

Adsorption performance and mechanism in binding of Reactive Red 4 by coke waste

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Abstract

The protonated coke waste was used as a new type of adsorbent for the removal of Reactive Red 4. To identify the binding sites in the protonated coke waste, the waste was potentiometrically titrated. As a result, four types of functional groups were present in the waste, which was confirmed by FT-IR analysis. Among functional groups, primary amine groups ($-\text{NH}_2$) were likely the binding sites for anionic Reactive Red 4. It was also found that sulfonate, carboxyl and phosphonate groups played a role in electrostatic interference with the binding of dye molecules. The maximum adsorption capacities of the coke waste were 70.3 ± 11.1 and 24.9 ± 1.8 mg/g at pH 1 and 2, respectively. Kinetic study showed a pseudo-first-order rate of adsorption with respect to the solution. The uptake of Reactive Red 4 was not significantly affected by the high concentration of salts. These results of adsorption performance indicate the coke waste as a potentially economical adsorbent for dye removal.

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1. Introduction

Textile industries consume large volumes of water and chemicals for the wet processing of textiles. The presence of very low concentrations of dyes in effluent discharged from these industries is highly visible and undesirable [1]. Moreover, it may also affect photosynthetic activity in aquatic systems by reducing light penetration [2,3]. Also, several commonly used dyes have been reported to be carcinogenic and mutagenic for aquatic organisms [4]. Thus, the removal of textile dyes from wastewater is one of the most important environmental issues to be solved today. However, dye-contained wastewater is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents [5].

Various physical, chemical, and biological methods have been used for the treatment of dye-containing wastewater. Chemical oxidation by Fenton reagent, ozone, UV plus H_2O_2 or NaOCl usually results in aromatic ring cleavage and may generate chemical sludge or by-products that are likely to be more toxic [6]. Aerobic biological treatment is known to be ineffective for dye removal but anaerobic bioremediation enables water-soluble dyes to be decolorized [7]. Physical adsorption technology provides an attractive alternative for the treatment of contaminated waters, especially if the adsorbent is inexpensive and does not require an additional pre-treatment step (such as activation) before its application. Currently, the most commonly used adsorption agent in industry is activated carbon that was successfully tested also for the dye removal from waters [8,9]. However, the activated carbon is considered as an expensive adsorbent, which makes the wastewater treatment a cost-challenging step especially in developing countries and problems with regeneration of the spent activated carbon hamper its large-scale application. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents.

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Many studies have been undertaken to find low-cost adsorbents which include peat [10], bentonite [10], steel-plant slag [10], fly ash [10], China clay [11], maize cob [12], wood shavings [13], silica [14], waste slurry [15,16], aluminum industry waste [17], bottom ash [18,19], and de-oiled soya [18,20]. However, these low-cost adsorbents generally have low uptake which means that large amounts of adsorbents are needed. Although good adsorption capacities for reactive dyes (60–420 mg/g) are found for quaternized organic materials such as cellulose, sugarcane bagasse, rice husk, and coconut husk, successful regeneration has not been reported [21]. Therefore, new, economical, easily available and highly effective adsorbents still need to be found.

The coke waste is generated in a great quantity from the coke plant in China. After an aerobic treatment at wastewater treatment process, this waste is currently reclaimed. Thus, the main objective of this work is to utilize coke wastes as a low-adsorbent for adsorption of a reactive dye, specifically Reactive Red 4 (RR 4) from aqueous solution, and to discuss interactions between the binding sites of the biomass and RR 4 molecules.

2. Materials and methods

2.1. Preparation of the protonated coke waste

The waste biomass was taken from a biological coke wastewater treatment plant. After ground with a size less than 0.5 mm, the biomass was treated with 1 M HNO₃ solution for 24 h, replacing the natural mix of ionic species with protons. The acid-treated coke waste was washed several times with deionized distilled water to remove the excess of acid. It was then dried in an oven at 60 °C for 24 h to yield protonated coke waste. The resulting dried coke waste was stored in a desiccator and used as an adsorbent in the adsorption experiments.

2.2. Preparation of dye solution

All chemicals used in this study were of analytical grade. Reactive Red 4 can be abbreviated as RR 4, which was used as a model reactive dye in this work, was purchased from Sigma–Aldrich Korea Ltd. (CI 17757, Yongin, Korea). As shown in Fig. 1, RR 4 has four sulfonate groups, which have negative charges in aqueous solution. The general characteristics of RR 4 are chemical formula = C₃₂H₂₃ClN₈Na₄O₁₄S₄, molar mass = 995.23, color index number = 18105, and maximum light absorption at λ_{max} = 517 nm.

