

## Sorption of an anionic dye by uncalcined and calcined layered double hydroxides: a case study

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Received 18 October 2004; received in revised form 30 December 2004; accepted 31 December 2004

### Abstract

Layered double hydroxides (LDHs) with a Mg/Al molar ratio of 2:1 were synthesized by using a co-precipitation method and their calcined products (CLDHs) were obtained by heating Mg/Al-LDHs at 500 °C. Sorption of a weak acid dye, Brilliant Blue R (BBR), by LDHs and CLDHs indicated equilibrium time required for BBR sorption by CLDHs was less than 12 h, regardless of initial concentration of BBR, whereas BBR sorption by LDHs was longer than 20 h. Sorption capacity of CLDHs was much larger than that of LDHs. Therefore, CLDHs could be used to remove anionic dyes of relatively high concentrations while LDHs may only be used to remove anionic dyes of low concentrations. Isotherms for BBR sorption by CLDHs and LDHs were well described using the Freundlich and Langmuir equations, respectively. When the initial pH of BBR solutions was lower than 8.0, the final pH of the solution after sorption was enhanced and stabilized at 10.6–10.8. The effect of initial pH (<8.0) on BBR removal was negligible, which would be environmentally important for precipitation/co-precipitation of co-existing metal cations. The effects of both Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> on BBR sorption by CLDHs were minimal; but the presence of CO<sub>3</sub><sup>2-</sup> markedly reduced BBR removal. Thermal regeneration for re-use of LDHs and CLDHs after BBR sorption was feasible only within the first two cycles, after which the regenerated materials suffered from a large loss in their sorption capacities.

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**Keywords:** Adsorption; Hydrotalcite; Dye sorption; Calcined layered double hydroxides; Decolorization

### 1. Introduction

Synthetic dyes have long been used in dyeing, paper and pulp, textile and other industrial applications [1]. Dye effluents from these industries pose certain hazards and environmental problems. They are not only aesthetic pollutants, but coloration of water by the dyes may interfere with light penetration affecting aquatic ecosystems [2]. Hence, color removal from dye effluents is one of the several major environmental concerns. Traditionally, biological, physical and chemical methods have been applied for dye removal [3–5]. However, many dyes are poorly biodegradable or recalcitrant to environmental conditions due to their complex structure and xenobiotic properties. Furthermore, many dyes are toxic

to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities [6]. Chemical and electrochemical oxidations, coagulation and reverse osmosis are generally not feasible on a large scale due to economic consideration. Adsorption, however, is an effective method for dye removal. Activated carbon is perhaps the most widely used adsorbent because of its high specific surface area, high adsorption capacity and low-selectivity for both inorganic and organic pollutants [7,8]. Unfortunately, activated carbon adsorption is an expensive method due to its high price and the difficulties involved in its regeneration for re-use. In recent years, many low-cost natural materials such as natural clay, materials produced from agricultural by-products and industrial solid wastes such as fly ash and coal, as dye adsorbents have attracted interests of environmental scientists [2,9–11]. However, these materials generally have low adsorption capacities and hence, large adsorbent dosage is re-

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quired to achieve a low dye concentration of the effluents. Difficulties involved in regeneration of these low-cost adsorbents for re-use also increase economic burdens disposing of the used adsorbents.

