate of sorption (Sulak et al., 2007). We noted a close linear relationship between the amount of dye adsorbed and the particle size value, which is validated by the R^2 value being close to 1 (0.9843) (Fig. 7).

3.2.8. Effect of the contact time

The amount of BB41 removed over different contact times is presented in Fig. 8 for WB particle sizes from 0.125 to



Figure 7 Relationship between the brick waste particle size and the amount of removed basic blue 41.



Figure 8 Progress of the basic blue 41 removal over time using brick waste at different initial dye concentrations (a) 25 mg/L, (b) 300 mg/L and (c) 600 mg/L.

0.225 mm at three different concentrations: 25, 300 and 600 mg/L. The amount of BB-41 removed increased with the contact time across all of the initial concentrations. Additionally the amount of adsorbed BB-41 increased when the initial concentrations increased, which was due to an increase in mass transfer driving force and the resultant increase in BB-41 adsorption. For the first 60 min, the amount uptaken increased as the contact time increased, but afterwards it gradually approached a more or less constant value, denoting attainment of equilibrium. These observations indicated that the initial BB-41 concentration had no effect on the equilibrium time. Additionally, we noted that up to 50-70% of the total amount of uptake occurred in the first 60 min. The uptake of BB-41, which occurred at an early stage, could be related to an increased number of vacant sites available early on. However, as time proceeded, the number of adsorption sites was reduced because the dye particles accumulated in the vacant sites, leading to decreased sorption rates from 60 to 400 min.

3.3. Kinetics of adsorption

Kinetics models were used to examine the rate of the adsorption process and to identify the rate determining step. In the present work, the kinetic data have been analysed using pseudo-first- and pseudo-second-order models. The first order equation reported by Lagergren (Lagergren, 1898) is generally expressed as follows:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{1}$$

A plot of $\ln(q_e - q_t)$ against t should yield a linear relationship with a slope of k_1 and an intercept of $\ln q_e$. The values q_e and q_t are the amounts of BB-41 adsorbed (mg/g) at equilibrium and

Table 3	Comparison of adsorption	kinetic parameters for the first and	d second-order equations of BB-41 onto WB.

$C_i ({ m mg/L})$	First orde	First order					Second order		
	q_{ex}	k_1	$q_{\rm cal}$	R^2	q_{ex}	<i>k</i> ₂	$q_{\rm cal}$	h	R ²
25	2.5	0.0063	1.80	0.9316	2.5	0.00416	2.99	0.0371	0.997
300	15.20	0.0185	12.45	0.9388	15.20	0.0028	16.36	0.6390	0.998
600	23.11	0.0214	16.86	0.9382	23.11	0.00128	24.81	0.791	0.997

at time t (min), respectively, and k_1 is the rate constant of the pseudo-first-order sorption (min⁻¹).

The pseudo-second-order kinetic rate equation is expressed as follows,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where, q_e is the amount of BB-41 adsorbed at equilibrium per unit weight of sorbent (mg·g⁻¹); q_t is the amount of BB-41 adsorbed at any time (mg·g⁻¹) and h $(k_2q_e^2)$ is the initial sorption rate (mg/g min) and k_2 is the rate constant of pseudo-second order kinetics (g/mg min). The slope and intercept of plot of $\frac{1}{q_e}$ against (*t*) were used to determine q_e and k_2 , respectively (Ho and McKay, 1999). The constant k_2 was used to calculate the initial sorption h $(k_2q_e^2)$

The Lagergren rate constants determined from the slope of Eq. (3) and correlation coefficient are presented in Table 3. The rate constant k_1 increased with increases in initial BB-41 concentration, and rate constant k_1 was found to fit this relationship with a correlation coefficient of 1 as follows:

$$k_1 = -6.03 \times 10^{-8} C_i^2 + 6.37 \times 10^{-5} C_i + 0.0047$$
 (3)

The correlation coefficients were close to 0.9332 for all of the initial concentrations, therefore demonstrating the applicability of the pseudo-first-order model for predicting the kinetics of the BB-41 adsorption onto WB material. Additionally, the values for the calculated q_e (cal) from the slope of the model were lower than q_e (exp).