Stock solutions of RR 4, without further purification, were prepared by dissolving accurately weighed samples of dye in deionized distilled water to give a concentration of 1500 mg/l and diluting when necessary.

2.3. Dye adsorption experiments

In order to carry out the adsorption experiments, a constant mass of protonated coke waste (0.15 g) was weighed into a 50 ml plastic bottle (high-density polyethylene) and 30 ml of dye solution were added to it. The mixture was shaken at 160 rpm at a

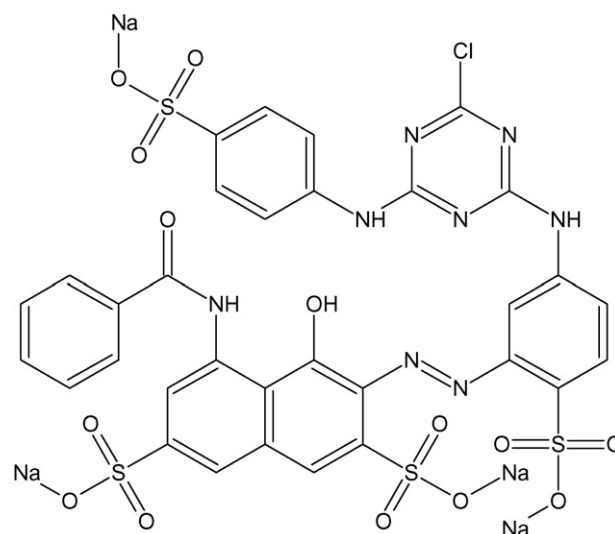


Fig. 1. Chemical structure of Reactive Red 4.

temperature of 25 ± 2 °C for 48 h to reach equilibrium. Then, the final pH was measured and sample was taken, centrifuged at 3000 rpm for liquid–solid separation. The supernatant portion was used for the analysis of the residual concentration of RR 4 after an appropriate dilution. The residual RR 4 concentration of the sample was analyzed using spectrophotometer (UV-2450, Shimadzu, Kyoto, Japan) at 517 nm.

The pH edge experiments were conducted with 100 mg/l of initial RR 4. The pH was intentionally altered by means of the addition of 1 N NaOH or 1 N HNO₃. The effect of the salt concentration on the adsorption capacity of the protonated coke waste was studied with the addition of sodium chloride at different concentrations 0–0.3 M to dye solutions. The concentration of NaCl used ranged from 0 to 0.3 M. The solution pH was maintained at pH 2 using 1 N HNO₃ during the experiment. The adsorption capacity of the adsorbent was determined at pH 1 and 2, varying the dye concentration within the range 50–1500 mg/l, which resulted in different final dye concentrations after adsorption equilibrium had been achieved. The dye uptake (q_e , mg/g) was calculated from the mass balance, as follows:

$$q_e = \frac{V_i C_i - V_f C_f}{M} \quad (1)$$

where V_i and V_f are the initial and final (initial plus added acid or base solution) volumes (l), respectively, C_i and C_f are the initial and final concentrations of RR 4 (mg/l), respectively, and M is the mass of adsorbent used (g).

Kinetic experiments were carried out by agitating 30 ml of dye solution containing 100 mg/l of dye concentration and 0.15 g of the biomass in a vessel maintained at 25 ± 2 °C, pH 2 and a constant agitation speed of 160 rpm. After stirring the vessel for predetermined time intervals, the samples were taken and centrifuged for liquid–solid separation and finally measured for dye concentration. The amount of adsorption at any time, q_t (mg/g), was calculated by

$$q_t = \frac{V_i C_i - V_t C_t}{M} \quad (2)$$

where V_t (l) and C_t (mg/l) are the volume and the dye concentration at time t , respectively.

2.4. Potentiometric titration experiments

The potentiometric titration was carried out with 10 g/l of biomass concentration. The protonated coke waste and 30 ml of water (CO₂-free) were placed in each bottle, where CO₂-free water was obtained by stripping water with nitrogen gas for 2 h with vigorous mixing. Different volumes of 1 N NaOH or 1 N HNO₃ were added to the protonated coke waste suspensions. After closing the bottle caps, the bottles were agitated using a shaker (200 rpm) at room temperature for 24 h. Preliminary tests revealed that 24 h was a sufficient time to achieve the proton sorption equilibrium. Thereafter, the equilibrium pH was measured using an electrode (Ingold). The control titration experiments with water solution were carried out without the protonated coke waste in order to compare them with the titration data when the protonated coke waste was present. During the titration experiments, the CO₂-free condition was maintained to avoid any influence of inorganic carbon on the solution pH. Detailed procedure and data treatment methods are available in the previous literature [22].

