



## Insight into removal kinetic and mechanisms of anionic dye by calcined clay materials and lime

Vipasiri Vimonses<sup>a,b</sup>, Bo Jin<sup>a,b,c,\*</sup>, Christopher W.K. Chow<sup>c</sup>

<sup>a</sup> School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

<sup>b</sup> School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

<sup>c</sup> Australian Water Quality Centre, SA Water Corporation, 250 Victoria Square, Adelaide, SA 5100, Australia

### ARTICLE INFO

#### Article history:

Received 28 August 2009

Received in revised form 7 December 2009

Accepted 9 December 2009

Available online 16 December 2009

#### Keywords:

Clay materials

Lime

Congo red

Removal kinetic mechanisms

### ABSTRACT

Our recent work reported that a mixed adsorbent with natural clay materials and lime demonstrated an enhanced capacity and efficiency to remove anionic Congo Red dye from wastewater. This study aims to investigate the removal kinetic and mechanisms of the mixed materials involved in the decolourisation of the dye to maximise their prospective applications for industrial wastewater treatment. The experimental results showed that dye removal was governed by combined physiochemical reactions of adsorption, ion-exchange, and precipitation. Ca-dye precipitation contributed over 70% total dye removal, followed by adsorption and ion-exchange. The dye removal kinetic followed the pseudo-second-order expression and was well described by the Freundlich isotherm model. This study indicated pH was a key parameter to govern the removal mechanisms, i.e. adsorption/coagulation at acidic pH and precipitation at basic condition. Yet, the overall removal efficiency was found to be independent to the operation conditions, resulting in more than 94% dye removal. This work revealed that the mixed clays and lime can be applied as alternative low-cost adsorbents for industrial wastewater treatment.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

The production of commercial dyes is estimated to be over  $7 \times 10^5$  to  $1 \times 10^6$  tons/annum [1]. It is estimated that 2% of the dyes produced are discharged directly into the ecosystem, and 10% of the total dyes are subsequently lost during the colouration process [2]. The contamination of the commercial dyes in water stream creates an offensive concern to the human health and aquatic biota as a result of their indigenous toxic, mutagenic and carcinogenic consequences. Even at low concentration it could be highly visible, and can cause an aesthetic pollution and disturbance to the ecosystem and water sources.

In general, decolourisation and degradation of the dyes and dye intermediates by a conventional treatment such as activated sludge process is facing difficulties owing to their high physiochemical stability and recalcitrant nature [3]. Several treatment methods have been developed and used for removing the dyes from wastewater; including coagulation/flocculation, adsorption, advanced oxidation processes, ozonation, membrane filtration and biological treatment [4]. However, these processes are found to be

infeasible for an industrial application due to their low efficiency, high operating cost and environmental impact [5].

Adsorption is one of the prominent methods used in wastewater treatment for dye removal due to its simplicity in operation and availability of a wide range of adsorbents. The increasing demand of efficient and economical treatment technology has given rise to a search of alternative low-cost adsorbents to substitute the use of commercial activated carbon that are expensive and difficult to be regenerated.

Among the alternative low-cost adsorbents, clay adsorption is considered as the most economical option for dye removal [6]. The use of clay minerals is of a great interest according to their variety of structural and surface properties, high chemical stability, and large specific surface area [7]. A number of clay materials: sepiolite [8], montmorillonite [9], smectite [10], bentonite [7] and zeolite [11] have been investigated for dye removal. However, their practical applications in wastewater treatment are still impeded for several reasons. One of those is due to their low removal capability. Therefore, large amount of adsorbents are required in a treatment process, resulting in a high volume of sludge production.

A mixture of natural clays (bentonite, kaolin and zeolite) and lime was investigated and reported in our recent communication [12]. The results revealed that the mixed adsorbents at different ratios demonstrated an enhanced removal capacity and efficiency of Congo Red (CR). The clay mixtures showed a 10–20 times higher removal capacity than the bentonite, kaolin and zeolite, which was

\* Corresponding author at: School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia. Tel.: +61 8 8303 7056; fax: +61 8 8303 6222.

E-mail address: [bo.jin@adelaide.edu.au](mailto:bo.jin@adelaide.edu.au) (B. Jin).

**Table 1**  
Mineral constituents of the clay mixtures.

Mineral constituents (%)	Adsorbent mixture		
	1	2	3
Ca(OH) <sub>2</sub>	65	70	70
Na bentonite	15	15	10
Kaolin	15	10	10
Zeolite	5	5	10
Total	100	100	100

used along. The mixed clays and lime could be alternative adsorbents to removal recalcitrant organic contaminants such as anionic dyes for industrial wastewater treatment. It is important to extend the study to attain a better understanding of the removal kinetics and mechanisms of the clay mixtures. These results are very beneficial to optimise the wastewater treatment process using the clay mixtures.

## 2. Materials and methods

### 2.1. Materials

Three clay mixtures made-up of Australian clay minerals: sodium bentonite, kaolin and zeolite with certain amount of lime were prepared and pre-activated according to the optimised condition reported in our previous study [12]. The clay constituents of the mixtures are given in Table 1. Sodium bentonite and kaolin clays were obtained from Unimin Australia Ltd, and Escott zeolite was provided by Zeolite Australia Ltd. Calcium hydroxide (Ca(OH)<sub>2</sub>) powder was purchased from Unilab (Ajax Finechem).

Congo Red (C<sub>32</sub>H<sub>22</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, Labchem Ajax Finechem Australia) was prepared to desired concentration by the addition of double-deionised water obtained from Barnstead nanopure Diamond Water ion-exchange system with 18.2 MΩ cm resistivity.

### 2.2. Characterisation of surface properties of clay materials

The specific surface area (SSA) of the materials was measured using Brunauer–Emmett–Teller (BET) method. Results were obtained by means of pure liquid N<sub>2</sub> adsorption at 77 ± 0.5 K using a Gemini V2.00 surface analyser (Micromeritics, USA). Prior to analysis, all samples were degassed under vacuum at 105 °C for 12 h.