The applications of layered double hydroxides (LDHs) as adsorbents to selectively remove anionic pollutants from aqueous solutions have attracted considerable attention in the recent decade [12–14]. LDHs, also called hydrotalcite-like compounds or anion clays, consist of brucite-like hydroxide sheets. Many cations can be incorporated in the brucite-like sheets. The general formula is  $[M_{1-x}^{II}M_x^{III}(\text{OH})_2](A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ , where  $M^{II}$  is divalent cation like  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , etc.,  $M^{III}$  trivalent cations like  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , etc., and  $A^{n-}$  is anion. Due to partial substitutions of  $M^{III}$  for  $M^{II}$ , the hydroxide sheets are positively charged and require intercalation of anions such as  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$  or  $\text{NO}_3^-$  to remain overall charge neutrality. Previous research has shown that LDHs can uptake some inorganic or organic anionic pollutants by exchange with interlayer anions [15,16], but the efficiency of uptake is affected considerably by the properties of interlayer anions. Generally, LDHs have greater affinities for multivalent anions than for monovalent anions. For example,  $\text{CO}_3^{2-}$  is preferentially adsorbed and not readily replaceable by other anions [16–18]. By heating to 450–500 °C, LDHs are converted into mixed metal oxides. An important property of calcined-LDHs (CLDHs) is the so-called “memory effect”, that is, the calcined products can easily reconstruct the original layered structure in an aquatic environment, by which anions are intercalated [19]. Used as sorbents, CLDHs are receiving greater interests in the environmental community [12–19] because of their high anion retention capacity and simple thermal regeneration procedure. However, studies on sorption of anionic dyes by LDHs and particularly, CLDHs are limited [15,20].

LDHs are rare in nature; however, they can be easily synthesized by the co-precipitation method under laboratory conditions [13,21]. In the present study, the removal of an anionic dye, e.g., weak acid Brilliant Blue R (BBR), by synthesized LDHs and their calcined products (CLDHs) was investigated.

## 2. Materials and methods

### 2.1. Preparation of Mg/Al- $\text{CO}_3$ -LDHs

A co-precipitation method following Reichle with some modifications [21] was used to prepare Mg/Al- $\text{CO}_3$ -LDHs. Briefly, 3.5 mol NaOH and 0.943 mol  $\text{Na}_2\text{CO}_3$  were dissolved in 1000 mL deionized water to which 700 mL mixed solution containing 0.5 mol  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 1.0 mol  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Mg:Al molar ratio = 2:1) was added at a rate of 1.0 mL/min under vigorous stirring. The resulting slurry was aged at 80 °C for 37 h while stirring. After cooling to room temperature, the slurry was centrifuged and washed us-

ing deionized water at least eight times to remove free ions. Then the material was dried at 105 °C, ground and passed through a 100-mesh sieve. Part of the resulting material was calcined at 500 °C for 8 h to obtain CLDHs.

### 2.2. Sorption experiments

BBR (purity >99%) was provided by the Qingdao Shuangtao dyestuff factory and used as received. The chemical structure of BBR is shown in Fig. 1. BBR solutions were prepared by dissolving BBR in deionized water. The initial pH value of BBR solutions is about 6.8. A series of BBR solutions of desired pH values was obtained by adjusting with dilute HCl or NaOH solutions.

BBR sorption experiments were carried out using a batch method. The effects of contact time, solution pH and BBR concentration on BBR sorption were investigated. The effect of contact time was used to determine kinetic model of BBR sorption and equilibrium time. Thirty milligrams CLDHs or 100 mg LDHs and 50 mL BBR solutions (typically ranging from 90 to 600 mg/L) were added to 100 mL conical beakers. After capping and vigorously shaking by hand, the conical beakers were placed in a water bath at 25 °C and gently shaken for specific time period or until adsorption equilibrium. The initial pH values of BBR solutions were not adjusted except in investigating the effect of pH on BBR sorption. The suspensions were filtered and BBR concentrations determined using a Hewlett-Packard 8453 UV-vis spectrophotometer at  $\lambda_{\text{max}} = 627 \text{ nm}$ . Amounts of sorbed BBR were calculated by the differences between originally added BBR concentrations to that remaining in solution; pH values of the filtrates were measured immediately after filtration.