2.5. FT-IR analysis

In order to identify the functional groups of protonated coke waste, the adsorbent was analyzed and interpreted by FT-IR spectroscopy. The spectra were recorded in a Fourier transform infrared spectrometer (FT/IR-Nicolet NEXUS-470) within the range of 400–4000 cm⁻¹ with the samples prepared as KBr discs.

2.6. Estimation of model parameters

The parameters of the Langmuir equation were obtained by fitting the model to the experimental data using the Marquardt–Levenberg nonlinear regression algorithm [23] and the kinetic models were calculated using linear regression algorithm. The computer software, Sigma Plot (Version 4.0, SPSS, USA), was used for the nonlinear and linear regression.

3. Results and discussion

3.1. pH edge and mechanism of RR 4 adsorption

The pH edge experiments were carried out to study the equilibrium relationship between the dye uptake and final pH, which was helpful in understanding the pH dependence of adsorption [24]. The variation in the adsorption of RR 4 was studied in the range of pH 1–10, and the result is shown in Fig. 2. As shown in Fig. 2, the pH of the dye solution significantly affected the uptake of RR 4 by the protonated coke waste. As the pH was decreased, the uptake of RR 4 increased and maximum RR 4 uptake was obtained at pH 1. However, the uptake of dye molecules was negligible at pH ≥ 7 . Also, the dye-loaded coke waste was regenerated at pH 9 with desorption efficiency of almost 100% (data

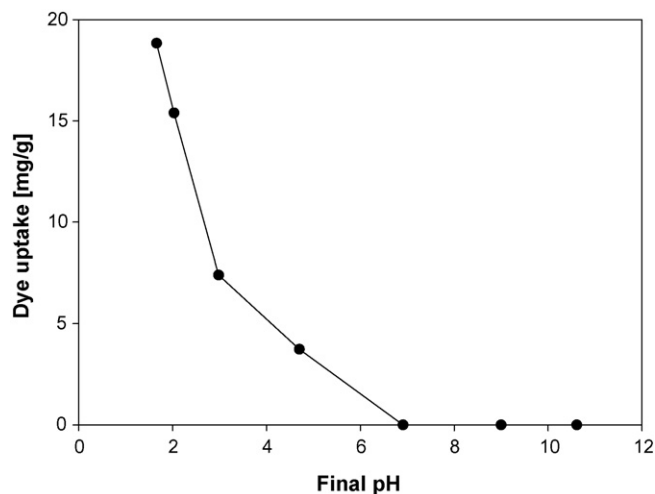


Fig. 2. Effect of pH on the adsorption of Reactive Red 4. Dye concentration: 100 mg/l; adsorbent dose: 0.15 g/30 ml; temperature: 25 \pm 2 $^{\circ}$ C; contact time: 48 h.

not shown). Therefore, it can be noted that in a practical process, the adsorption step can be operated at an acidic condition and the dye-loaded coke waste can be regenerated at a basic condition.

Four sulfonate groups of RR 4 are easily dissociated and have negative charges in the aquatic environment. Therefore, the negative sites of the protonated coke waste such as sulfonate, carboxyl and phosphonate groups may not play a role in RR 4 binding. Meanwhile, positively charged amine groups are believed to be the binding sites for anionic RR 4. These groups are likely to bind the negative sulfonate groups (dye-SO₃⁻) by electrostatic attraction. The observed results were similar to those in our earlier study using fermentation wastes composed of *Corynebacterium glutamicum* biomass [25]. Other types of adsorbents, such as fungal biomass [26] and chitosan [27,28], which have also been reported to uptake anionic dyes and the binding sites were suggested to be protonated amines. As the solution pH decreases, the number of binding sites (positively charged amine) increases and; thereby, the uptake of RR 4 increases. The negative logarithm value (pK_H) of dissociation constant value of amine groups was 10.33 \pm 0.07. Accordingly, the amine groups should be fully protonated at a pH less than approximately 9. However, the RR 4 uptake around pH 7 was not significant (Fig. 2). This is likely to have been due to electrostatic repulsion between the negative sulfonate groups (dye-SO₃⁻) of the RR 4 and the negative sulfonate, carboxyl and phosphonate groups of the protonated coke waste. Thus, the main mechanism of RR 4 adsorption is considered to be electrostatic interaction.