X-ray diffraction (XRD) analysis was carried out to determine the phases of the clay minerals. The measurements were performed on a Philips PW diffractometer (Co X-rays λ = 1.7902 Å) over the range of 5–90° 2θ for the solid powder samples. Samples were spiked with 10 wt% of zinc oxide before analysis to facilitate the calculation for the weight percent of the amorphous phase.

The morphological features and surface characteristics of samples were obtained from scanning electron microscopy (SEM) using a Philips XL30 Scanning Electron Microscope at an accelerating voltage of 10 kV. The samples were coated with platinum under vacuum prior to analyses.

### 2.3. Experimental procedure

CR removal capacity of the clay mixtures was carried out in a batch system. 0.05 g of the adsorbent was added to 50 mL of the 150 mg L<sup>-1</sup> CR solution, unless otherwise stated. The mixture suspension was shaken at 150 rpm in a rotary shaker (Ratek OM 15 orbital mixer, Australia) at 30 ± 1 °C. Experiments were carried out over 24 h to ensure that equilibrated reaction was obtained, except for kinetic study where the samples were withdrawn from the experimental flask at pre-determined time intervals. At the end of the equilibration period, the mixture was separated by centrifuga-

tion (Eppendorf Centrifuge 5415R, Germany) at 13200 rpm for 20 min. The supernatants were then filtered using Millex VX filter (Millipore 0.45 μm) to ensure the solutions were free from adsorbent particles before measuring the residual dye concentration.

The role of Ca<sup>2+</sup> in colour elimination was also investigated in this study. The supernatants were separated from the mixture suspension (0.1 g clay mixtures in 100 mL deionised water) by centrifugation and filtration after equilibration overnight. The supernatants were then mixed thoroughly with the desired CR solution at a ratio of 1:1 (20 mL:20 mL) in a rotary shaker for 24 h. The sample was subsequently separated and the dye residuals were measured as described above. All experiments were carried out in triplicate, and the average values were taken to minimise random error.

## 2.4. Analytical method

### 2.4.1. Measurement methods

Dye concentration was determined colorimetrically by measuring at maximum absorbance of 496.5 nm using a UV–vis spectrophotometer (model γ, Helios, UK). A calibration curve was plotted between absorbance and concentration of the dye solution to obtain an absorbance–concentration profile. The percentage removal and the adsorption of the dye were calculated from the concentration changes. The concentration of Ca<sup>2+</sup> ion was determined according to the EDTA titrimetric method [13].

### 2.4.2. Determination of removal mechanism using isotherm and kinetic models

From previous study [12], clay mixtures were proven to have superior removal capacity potential over natural clay adsorptions, suggesting that decolourisation of dye may involve different physiochemical reactions. In order to understand the comprehensive removal mechanisms and interactions of the clay mixtures toward CR, several isotherms and kinetics models were employed. In this study, the Freundlich and Langmuir adsorption isotherms, and the pseudo-first and second-order kinetics were selected to interpret the removal behaviour of the clay mixtures. The modelled results were then determined the error analysis, in which the linearization and the non-linear-regression Chi-square (X<sup>2</sup>) test were employed as a criterion for the quality of fitting to the studied models. Detailed interpretation will be presented in Section 3.

### 2.4.3. Error analysis

Due to the inherent bias resulting from linearization of the isotherm model, the non-linear-regression Chi-square (X<sup>2</sup>) test was employed as a criterion for the quality of fitting. This statistical analysis is based on the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models [14]. The Chi-square can be represented by Eq. (1).

$$X^2 = \sum \left[ \frac{(q_{ee} - q_{ec})^2}{q_{ec}} \right] \quad (1)$$

where  $q_{ee}$  is the equilibrium adsorption capacity from the experiment (mg g<sup>-1</sup>), and  $q_{ec}$  is the equilibrium capacity calculated according to the dynamic model (mg g<sup>-1</sup>). A small value of X<sup>2</sup> indicates that data from the model is similar to the experimental value, whereas a large value of X<sup>2</sup> points out the difference between them. In order to confirm the best-fit isotherms and kinetic models for the adsorption system, there is need to analyse the data set using the Chi-square test, combined with the values of the determined coefficient (R<sup>2</sup>).