The effects of CLDHs dosage and competitive sorption of inorganic anions  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  on BBR sorption by CLDHs were also investigated. In the experiments investigating the effect of CLDHs dosage on BBR sorption, various amounts of CLDHs (20, 30, 40 and 45 mg) and 50 mL BBR solution of 600 mg/L without pH adjusting were added to 100 mL conical beakers and shaken until equilibrium. Suspensions were filtered and BBR concentrations determined as discussed above. In the experiments investigating the effect of competitive sorption of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  on BBR sorption, the solutions of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  were

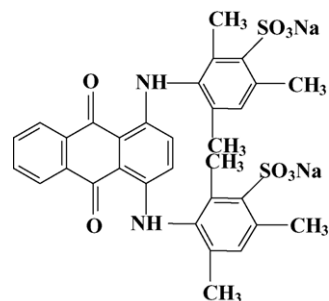


Fig. 1. Chemical structure of Brilliant Blue R (BBR) dye.

prepared by dissolving  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$  in deionized water, respectively. A series of 50 mL mixed solutions with constant BBR concentration (380 mg/L), but differing concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  or  $\text{CO}_3^{2-}$  and 30 mg CLDHs were added to conical beakers. The molar ratios of inorganic anion to BBR vary from 0 to 12. After capping and vigorously shaking by hand, the conical beakers were placed into a water bath at 25 °C and gently shaken until adsorption equilibrium (12 h). Suspensions were filtered and BBR concentrations determined as discussed above.

### 2.3. X-ray diffraction analysis

After equilibrium sorption, LDHs and CLDHs were washed three times using deionized water to remove any free BBR and then dried at 60 °C for X-ray diffraction (XRD) analysis. The XRD patterns of LDHs and CLDHs both before and after sorption experiments were obtained using a Rigaku D/max-rB diffractometer (Cu  $K\alpha$ , 40 kV, 100 mA, 7°  $\text{min}^{-1}$ ).

### 2.4. Regeneration of used CLDHs and their sorption efficiencies

In the present study, only used CLDHs are regenerated using a thermal recycle method similar to Crepaldi et al. [13]. The efficiency of BBR sorption by the regenerated materi-

als after several sorption and combustion cycles was also investigated. After completing equilibrium sorption experiments described in Section 2.2, the suspensions were recovered and calcined at 500 °C and the calcined materials were then re-dispersed in BBR solutions of known concentrations. This procedure was repeated three times and amount of BBR sorbed after each dispersion–calcination cycle was determined.

## 3. Results and discussion

### 3.1. Characterization of LDHs and CLDHs

Typical XRD patterns of LDHs and CLDHs both before and after sorption experiments are shown in Fig. 2. The XRD pattern of the original LDH (Fig. 2a) consists of both sharp and symmetrical peaks with some asymmetrical peaks at high angle, indicating good crystallinity [19,22]. The basal spacing ( $d_{003}$ ) of LDHs is 7.43 Å, which is smaller than values reported by other authors [13,14,23]. After BBR sorption, the XRD patterns of the recovered LDHs (Fig. 2b) are almost unchanged compared with the original LDHs (Fig. 2a), but their basal spacing ( $d_{003} = 7.55$  Å) is somewhat larger. The XRD pattern of CLDHs (Fig. 2d) shows that layered structure of the original LDHs is completely destroyed and indicates only MgO peaks [13,19], suggesting an almost total decomposi-