The kinetics of BB-41 adsorption on BW were better described by pseudo-second order kinetic model than the pseudo-first order model. The linearity of the plot also demonstrated the applicability of the pseudo-second order kinetic model, which had an average regression coefficient of R_2^2 (0.9982) that was higher than the R_1^2 (0.9332) from the first model. These results suggested that the removal process is caused by chemisorption (Ho, 2003). Additionally, the value of q_e (exp) found using a pseudo-second order kinetic model was close to q_e (cal), with an average percentage error of 7%. The initial sorption rate (h) and the equilibrium adsorption capacity were increased when the initial BB-41 concentration increased. Similar observations were reported previously with different adsorbents. (Ho, 2003; Vadivelan and Vasanth, 2005).

The pseudo-second order kinetic model could not identify the diffusion mechanism, and the kinetic results were subsequently analysed with the intraparticle diffusion model. The possibility of the occurrence of intraparticle diffusion was explored with the Weber and Morris intra particle diffusion model (Weber, 1972):

$$q_t = k_p t^{1/2} + A \tag{4}$$

where q_t = amount of BB-41 adsorbed at time t (mg g⁻¹), k_p = intra particle diffusion rate constant (mg g⁻¹ min^{-1/2}), and A = intercept and corresponds to thickness of boundary layer.

If a plot of adsorbate uptake versus the square root time generates a linear relationship and passes through the origin, then intraparticle diffusion is the rate limiting step. Otherwise, some degree of boundary layer control must exist and the extent of thickness of boundary layer can be examined from the values of intercept. The K_p (mg/g min^{0.5}) value can be obtained from the slope of the plot of q_t (mg/g) versus $t^{0.5}$. From Fig. 9, the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggested that the sorption proceeds via surface sorption and intraparticle diffusion (Weber, 1972).

3.4. Adsorption isotherms

The analysis of the isotherm data fitted to different models is an important step for finding a model that can be applied to design purposes (Ismadji and Bhatia, 2000). The Langmuir



Figure 9 Intraparticle diffusion plot for basic blue 41 on brick waste at different initial dye concentrations, (a) 25 mg/L, (b) 300 mg/L and (c) 600 mg/L.

and Freundlich models are the most frequently employed models used to describe the experimental data of adsorption isotherms. The Langmuir isotherm model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant and that there is no transmigration of adsorbate across the plane of the surface (Langmuir, 1916). The Langmuir isotherm represents the equilibrium distribution of dye molecules between the solid and liquid phases. The linearised Langmuir isotherm allows the calculation of adsorption capacities (q_{max}) and the Langmuir constants (K_L) and is equated by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}} \tag{5}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is equilibrium concentration of the adsorbate (mg/L), and q_{max} (mg/g) and K_L (L/mg). These constants can be evaluated from the intercept and slope of the linear plot for the experimental data of C_e/q_e versus C_e (Langmuir, 1916).

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces; the adsorption capacity (q_e) is related to concentration at equilibrium (C_e) of BB-41 dye (Freundlich, 1906). A linear form of the Freundlich equation is generally expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

where K_F indicates the adsorption capacity and n is the adsorption intensity. The magnitude of n reveals the favourability of the adsorption. The values of 0 < 1/n < 1, represent favourable adsorption conditions (Cerofolini et al., 1978). The plot of $\ln q_e$ versus $\ln C_e$ is employed to evaluate the intercept K_F and the slope 1/n.

The values of the Langmuir and Freundlich isotherms constants for BB-41 on WB are presented in Table 3. When comparing the Langmuir and Freundlich isotherms, the experimental data fitted better with the Langmuir equation. The best equilibrium model was chosen based on the linear square regression correlation coefficient, R^2 . (Table 3) The magnitudes of the K_L parameters of the Langmuir isotherm represented the interaction energies between the BB-41 and adsorption sites of WB. In our case, the lower value of the K_L parameter indicated the presence of weak interaction energy between the BB-41 and the surface of WB.