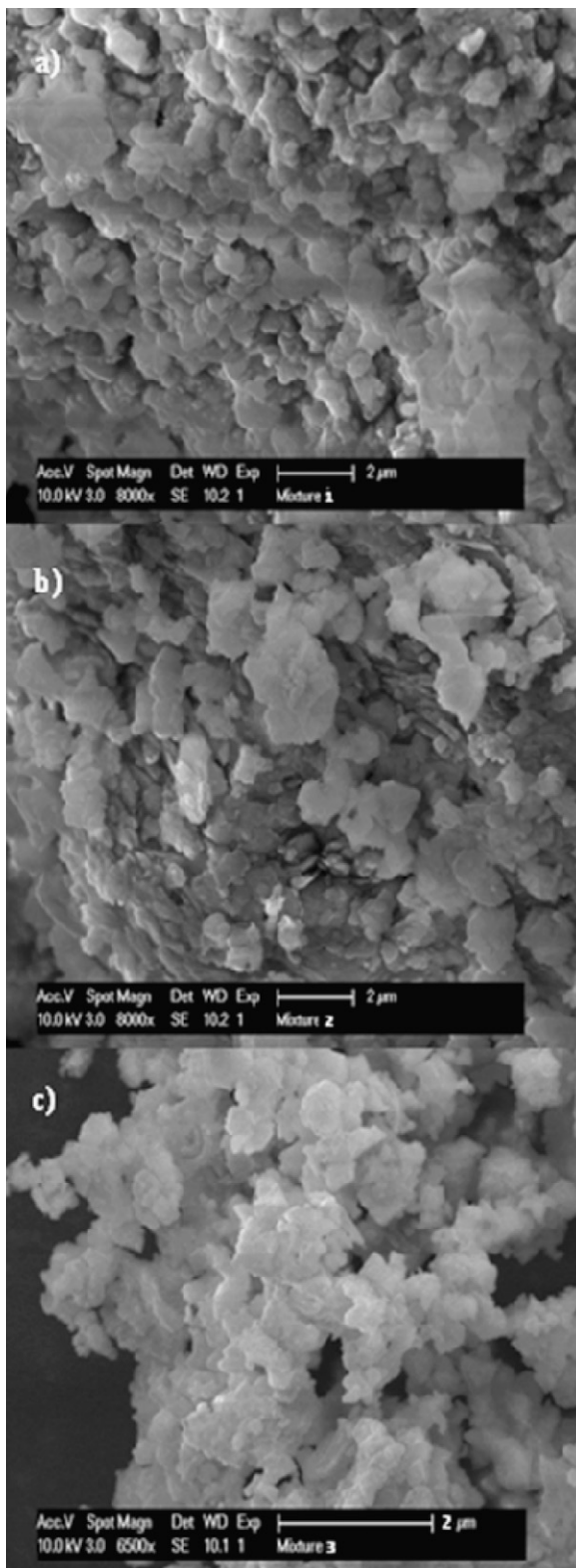


Fig. 1. SEM images of (a) Mixture 1, (b) Mixture 2, and (c) Mixture 3.

### 3. Results and discussion

#### 3.1. Characterisation of mixed materials

The surface morphology of the mixtures was shown in Fig. 1. Porosity of the mixed materials was observed for all mixtures. This

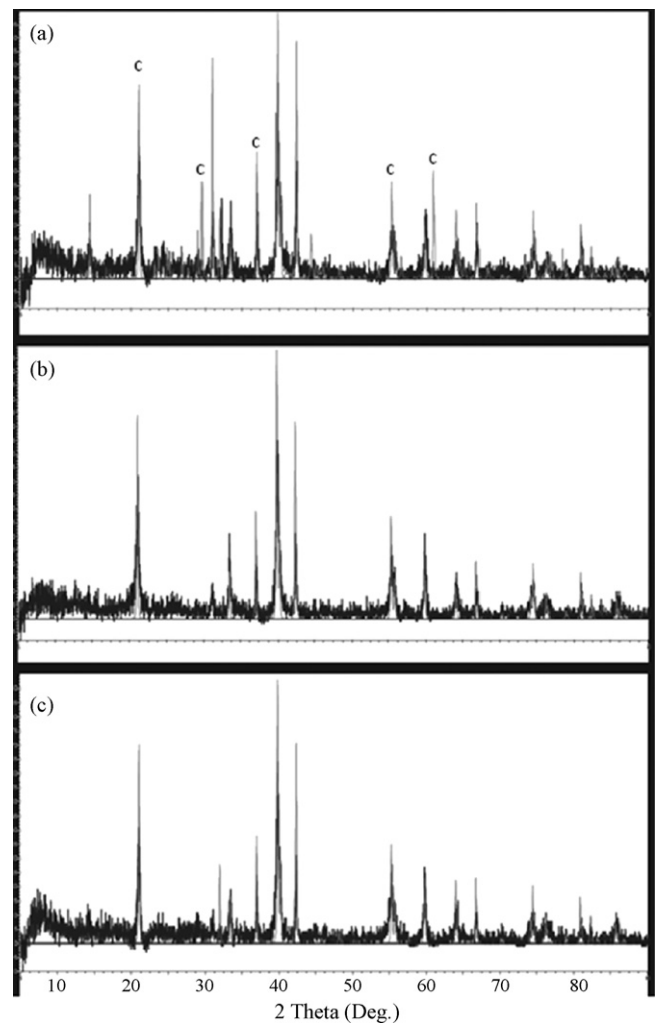


Fig. 2. X-ray diffraction patterns of adsorbent mixtures (a) Mixture 1, (b) Mixture 2, and (c) Mixture 3. C: calcium derivatives.

can be related to a porous nature of the clay minerals, of which those pores can be classified as micropore sizes, depending on the types of clays, and their geographic source of origin. Calcium hydroxide can be dehydrated and converted into calcium oxide during calcination treatment and consequently formed a porous Ca-based material. These pores are anticipated to be responsible for the dye decontamination. The SSA of the mixtures was also monitored in this case, and reported as 20.7, 25.1 and 19.6 m<sup>2</sup> g<sup>-1</sup> for Mixtures 1, 2 and 3, respectively. Mixture 2 had a higher SSA than others. This can be explained due to the large proportion of bentonite (25.70 m<sup>2</sup> g<sup>-1</sup>) and kaolin (20.28 m<sup>2</sup> g<sup>-1</sup>) and a small amount of zeolite (8.31 m<sup>2</sup> g<sup>-1</sup>). This result was concurred with the SSA of the clay minerals studied in our previous work [12].

The XRD measurement in Fig. 2 exhibits the changes in crystalline profile of the clay mixtures relative to those of natural clays [12]. Formation of calcium derivatives as a resultant lime was observed. The results revealed that Mixture 1 contained the highest crystalline content (65.4%), followed by Mixture 2 (41.1%) and Mixture 3 (27.8%). This is markedly attributed to the difference in clay content of the mixtures as given in Table 1. Kaolin and zeolite are the major contributors of the crystalline content, comparative to bentonite as discussed previously [12]. The relative proportion of the crystalline and amorphous phase of the mixtures is suggested as a rather combined removal mechanisms i.e. dye adsorption on the crystal surface or edge of the clay, cation-exchange between

**Table 2**  
Adsorption isotherm parameters of CR removal by the clay mixtures.

Materials	Freundlich				Langmuir			
	$K_F$	$n$	$r^2$	$\chi^2$	$K_L$	$q_m$	$r^2$	$\chi^2$
Mixture 1	89.91	1.72	0.9955	11.1782	0.31	434.78	0.9435	142.0034
Mixture 2	97.50	1.49	0.9925	14.1682	0.19	666.67	0.9689	43.8319
Mixture 3	102.75	1.67	0.9919	17.7177	0.26	555.56	0.9598	59.5084

dye and foreign ions within the clay interlayer, or other chemical interaction etc.