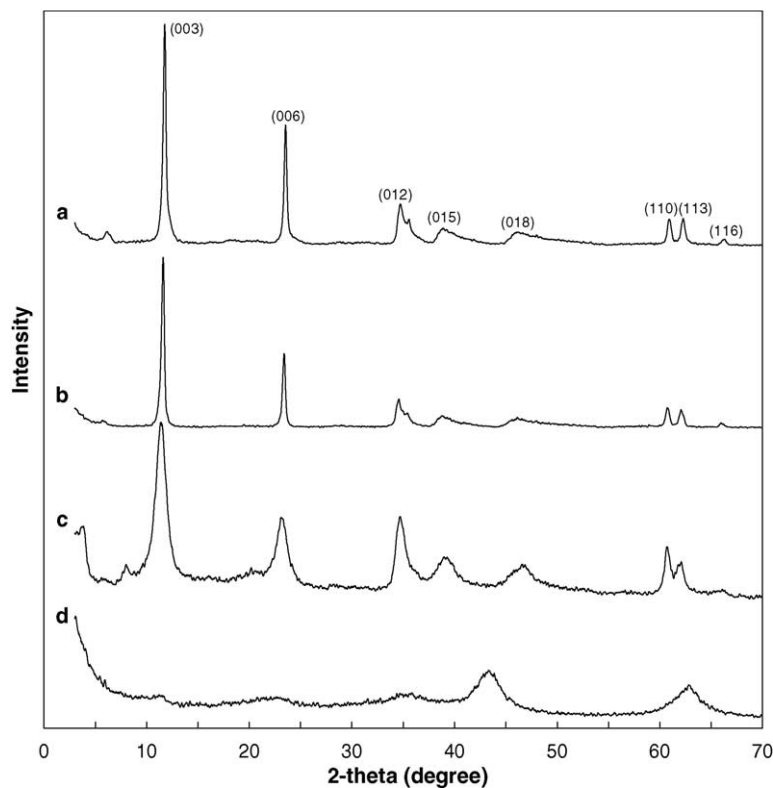


Fig. 2. X-ray diffractograms of layered double hydroxides (LDHs) and calcined LDHs (CLDHs) before and after Brilliant Blue R (BBR) sorption. (a) LDHs; (b) LDHs after BBR sorption; (c) CLDHs after BBR sorption; (d) CLDHs.

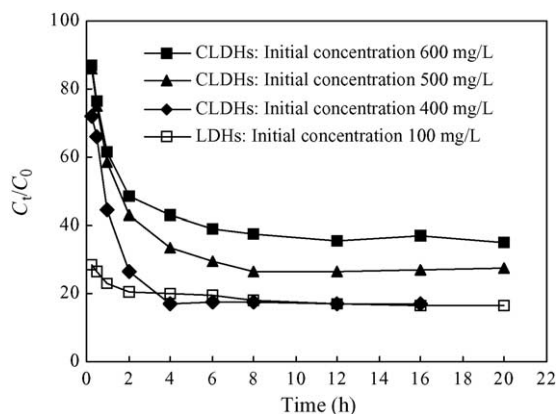


Fig. 3. Effect of contact time on the uptake of Brilliant Blue R (BBR) by layered double hydroxides (LDHs) and calcined LDHs (CLDHs) at different initial concentrations.

tion of the original LDHs and elimination of most interlayer carbonate anions and water. After BBR sorption by CLDHs, the layered structure of the recovered products was reconstructed (Fig. 2c). However, the peaks, particularly (003) and (006), were broadened and the intensity of the peaks decreased in comparison with the original LDHs (Fig. 2a), indicating some reductions in crystallinity following calcination and re-hydration. After the reconstruction, the basal spacing ( $d_{003}$ ) was 7.76 Å.

### 3.2. Effect of time on BBR sorption

Effect of sorption time on BBR removal by LDHs and CLDHs is shown in Fig. 3. For CLDHs, amounts of BBR sorbed increased rapidly within the initial 3 h and remained almost unchanged after 9 h, indicating an equilibrium state. Initial concentrations of BBR had no significant effect on the equilibrium time. For LDHs, amounts of BBR sorbed increased rapidly within initial 4 h followed by a slow increase in the following 18 h. In order to ensure a complete sorption equilibrium, 12 and 24 h were chosen for CLDHs and LDHs, respectively, in each batch equilibrium sorption experiment. An emphasis was placed on characterizing CLDHs rather than LDHs in the following sections because of its much higher sorption capacity.