As shown in Table 3, the $\frac{1}{2}$ values, which reflected the intensity of adsorption, are lower than 1, indicating that the surface of the WB is heterogeneous and large enough for effective separation (Freundlich, 1906).

The predicted Langmuir and Freundlich isotherm equations for BB-41 onto WB with diameters of 1.25 ± 0.064 mm are given by Eqs. (7) and (8).

$$q_e = \frac{2.301C_e}{1+0.0828C_e} \tag{7}$$

$$q_e = 1.49 C_e^{0.223} \tag{8}$$

Fig. 10 shows the Langmuir and Freundlich curves generated using Eqs. (8) and (9) representing BB-41 adsorption on WB at a temperature of 30 °C alongside the experimental data. The equilibrium data were very well represented by the Langmuir isotherm equation compared to Freundlich equation, and confirmed that the monolaver coverage process occurred with BB-41 on the WB. The experimental data for the adsorption equilibrium of BB-41 and WB using different particle sizes can be interpreted with the linearised Langmuir model $(R^2 > 0.99)$ compared to Freundlich one. The values of the



Figure 10 Experimental and theoretical removal isotherms for BB-41 with brick waste.

Table 4 Langmuir and Freundlich constants, for the removal of basic blue 41 onto WB at different particle sizes.								
Samples	Langmuir Model			Freundlich m	Freundlich model			
	q_m	K_L	R^2	1/n	K_L	R^2		
WB 2 \pm 1 mm	4							
WB 1 \pm 0.5 mm	15	0.034	0.9989	0.419	1.32	0.9471		
WB $0.5 \pm 0.225 \text{ mm}$	22	0.0515	0.9818	0.5868	1.58	0.9646		
WB 0.225 \pm 0.125 mm	25	0.0828	0.9953	0.223	1.49	0.9848		
WB $0.125 \pm 0.065 \text{ mm}$	29	0.096	0.9931	0.2820	1.78	0.9865		
WB 0.065 \pm 0.0044 mm	32	0.112	0.9921	0.2121	1.85	0.9854		

 q_{max} of BB-41 on the WB materials were between 11 mg and 35 mg/g, depending on the WB particle diameters that have a maximum diameter of 0.065 ± 0.0044 mm (Table 4). The maximum adsorption value was improved by increasing the adsorption temperature; this value reached 60 mg/g at 60 °C. The q_{max} values indicated that the removal capacity of brick waste was higher than the removal capacities of other low cost adsorbent materials for basic blue.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L , (Cerofolini) which is defined by $R_L = \frac{1}{1+K_LC_l}$. Where C_i is the BB-41 concentration (mg/L) and b is the

Where C_i is the BB-41 concentration (mg/L) and b is the Langmuir constant (L/mg). The shape of the isotherm depends on the value of R_L as follows: the isotherm is unfavourable $(R_L > 1)$, linear $(R_L = 1)$, favourable $(0 < R_L < 1)$ and reversible $(R_L = 0)$. In our case, the value of R_L in all cases lies between 0 and 1, indicating that the BB-41 adsorption on unmodified or modified brick waste was favourable.

4. Conclusions

The brick waste could be used to remove basic blue 41 dye from an aqueous solution. The removal capacity increased with an increase in the initial concentration, temperature and the mass of brick waste used. The pH of the initial dye solution affected the removal capacity at values between 2 and 4 but remained unchanged at higher pH values. Above pH = 10, the basic blue dye reacted with the sodium hydroxide to form a brown precipitate. The chemical treatment of brick waste affected its removal properties, especially when treated with sodium hydroxide solution; a twofold increase in the removal of basic blue 41 was achieved. Treatment with sulphuric acid increased the specific surface area, but this parameter was not essential for the removal of basic blue 41; in fact, a decrease in dye removal was obtained.

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