### 3.2. Removal capacity of clay mixtures

To assess the removal capacity of the clay mixtures toward CR, the experiment was carried out at different CR concentrations (40–600 mg L<sup>-1</sup>). The residual dye was measured and the results are given in Fig. 3. The results indicated that removal efficiency was gradually decreased with the CR concentration increased. This can be interpreted as the adsorptive sites were the limiting factor. However, from our results, more than 95% decolourisation of dye can still be achieved even at 600 mg L<sup>-1</sup> CR. This removal capacity was equivalent to 575.49, 586.51, and 583.43 mg g<sup>-1</sup> of the Mixtures 1, 2, and 3, respectively. Such a great CR removal profile of the clay mixtures was much higher than those using other natural or modified clays reported in the literatures. For instance, a removal capacity was reported as 158.7 mg g<sup>-1</sup> for bentonite [15], 5.6 mg g<sup>-1</sup> using kaolins [16], 350 mg g<sup>-1</sup> by modified-montmorillonite [9], and 4.3 mg g<sup>-1</sup> with zeolite [11].

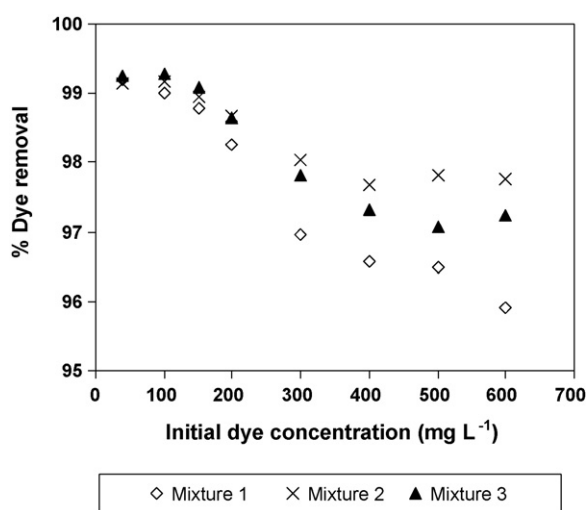
### 3.3. Adsorption isotherms and kinetic reactions of clay mixtures

#### 3.3.1. Adsorption isotherm study

To investigate an interaction of CR molecules and the mixed adsorbents, two well-known models, the Freundlich [17] and Langmuir [18] isotherms, were selected to explicate dye–clay interaction in this study.

**3.3.1.1. Freundlich isotherm.** The Freundlich isotherm describes the non-ideal adsorption of a heterogeneous system and reversible adsorption [19]. The model can be expressed as

$$q_e = K_F C_e^{1/n} \quad (2)$$



**Fig. 3.** Removal efficiency of the clay mixtures at different initial Congo Red concentrations (adsorbent dosage 1 g L<sup>-1</sup>).

where  $q_e$  is the amount of dye adsorbed per unit of adsorbent (mg g<sup>-1</sup>),  $C_e$  is the concentration of dye solution at adsorption equilibrium (mg L<sup>-1</sup>),  $K_F$  (mg<sup>1-1/n</sup> L<sup>1/n</sup> g<sup>-1</sup>) and  $n$  is the Freundlich adsorption isotherm constant. The favourable adsorption of this model can be characterised such that if a value for  $n$  is above unity, adsorption is favourable and a physical process [7].

**3.3.1.2. Langmuir isotherm.** The Langmuir isotherm is based on the assumption of a structurally homogeneous adsorbent and the monolayer coverage. That is, once a dye molecule occupies a site, no further adsorption can take place at that site. The equation is given as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where  $q_m$  is the maximum amount of adsorption which completes monolayer coverage on the adsorbent surface (mg g<sup>-1</sup>), and  $K_L$  is the Langmuir constant (L mg<sup>-1</sup>). The Langmuir constants  $K_L$  and  $q_m$  can be determined from the linear plot of  $1/q_e$  versus  $1/C_e$ .

In this present work, both linear and non-linear-regression were employed. The obtained results were found to be conflict in case of the Langmuir model, in which the linear-regression showed the well-fit to the model, while the non-linear-regression was not. It can be seen by the  $r^2$  values obtained from linear-regression were conflicted with  $\chi^2$  of non-linear one as given in Table 2. This indicated non-universal validity of the linear-regression for the Langmuir model, and therefore the non-linear-regression of this model is essentially required to verify the accuracy.

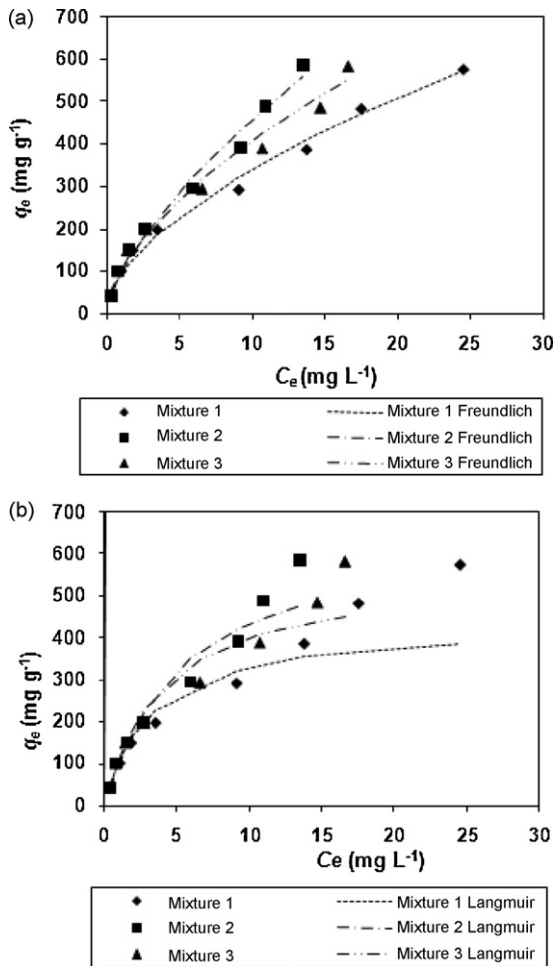
Fig. 4a and b shows that the adsorption of CR onto the three mixtures was better described by the Freundlich model for the entire concentration range. Whereas, fitting to the Langmuir isotherms may not be applicable, especially at a high dye concentration. The initial fit to the Langmuir model at a low CR concentration may be due to yet unsaturated adsorptive sites on the mixture surface. As the dye concentration increased, the adsorptive sites became more and more occupied, and ultimately reached the maximum capacity of the surface adsorption. Table 2 presents the calculated values of Freundlich and Langmuir model's parameters. These results showed that the uptake of CR by the mixtures exceeded the amount predicted by the monolayer coverage, suggesting that either multilayer adsorption or other possible removal mechanisms e.g. precipitation were involved. The better fit to the Freundlich model was revealed by the values of  $n$  above unity. A good agreement with this adsorption isotherms was confirmed by correlation  $r^2 > 0.99$  and the smaller Chi-square ( $\chi^2$ ) values for the three mixtures, in relative to the Langmuir model's parameters as illustrated in Table 2.