3.2. Characterization of binding sites

The titration curve displays its distinct characteristics depending upon types and amounts of functional groups present in the protonated coke waste (Fig. 3). From potentiometric titration data, the proton uptake as a function of solution pH can be obtained based on the method suggested in the previous work [22,29]. The protonated coke waste can be considered to contain

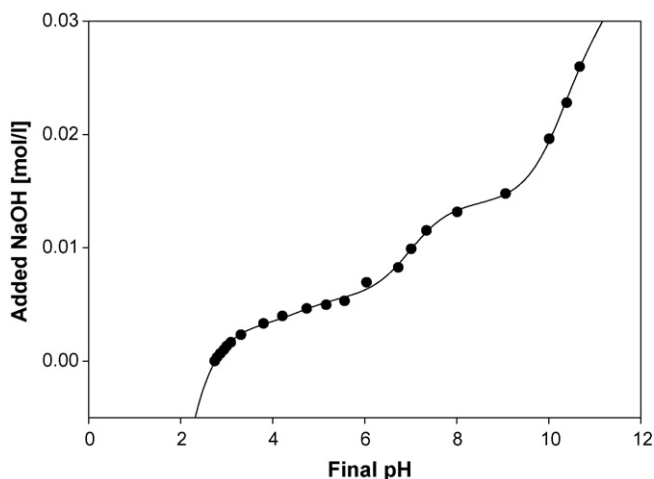
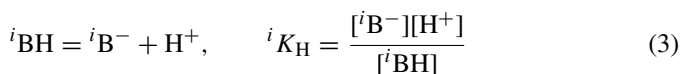


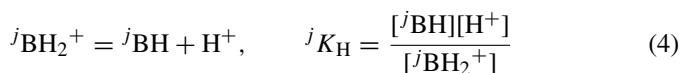
Fig. 3. Proton isotherm of the protonated coke waste. The proton isotherm was obtained from the potentiometric titration data of the protonated coke waste. The solid line represents the theoretical curves predicted from proton-binding model.

some neutral and/or positively charged groups that also contain protons.

Assuming a certain neutral group ($i\text{BH}$), its reaction with a proton and its related equilibrium constant (iK_{H}) are defined as follows:



Also, a certain positively charged group ($j\text{BH}_2^+$) may be present in the protonated coke waste (for example, $-\text{NH}_3^+$):



The total uptake of protons (q_{H}) by the protonated coke waste is the sum of proton uptake by all kinds of negative and positive groups:

$$q_{\text{H}} = \sum_{i=1} [i\text{BH}] + \sum_{j=1} [j\text{BH}_2^+] \\ = \sum_{i=1} \frac{i b [\text{H}^+]}{i K_{\text{H}} + [\text{H}^+]} + \sum_{j=1} \frac{j b [\text{H}^+]}{j K_{\text{H}} + [\text{H}^+]} \quad (5)$$

where $i b$ and $j b$ are weight-specific numbers (mol/g) of i th neutral and j th positively charged functional groups, respectively. Detailed derivation procedures of the proton-binding model (Eq. (5)) are available in Ref. [22].

The proton-binding model was well fitted to the experimental data (Fig. 3) as the high value of correlation coefficient ($r^2 = 1.000$). As a result, the four-site model (three types of negative groups and one positive group) was able to completely describe the potentiometric titration data (Fig. 3), whereas three-, two- or one-site functional group models lacked representation of the data (data not shown). The estimated parameters of the proton-binding model are summarized in Table 1.

The first group was estimated to be a sulfonate group ($\text{B}-\text{SO}_3^-$) and the dissociation constant ($\text{p}K_{\text{H}}$) of sulfonate

Table 1
Estimated parameters of the proton-binding model^a

Functional groups ^b	First group	Second group	Third group	Fourth group
Charge	–	–	–	+
$\text{p}K_{\text{H}}$ (–) ^c	1.93 (0.12)	4.61 (0.29)	6.99 (0.06)	10.33 (0.07)
b (mmol g ^{–1}) ^d	1.2 (0.0)	0.2 (0.0)	0.8 (0.0)	1.7 (0.1)

^a The coefficient of determination was 1.000. Standard errors of the estimated parameters are given in parentheses.

^b The first functional group was considered as sulfonate site; the second functional group indicates carboxyl site; the third group is possibly phosphonate site; the fourth group primary amine site.

^c The $\text{p}K_{\text{H}}$ values represent the dissociation constants of the functional groups.

^d The b values are the numbers of the functional groups.

group was 1.93 ± 0.12 . The second group, with a $\text{p}K_{\text{H}}$ value of 4.61 ± 0.29 , was believed to be a carboxyl group ($\text{B}-\text{COO}^-$), which have $\text{p}K_{\text{H}}$ values ranging from 3.5 to 5.0 in biological polymers [26]. The $\text{p}K_{\text{H}}$ value and number of the third binding site were estimated to be 6.99 ± 0.06 and 0.8 ± 0.0 mmol/g, respectively. This likely makes them phosphonate groups ($\text{B}-\text{HPO}_4^-$), as the phosphonate groups of phospholipids present in the plasma membrane of the biomass have a similar range of $\text{p}K_{\text{H}}$ value [30]. The last group (positively charged) was considered to be an amine group ($\text{B}-\text{NH}_3^+$), with $\text{p}K_{\text{H}}$ value of 10.33 ± 0.07 for various biomaterials ranging between 8 and 10 [26].

3.3. FT-IR spectroscopy

In order to confirm the existence of sulfonate, amine, carboxyl and phosphonate groups in the protonated coke waste, a FT-IR study was carried out. As shown in Fig. 4, the FT-IR spectrum displays a number of absorption peaks, indicating the complex nature of the protonated coke waste examined.

The spectrum of FT-IR showed characteristic symmetrical as well as asymmetrical stretching vibrations of the S=O group at 1390 and 1200 cm^{-1} [31]. The absorption peak at 1040 cm^{-1}

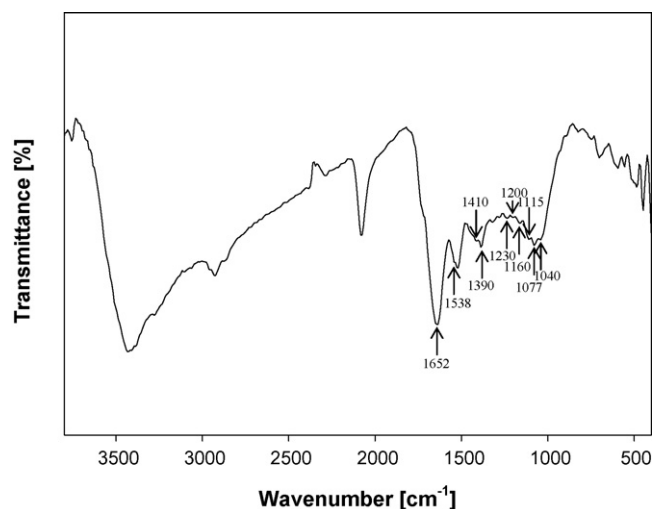


Fig. 4. Fourier transform infrared absorption spectrum of the protonated coke waste.

is characteristic of the aromatic SO_3H symmetric stretching vibrations. It has been known that the asymmetrical stretching vibrations of sulfonic acid groups appear at 1200 cm^{-1} [32]. The FT-IR spectroscopic analysis showed a strong band at $3800\text{--}2500\text{ cm}^{-1}$, indicative of $-\text{OH}$ in the carboxyl group [33–35]. A medium strength absorption peak at 1410 cm^{-1} can be assigned to the symmetrical stretching of the carboxylic acid [35]. Like many types of bacteria [36], the protonated coke waste showed a very weak band at $1730\text{--}1745\text{ cm}^{-1}$ featuring the $\text{C}=\text{O}$ vibrations of the carbonyl in carboxylic groups. Some absorption bands ($\text{P}=\text{O}$ stretching at 1160 cm^{-1} ; $\text{P}-\text{OH}$ stretching at 1077 cm^{-1} ; $\text{P}-\text{O}-\text{C}$ stretching at 1115 cm^{-1}) were considered to be indicative of a phosphonate group [37]. The FT-IR spectrum of the protonated coke waste showed some characteristic absorption bands of an amine group [38]: $\text{N}-\text{H}$ bending band at 1652 cm^{-1} ; $\text{H}-\text{N}-\text{C}$ stretching at 1538 cm^{-1} ; $\text{C}-\text{N}$ stretching band at 1230 cm^{-1} . An $\text{N}-\text{H}$ stretching band in the range $3500\text{--}3300\text{ cm}^{-1}$ was not visible, possibly due to being obscured by the strong and large band of the carboxyl group within the range $3800\text{--}2500\text{ cm}^{-1}$.

3.4. Effect of the salt concentration

In general, reactive dyes are applied to fabric in a high salt concentration in order to lower the dye solubility [39]. NaCl is mainly used as a salt to enhance the bath dye exhaustion. Therefore, unfixed dye in wastewater is accompanied by a high concentration of salts that are likely to interfere with dye adsorption. The effect of the salt concentration in the synthetic wastewater on the uptake of RR 4 was investigated (Fig. 5). At the initial RR 4 concentration of 50 mg/l , the effect of the salt concentration on the dye uptake was negligible. As the initial concentration of RR 4 was increased to 500 mg/l , the uptake did not significantly decrease. It is to indicate that Cl^- ions do not compete with sulfonate groups of RR 4 molecules for amine sites of coke waste. In addition, it can be noted that an elevated ionic strength with

NaCl does not electrostatically interfere with the binding of RR 4 to the coke waste significantly. From a practical point of view, this result implies that the protonated coke waste can be used for the removal of RR 4 from salt-containing wastewaters.