#### 3.3.2. Kinetic study

Several mathematical kinetic models were derived to determine the mechanism of dye adsorption from aqueous solutions. In this study, the pseudo-first-order and pseudo-second-order kinetic models were selected to investigate the dye removal dynamics due to their good applicability in many cases [20]

**3.3.2.1. Pseudo-first-order model.** Pseudo-first-order equation or Lagergren's kinetics equation [21] is based on the assumption that





**Fig. 4.** Adsorption isotherm of Congo Red adsorption by the clay mixtures. (a) Freundlich model and (b) Langmuir model (adsorbent dosage 1 g L<sup>-1</sup>).

the rate of change of adsorptive solute uptake with time is directly proportional to the difference in saturation concentration and the amount of adsorptive solid uptake with time.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

when  $q_t = 0$  at  $t = 0$ , Eq. (4) can be integrated into following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

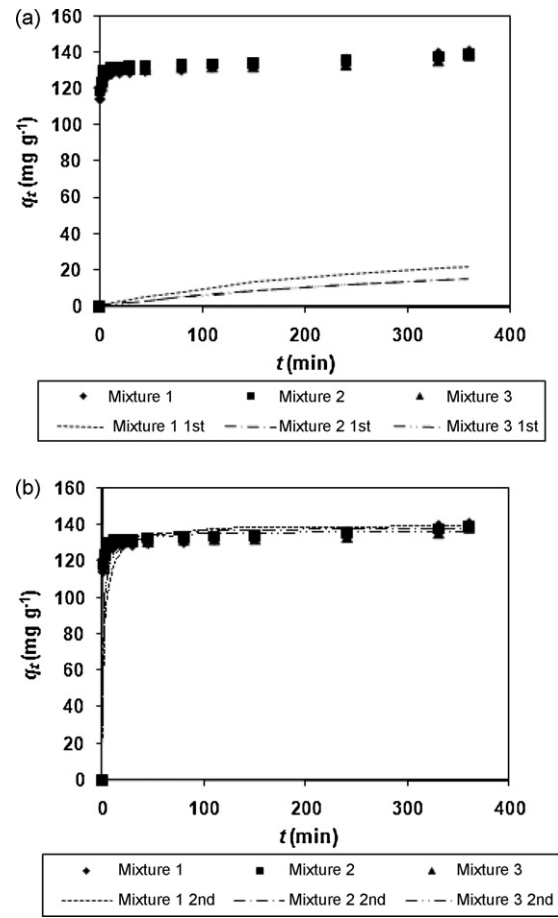
where  $q_t$  is the amount of dye adsorbed per unit of adsorbent ( $\text{mg g}^{-1}$ ) at time  $t$ ,  $k_1$  is the pseudo-first-order rate constant ( $\text{min}^{-1}$ ), and  $t$  is the contact time (min). The adsorption rate constant ( $k_1$ ) can be calculated from the plot of  $\log(q_e - q_t)$  against  $t$ .

**3.3.2.2. Pseudo-second-order model.** Ho and McKay [22] expressed the pseudo-second-order kinetic as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

**Table 3**  
Kinetic model parameters for the removal of Congo Red by the clay mixture.

Materials	$q_e$ (exp)	Pseudo-first-order				Pseudo-second-order				
		$q_{e1}$	$k_1$	$r^2$	$X^2$	$q_{e2}$	$h$	$k_2$	$r^2$	$X^2$
Mixture 1	148.20	28.51	0.0041	0.5181	502.45	140.85	61.35	0.0031	0.9994	0.3837
Mixture 2	148.44	23.60	0.0030	0.3167	660.16	138.89	106.38	0.0055	0.9998	0.6564
Mixture 3	148.62	25.10	0.0025	0.2763	607.97	136.97	101.01	0.0054	0.9996	0.9875



**Fig. 5.** Kinetic model of Congo Red removal by the clay mixtures. (a) The pseudo-first-order and (b) the pseudo-second-order (adsorbent dosage 1 g L<sup>-1</sup>, initial dye concentration 150 mg L<sup>-1</sup>).

Integrating Eq. (6) and noting that  $q_t = 0$  at  $t = 0$ , the obtained equation can be rearranged into linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where  $k_2$  is the pseudo-second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The initial adsorption rate,  $h$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) at  $t \rightarrow 0$  is defined as

$$h = k_2 q_e^2 \quad (8)$$

$h$ ,  $q_e$  and  $k_2$  can be obtained by linear plot of  $t/q_t$  versus  $t$ .