3.5. Adsorption isotherm

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Although empirical models such as the Langmuir equation cannot provide any mechanistic understanding of the adsorption phenomena, the model may be conveniently used to estimate the maximum uptake of dye from experimental data. The Langmuir adsorption model was tested to express the isotherm data. It is based on four basic assumptions:

1. sorbate is adsorbed at a fixed number of well-defined sites;
2. each site can hold one sorbate molecule;
3. all sites are energetically equivalent;
4. there is no interaction between molecules adsorbed on neighboring sites.

The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (6)$$

where q_e is the amount of adsorbed dye, c_e the equilibrium concentration of the dye in solution, q_m the maximum monolayer adsorption capacity and b is the constant related to the free energy of adsorption.

The Langmuir parameters were estimated using the nonlinear regression method (Fig. 6) and are summarized in Table 2. As the pH decreased, the RR 4 uptake increased and at pH 1, the maximum uptake was estimated to be $70.3 \pm 11.1\text{ mg/g}$. To evaluate the adsorption capacity levels of the protonated coke waste, the maximum adsorption capacities of RR 4 were compared with

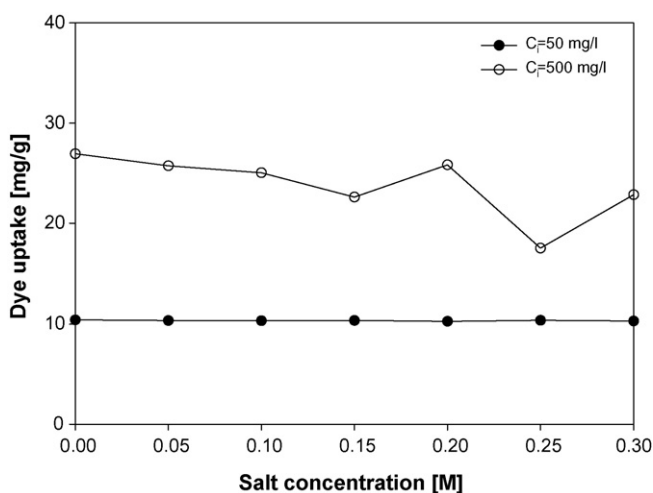


Fig. 5. Effect of the salt concentration on the uptake of RR 4 at different initial concentrations of RR 4. The solution pH was controlled at pH 2. Initial RR 4 concentration: 50 mg/l (●); 500 mg/l (○). Adsorbent dose: $0.15\text{ g}/30\text{ ml}$; temperature: $25 \pm 2\text{ }^\circ\text{C}$; contact time: 48 h .

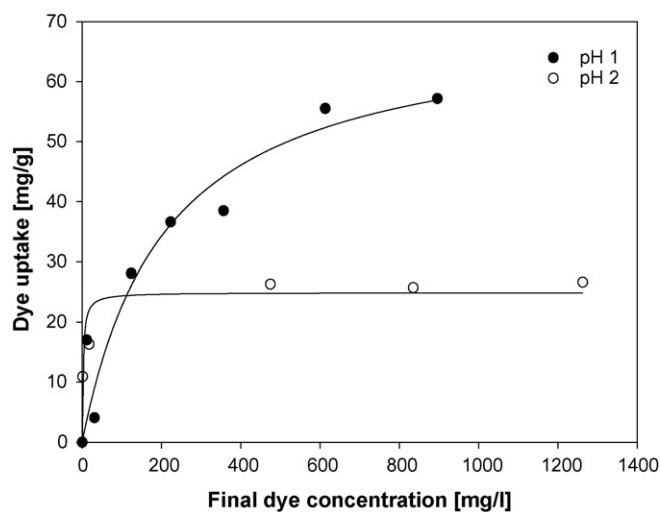


Fig. 6. Isotherms of RR 4 on the protonated coke waste at pH 1 and 2. The lines were produced according to the Langmuir model. Experimental data: pH 1 (●); pH 2 (○). Adsorbent dose: $0.15\text{ g}/30\text{ ml}$; temperature: $25 \pm 2\text{ }^\circ\text{C}$; contact time: 48 h .

Table 2
Estimated parameters of the Langmuir model^a

pH	q_m (mg/g)	b (l/mg)	r^2
1	70.3 (11.1)	0.005 (0.002)	0.923
2	24.9 (1.8)	0.434 (0.256)	0.922

^a Standard errors of the estimated parameters are given in parentheses.

other adsorbents reported elsewhere. The maximum uptake of RR 4 by protonated coke waste was slightly lower than that of *Corynebacterium glutamicum* biomass ($q_m = 104.6$ mg/g) [40] and higher than that of F-400 ($q_m = 13.6$ mg/g; Calgon Co., USA) [41]. Also, quaternized sawdust also showed that the maximum RR 4 adsorption capacity of 218 mg/g at pH 7. This adsorbent was used after chemical treatment using *N*-(3-chloro-2-hydroxypropyl)trimethylammonium chloride as a quaternization reagent [41].

The effect of isotherm shape can be used to predict whether a adsorption system is 'favourable' or 'unfavourable' both in fixed-bed systems as well as in batch processes. The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L :

$$R_L = \frac{1}{1 + bC_i} \quad (7)$$

where R_L is a dimensionless separation factor, C_i the initial concentration (mg/l) and b is the Langmuir constant (l/mg). The parameter R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). All values of R_L , calculated from Eq. (7), were found less than unity. Positive values of R_L , which are less than 1, confirm the favorability of the adsorption isotherm.

3.6. Adsorption kinetics

To determine equilibrium time for RR 4 adsorption, time intervals were assessed until no adsorption of RR 4 on protonated coke waste takes place. Fig. 7 shows the extent of dye adsorption as a function of reaction time. Results show that dye uptake increased with time and reached equilibrium value at about 42 h. After that, dye uptake became much less significant.

The kinetic data were described using the pseudo-first-order and pseudo-second-order rate equation [42]. The pseudo-first-order model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time. This pseudo-first-order rate equation is

$$\log(q_1 - q_t) = \log q_1 - \frac{k_1 t}{2.303} \quad (8)$$

where q_t and q_1 are the grams of solute sorbed per gram of adsorbent at any time and at equilibrium (mg/g), respectively, and k_1 is the rate constant of first-order adsorption (l/min). The pseudo-first-order equation has been extensively used to describe the adsorption kinetics.

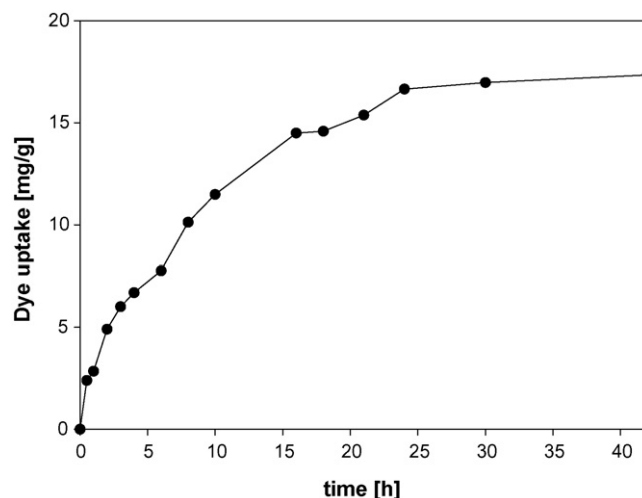


Fig. 7. Effect of the contact time on RR 4 adsorption rate by protonated coke waste. Dye concentration: 100 mg/l; adsorbent dose: 0.15 g/30 ml; pH 2; temperature: 25 ± 2 °C.

The value of the adsorption rate constant (k_1) for RR 4 adsorption by protonated coke waste was determined from the plot of $\log(q_1 - q_t)$ against t (Fig. 8(A)). The parameters of pseudo-first-order model were summarized in Table 3. The theoretical q_1 value of 17.69 ± 1.08 mg/g agreed with the experimental q_e value of 17.35 mg/g. Also, the high value of correlation coefficient ($r^2 = 0.975$) showed that the data conformed well to the pseudo-first-order rate kinetic model.

Another model for the analysis of adsorption kinetics is pseudo-second-order. The rate law for this system is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (9)$$

where q_2 is the gram of solute sorbed per gram of adsorbent at equilibrium (mg/g), and k_2 is the pseudo-second-order rate constant of adsorption (g/(mg min)). The initial adsorption rate, h (mg/(g min)), at $t \rightarrow 0$ is defined as

$$h = k_2 q_2^2 \quad (10)$$

The plot of t/q versus t gives a straight line with slope of $1/q_2$ and intercept of $1/k_2 q_2^2$ (Fig. 8(B)). There is no need to know any parameter beforehand and the grams of solute sorbed per gram of adsorbent at equilibrium (q_2) and adsorption rate constant