Table 3 illustrates the calculated values of the kinetic parameters, the related correlation coefficient ( $r^2$ ) and Chi-square ( $X^2$ ) obtained from the two kinetic models. The results showed that the application of the first-order kinetic was not valid for dye removal by the clay mixtures. This can be seen by the significant digression between the predicted and experimental plots shown in Fig. 5(a). The poorly fitted kinetic profile was also proven by the large deviation of  $X^2$  values and the  $q_e$  values calculated from the model which were considerably lower than those obtained from the experimental results. In contrast, the pseudo-second-order kinetic exhibits an

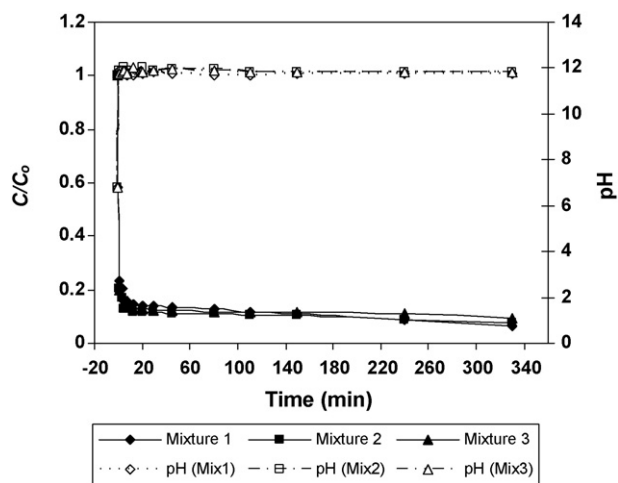


Fig. 6. Kinetic reaction of Congo Red removal by the clay mixtures (adsorbent dosage  $1 \text{ g L}^{-1}$ , initial dye concentration  $150 \text{ mg L}^{-1}$ ).

excellent agreement between the theoretical and experimental  $q_e$  values (Fig. 5b and Table 3). A better fit to the later model of the clay mixtures was verified by the integrated linearization method with  $r^2 > 0.999$  and very small values of  $X^2$ . It can be concluded that the CR removal kinetic by the clay mixtures was better described by the pseudo-second-order rather than the pseudo-first-order. Özacar and Şengil [23] suggested that such CR removal might take place via surface exchange reaction until the surface function sites are fully occupied. Then, the dye molecules diffuse into the interlayer space for further reactions such as ion-exchange and complexation interactions.

The results in Fig. 6 revealed that colour elimination using all mixtures can occur very rapidly, in which 84.3%, 87.1% and 86.3% of dye was removed within the initial 5 min by Mixtures 1, 2, and 3, respectively. Then, the removal progressively increased with time, in which more than 90% removal can be achieved in 150 minutes. Although the removal capacities of all the mixtures were similar, by taking into account the adsorption rate ( $h$ ) of all the mixtures, it was found that Mixture 2 had the highest initial decolourisation rate, followed by Mixtures 3 and 1, respectively. Such results indicated that Mixture 2 is the most suitable adsorbent employed for a large-scale treatment, where adsorption contact time is considered as a critical operation parameter.

In addition to the CR removal kinetic study, the variation in pH in clay mixture suspension with time was also monitored. It can be seen that the mixtures showed a strong alkaline property in the solution with a pH ranging from 11.5 to 12.1. An abrupt increase in the pH of the dye solution was observed instantly after the addition of the mixtures and subsequently remained unchanged towards the end of reaction. This rapid increase in the solution pH was most likely attributed to the dissolution of  $\text{OH}^-$  from the calcium compounds into the solution. The responding of large fraction of dye removal in short period of time to the fast liberation of  $\text{Ca}^{2+}$  indicated that this primary removal stage was probably governed by chemical precipitation. Whereas, a further removal at low dye concentrations, but sustained over a longer periods, was expected to be a result of chemisorption. The similar removal profile was also reported on removal of phosphate by Ca-rich fly ash [24].

### 3.4. Removal mechanisms

The CR is a relatively large molecule and negatively charged at pH greater than 5 [25]. The adsorption capacity of CR on natural clays was found to decrease as the pH increased due to the electrostatic repulsion between negatively charged surface of the clay

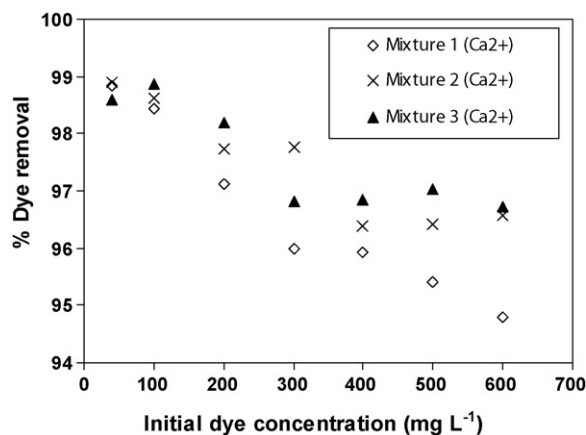


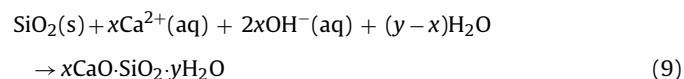
Fig. 7. Congo Red removal efficiency by Ca-supernatant of the mixtures.

and anion dye [12]. Nonetheless, the current experimental results revealed that the high removal efficiency of material mixture (99%) toward CR was given at  $\text{pH} > 11$ . This leads to the assumption of additional mechanisms involved in the dye removal process, apart from adsorption. The potential mechanism involved was expected to be related to the presence of calcium derived from calcium hydroxide as a major component of material mixture. Once calcium oxide was in contact with water, hydration reaction occurred and calcium hydroxide reformed.  $\text{Ca}(\text{OH})_2$  has a low solubility, of which the equilibrium solubility constant ( $K_{sp}$ ) is about  $5.5 \times 10^{-6}$  [26]. The partially dissolved  $\text{Ca}(\text{OH})_2$  results in dissociation of  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions.

In fact, the exchange sites and dissociation of CaO of the natural clays can generate  $\text{Ca}^{2+}$  ions. However, the  $\text{Ca}^{2+}$  contributions were dependant on the amount of  $\text{Ca}(\text{OH})_2$ . The effect of  $\text{Ca}^{2+}$  in solution on dye removal was investigated using the supernatants separated from the suspensions as described previously.