Table 3
Kinetic parameters for RR 4 biosorption by coke waste

Pseudo-first-order kinetic	
q_e (mg/g)	17.35
q_1 (mg/g)	17.69 (1.08)
k_1 (l/min)	2.1E-3
r^2	0.975
Pseudo-second-order kinetic	
q_2 (mg/g)	20.45 (0.67)
k_2 (g/mg min)	1.2E-4
h (mg/g min)	0.049 (0.004)
r^2	0.987

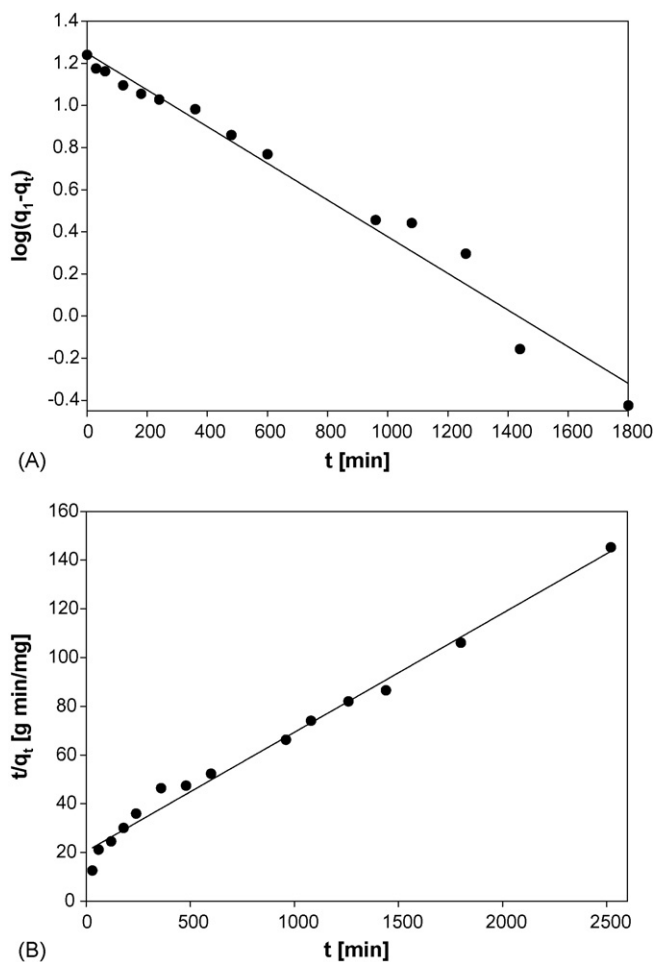


Fig. 8. Plots of sorption kinetic equations for RR 4 adsorption by protonated coke waste. (A) Pseudo-first-order kinetic; (B) pseudo-second-order kinetic. Dye concentration: 100 mg/l; adsorbent dose: 0.15 g/30 ml; pH 2; temperature: $25 \pm 2^\circ\text{C}$.

(k_2) can be evaluated from the slope and intercept, respectively. The values of the parameters k_2 , calculated q_2 , experimental q_e and initial adsorption rate h , together with the correlation coefficients, are presented in Table 3. Although the correlation coefficient ($r^2 = 0.987$) for the second-order kinetic model was higher than the first-order kinetic model, the theoretical q_2 value did not agree with the experimental q_e value in the case of pseudo-second-order kinetics. It is probable, therefore, that this adsorption system was not a second-order reaction at low dye concentration of 100 mg/l.

4. Conclusions

The protonated coke waste was utilized as a low-cost adsorbent for reactive dye RR 4 removal from aqueous solution. In this study we achieved a desorption efficiency of almost 100%, and the maximum uptake was estimated to be 70.3 ± 11.1 mg/g at pH 1. Considering that commercial adsorbents such as activated carbons are hardly regenerated, this coke waste has a great potential as a reusable dye adsorbent. Furthermore, it can be regenerated easily by adjusting the solution pH to a neutral con-

dition. Therefore, the biomass waste shows great promise for the treatment of dye-containing wastewater as a new, low-cost, easily available and highly effective adsorbent.

The surface of the protonated coke waste had four functional groups such as sulfonate, carboxyl, phosphonate, and amine groups. The negative sites of the protonated coke waste such as sulfonate, carboxyl and phosphonate groups may not play a role in RR 4 binding due to electrostatic repulsion between the negative sulfonate groups of the RR 4 and the negative groups of the protonated coke waste. However, positively charged amine groups could bind to anionic RR 4 by electrostatic attraction. Thus, amine sites of the protonated coke waste are believed to be the binding sites for anionic RR 4. Therefore, the main mechanism of RR 4 adsorption is considered to be electrostatic interaction.

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