Fig. 7 indicates that dissociated  $\text{Ca}^{2+}$  in the solution contributed significantly to the dye removal. The mechanism involves calcium ingredients in the mixture is likely to be the formation of Ca–CR precipitation through the reaction of the  $\text{Ca}^{2+}$  with the anionic CR molecules. This precipitation was confirmed by the reduction of Ca content in the solution. The similar phenomenon was also reported by Zhu et al. [27].

Another possible mechanism urging removal efficiency of the clay mixtures can be attributed to pozzolanic reactions [28,29]. The pozzolanic reaction generally involves a primary chemical adsorption of calcium compound on the surface of silanol groups [30]. In a strong alkaline medium,  $\text{SiO}_2$  in the clay structure is often dissolved and reacts with  $\text{Ca}^{2+}$  to form calcium silicates, which has large surface area and porous structure as shown in the equation below:



where  $x$  is 0.8–1.5, and  $y$  is 0.5–2.5 [31]. The formation of this porous material is believed to promote the adsorption of the dye onto the clay materials, and hence resulting in an enhancement in their removal capability.

The above results indicated that CR removal by the mixtures was controlled by two main mechanisms—(a) adsorption of dye on the mixture surface and (b) chemical precipitation between calcium ion and dye molecules. Comparison of removal efficiency of the mixtures and  $\text{Ca}(\text{OH})_2$ , it was found that chemical precipitation was likely the predominating mechanism in CR removal, especially at a

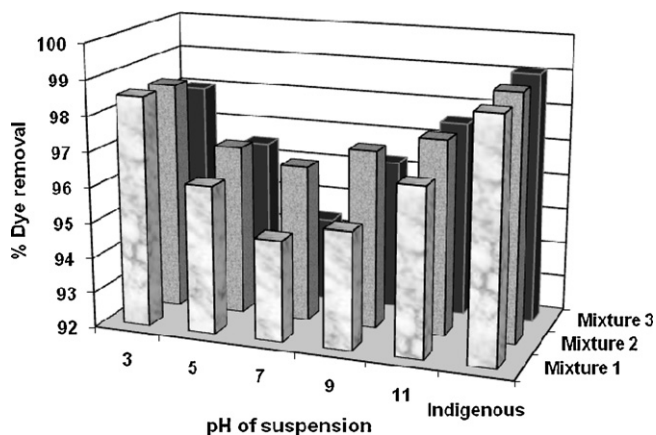


Fig. 8. Effect of pH on Congo Red removal by the clay mixtures (adsorbent dosage  $1 \text{ g L}^{-1}$ , initial dye concentration  $150 \text{ mg L}^{-1}$ ).

high initial dye concentration. Based on our previous investigation on the dye removal capacity by the natural clays [11] and lime [12], it was estimated that this precipitation process accounted for over 70% of the total removal of CR.

### 3.5. Effect of pH on removal mechanisms

In most adsorption processes, pH is often a key parameter determining the adsorption mechanism, and hence the removal efficiency of the adsorbents. The change of removal efficiency of the mixture was found to be insignificant with variation in the initial pH of the dye solution. This is due to the strong basic nature of the clay mixtures that can change the indigenous pH of the solution into the alkaline condition [12].

Thus, to further investigate the effect of pH on the removal mechanism of the clay mixtures, the dye-mixture suspensions were adjusted to a certain pH values i.e. 3, 5, 7, 9, 11, and indigenous pH ( $\sim 12$ ) using 1 M of NaOH and HCl. Fig. 8 showed that pH of the suspension affected the dye removal efficiency to some extent, in which Mixture 2 performed the best dye removal corresponding to the pH range. A high removal efficiency over 98% by all mixtures was attained at either strong acidity or alkalinity condition, suggesting there were different mechanisms taking place. At a high pH, the removal reaction would be dominated by chemical precipitation as discussed in previous section. In contrast, at a low pH, an increase in CR removal was major attributed to an electrostatic reaction between adsorbent surface and dye anionic molecules; whilst other possible mechanisms can be ascribed to acidification of the adsorbents.

Komadel [32] stated that the acidification of clay minerals can partly dissolve the material, resulting in increasing SSA and the porosity of the clay materials, and consequently improving their adsorption capacity. Meanwhile, this acid treatment results in releasing some elements such as iron, aluminium and silica from clays into the solution. Vandebusch [33] has suggested that dissolved calcium ions presented in the solution are likely to act as a coagulant for enhancement of the dye removal. The common calcium coagulants which can enhance dye coagulation process are often found to be calcium aluminosilicate ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), calcium trialuminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ), calcium monoferrite ( $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ ), and calcium silicide ( $\text{CaSi}_2$ ). From the current results, it is worth noting that the overall removal efficiency can still be maintained above 94% over the studied pH range regardless of the mechanisms involved. This removal character provides a significant advantage over other low-cost adsorbents, in which their applications are mostly limited by the pH of the solution.

## 4. Conclusion

The clay mixtures constituting of natural clays and lime demonstrated a significant enhancement in dye removal capacity and efficiency and was proven to have the potential applicability in wastewater treatment. This consecutive study was to provide an in-depth assessment of the possible removal kinetics and mechanisms of the mixture towards anionic dye CR. The results showed that the decolourisation of the dye was likely governed by a combination of physicochemical reactions such as adsorption, ion-exchange, and precipitation. The dye removal process was well-described by the Freundlich isotherm and the pseudo-second-order kinetic, in which the mixture with 70%  $\text{Ca}(\text{OH})_2$ , 15% sodium bentonite, 10% kaolin and 5% zeolite recorded the fastest decolourisation rate. Under a spontaneous condition, the precipitation of the dye with dissolved calcium ions was the dominant removal mechanism over the chemisorption of dye molecules onto the mixture surfaces. However, the predominant removal reaction of the dye can be varied depending upon the pH of the mixture suspension i.e. adsorption/coagulation at acidic pH and precipitation at basic condition. The change in overall removal efficiency was found to be insignificant over the studied pH range, in which more than 94% decolourisation was still maintained. This obtained comprehensive dye removal mechanisms from this study would assist in optimising the operating conditions and maximising the dye removal efficiency of the clay mixtures. This present work confirmed that it is feasible to employ the clay mixtures as alternative low-cost adsorbents for industrial wastewater treatment.

## Acknowledgement

This work was supported by the Australian Research Council Linkage Grant through the Water Environmental Biotechnology Laboratory (WEBL) at the University of Adelaide.

## References

- [1] Y. Anjaneyulu, N.S. Chary, D.S.S. Raj, Decolourization of industrial effluents—available methods and emerging technologies—a review, *Rev. Environ. Sci. Biotechnol.* 4 (2005) 245–273.
- [2] J. Easton, The dye maker's view, in: P. Cooper (Ed.), *Colour in Dyehouse Effluent*, Society of Dyers and Colourists, Bradford, UK, 1995, p. 1.
- [3] D. Brown, Effects of colorants in the aquatic environment, *Ecotoxicol. Environ. Saf.* 13 (1987) 139–147.
- [4] G.M. Walker, L. Hansen, J.A. Hana, S.J. Allen, Kinetics of a reactive dye adsorption onto dolomitic sorbents, *Water Res.* 37 (2003) 2081–2089.
- [5] S. Chakraborty, M.K. Purkait, S. DasGupta, S. De, J.K. Basu, Nanofiltration of textile plant effluent for color removal and reduction in COD, *Sep. Purif. Technol.* 31 (2003) 141–151.
- [6] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal—a review, *J. Environ. Manag.* 90 (2009) 2313–2342.
- [7] A.S. Özcan, B. Erdem, A. Özcan, Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite, *Colloids Surf. A: Physicochem. Eng. Aspects* 266 (2005) 73–81.
- [8] M. Alkan, Ö. Demirbaş, M. Doğan, Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite, *Micropor. Mesopor. Mater.* 101 (2007) 388–396.
- [9] L. Wang, A. Wang, Adsorption properties of Congo Red from aqueous solution onto surfactant-modified montmorillonite, *J. Hazard. Mater.* 160 (2008) 173–180.
- [10] I.K. Tonlé, E. Ngameni, H.L. Tchoumi, V. Tchiéda, C. Carteret, A. Walcarius, Sorption of methylene blue on an organoclay bearing thiol groups and application to electrochemical sensing of the dye, *Talanta* 74 (2008) 489–497.
- [11] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials, *Chem. Eng. J.* 148 (2009) 354–364.
- [12] V. Vimonses, B. Jin, C.W.K. Chow, C. Saint, Enhancing removal efficiency of anionic dye by combination and calcination of clay materials and calcium hydroxide, *J. Hazard. Mater.* 171 (2009) 941–947.
- [13] A. Klutes (Ed.), *Methods of Soil Analysis. Part I. Physical and Mineralogical Methods*, ASA and SSSA, Madison, 1986.
- [14] Y.S. Ho, Selection of optimum sorption isotherm, *Carbon* 42 (2004) 2115–2116.
- [15] E. Bulut, M. Özcan, I.A. Şengil, Equilibrium and kinetic data and process design for adsorption of Congo Red onto bentonite, *J. Hazard. Mater.* 154 (2008) 613–622.

- [16] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Adsorption of Congo Red by three Australian kaolins, *Appl. Clay Sci.* 43 (2009) 465–472.
- [17] H.M.F. Freundlich, Über die adsorption in lösungen, *Z. Phys. C: Chem.* 57 (1906) 385–470.
- [18] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [19] S. Wang, Z.H. Zhu, Characterisation and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, *J. Hazard. Mater.* B136 (2006) 946–952.
- [20] M. Özacar, Equilibrium and kinetic modelling of adsorption of phosphorous on calcined alunite, *Adsorption* 9 (2003) 125–132.
- [21] S. Lagergren, About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens Handlingar.* 24 (1898) 1–39.
- [22] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [23] M. Özacar, İ.A. Şengil, Equilibrium data and process design for adsorption of disperse dyes onto alunite, *Environ. Geol.* 45 (2004) 762–768.
- [24] S.G. Lu, S.Q. Bai, L. Zhu, H.D. Shan, Removal mechanism of phosphate from aqueous solution by fly ash, *J. Hazard. Mater.* 161 (2009) 95–101.
- [25] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Removal of Congo Red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses, *Chemosphere* 61 (2005) 492–501.
- [26] J. Chen, H. Kong, D. Wu, X. Chen, D. Zhang, Z. Sun, Phosphate immobilization from aqueous solution by fly ashes in relation to their composition, *J. Hazard. Mater.* B139 (2007) 293–300.
- [27] M.X. Zhu, L. Lee, H.H. Wang, Z. Wang, Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud, *J. Hazard. Mater.* 149 (2007) 735–741.
- [28] G. Gong, S. Ye, Y. Tian, Q. Wang, J. Ni, Y. Chen, Preparation of a new sorbent with hydrated lime and blast furnace slag for phosphorous removal from aqueous solution, *J. Hazard. Mater.* 166 (2009) 714–719.
- [29] R.B. Lin, S.M. Shih, C.F. Liu, Structural properties and reactivities of  $\text{Ca}(\text{OH})_2$ /fly ash sorbents for flue gas desulfurization, *Ind. Eng. Chem. Res.* 42 (2003) 1350–1356.
- [30] J. Fernández, M.J. Renedo, A. Pesquera, J.A. Irabien, Effect of  $\text{CaSO}_4$  on the structure and use of  $\text{Ca}(\text{OH})_2$ /fly ash sorbents for  $\text{SO}_2$  removal, *Powder Technol.* 119 (2001) 201–205.
- [31] H.F.W. Taylor, *Chemistry of Cement*, Academic Press/Harcourt Brace Jovanovich Publisher, London, 1990.
- [32] P. Komadel, Chemically modified smectites, *Clay Miner.* 38 (2003) 127–138.
- [33] M.B. Vandenbusch, Fly ash as a sorbent for the removal of biologically resistant organic matter, *Resour. Conserv. Recycl.* 6 (1992) 95–116.