Kinetic modeling not only allows estimation of sorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. In this respect, several ki-

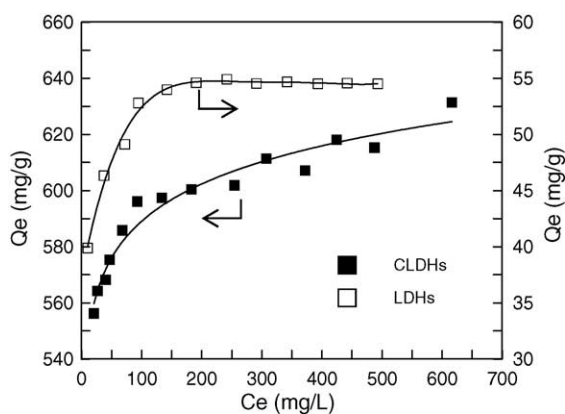


Fig. 4. Sorption isotherms for Brilliant Blue R (BBR) sorption by layered double hydroxides (LDHs) and calcined LDHs (CLDHs).

netic models including the pseudo-first-order equation (Eq. (1)) [24], pseudo-second-order equation (Eq. (2)) [24] and intraparticle diffusion model (Eq. (3)) [24] were tested.

$$\frac{1}{Q_t} = \left( \frac{k_1}{Q_m} \right) \left( \frac{1}{t} \right) + \frac{1}{Q_m} \quad (1)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_m^2} + \frac{1}{Q_m} t \quad (2)$$

$$Q_t = k_p t^{1/2} + C \quad (3)$$

where  $Q_t$  is the amount of BBR sorbed (mg/g) at a given time  $t$ ,  $Q_m$  the maximum adsorption capacity (mg/g),  $k_1$  and  $k_2$  the pseudo-first-order and pseudo-second-order rate constants, respectively,  $k_p$  the intraparticle diffusion rate constant and  $C$  is the intercept. The calculated kinetic parameters for BBR sorption by CLDHs and LDHs are given in Table 1. It seems that, of the three kinetic equations tested, the pseudo-second-order model best described the kinetic data for BBR sorption by both CLDHs and LDHs, based on the correction coefficient  $R^2$ .

### 3.3. Sorption isotherms and sorption mechanisms

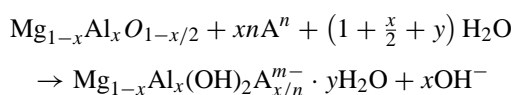
Sorption isotherms of BBR retention by CLDHs and LDHs are shown in Fig. 4. It is evident that sorption capacities of CLDHs are much larger than those of LDHs. For example, at a similar BBR equilibrium concentration of 100 mg/L, sorption capacity of CLDHs was more than 10 times greater

Table 1  
Kinetic parameters for sorption of BBR by CLDHs and LDHs

Initial concentration (mg/L)	$k_1$ ( $\text{h}^{-1}$ )	$q_1$ (mg/g)	$R_1^2$	$k_2$ (g/(mg h))	$q_2$ (mg/g)	$R_2^2$	$k_p$ (mg/(g h))	$C$ (mg/g)	$R_p^2$
CLDHs									
400	0.608	600.2	0.953	0.0026	615.2	0.999	111.6	231.5	0.753
500	1.23	711.3	0.997	0.0020	639.5	0.999	112.1	216.7	0.720
600	1.16	735.0	0.991	0.0017	672.2	0.998	112.1	235.2	0.730
LDHs									
100	0.043	136.7	0.890	0.0524	140.3	0.999	4.63	121.9	0.841

$R^2$ : correction coefficient.

than that of LDHs. These results suggest that CLDHs may be used to remove anionic dyes of relatively high concentrations, whereas LDHs may only be used to remove anionic dyes of low concentrations. For most dye wastewaters (typically ranging from 10 to 50 mg/L of dye concentrations [20]), both LDHs and CLDHs should be highly effective sorbents. The main mechanism for BBR sorption by LDHs is exchanged between BBR anions and previously adsorbed interlayer CO<sub>3</sub><sup>2-</sup> ions, though surface adsorption is presumed to be also involved [13]. Large affinities of LDHs for CO<sub>3</sub><sup>2-</sup> prevent the exchange to a great extent, resulting in low BBR sorption. The much larger sorption capacity of CLDHs than that of LDHs can be attributed to their peculiar property of structural reconstruction. The process can be expressed as [25]:



In this process, anions are intercalated and OH<sup>-</sup> ions are simultaneously released. Consequently, final pH of the aquatic solution will be enhanced. A longer equilibrium time required for BBR sorption by LDHs than by CLDHs is therefore understandable (Fig. 3). Both film diffusion and pore diffusion are involved in ion exchanges in LDHs; however, structural reconstruction and BBR intercalation occur almost simultaneously in CLDHs and the processes are rapid. Structural reconstruction was confirmed by XRD analysis (Fig. 2c). Larger basal spacings of reconstructed CLDHs (*d*<sub>003</sub> = 7.76 Å) in BBR solutions than basal spacings of LDHs (*d*<sub>003</sub> = 7.55 Å) after BBR sorption indicated that much more BBR anions were intercalated in reconstructed CLDHs.

Isotherms for BBR sorption by CLDHs and LDHs were modeled by two commonly used isotherm equations, Langmuir (Eq. (4)) [26] and Freundlich (Eq. (5)) [26].

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m C_e} + \frac{1}{Q_m} \tag{4}$$

$$Q_e = K_F C_e^n \quad \text{or} \quad \log Q_e = \log K_F + n \log C_e \tag{5}$$

where *Q<sub>e</sub>* (mg/g) is the amount of BBR sorbed at equilibrium, *Q<sub>m</sub>* (mg/g) the theoretical maximum monolayer sorption capacity, *C<sub>e</sub>* (mg/L) the equilibrium concentration of BBR in solution, and *K<sub>F</sub>*, *n* and *K<sub>L</sub>* are empirical constants. The calculated Langmuir and Freundlich isotherm constants are given in Table 2. Data for BBR sorption by CLDHs were fitted better by the Freundlich equation than by the Langmuir equation

Table 2  
Langmuir and Freundlich isotherm constants for sorption of BBR by CLDHs and LDHs

	Langmuir			Freundlich		
	<i>Q<sub>m</sub></i> (mg/g)	<i>K<sub>L</sub></i> (L/mg)	<i>R</i> <sup>2</sup>	<i>n</i>	<i>K<sub>F</sub></i> (L/g)	<i>R</i> <sup>2</sup>
CLDHs	613.6	0.411	0.871	0.0321	508.04	0.959
LDHs	54.59	0.254	0.934	0.0781	34.99	0.870

*R*<sup>2</sup>: correction coefficient.

based on the correction coefficient *R*<sup>2</sup>, whereas data for BBR sorption by LDHs were fitted better by the Langmuir equation.

### 3.4. Effect of pH

Effect of pH on BBR sorption at a fixed initial concentration of BBR (593 mg/L) and CLDH dosage (0.6 g/L) is shown in Fig. 5. When initial pH was between 3.5 and 11.5, BBR sorption decreased from 68 to 62%. When the initial pH was at >11.5, the percent sorbed increased. At an initial pH of 12.5, sorption was 65%. It may be concluded that the effect of initial pH over a wide pH range (3.5–13.0) on anionic dye removal by CLDHs is minimal probably due to OH<sup>-</sup> release while structural reconstruction of CLDHs in aqueous environments. In so far as weak acid or acid dye solutions are concerned, the effect of pH on anionic dye sorption by CLDHs may be insignificant because the pH values of the dye solutions are generally near 7.0. It should be noted that, however, the effect of pH on both cationic and anionic dye sorption by many other adsorbents, for example, fly ash and acid-activated bentonite was pronounced, according to previous studies [11,24].

The difference between initial and final pH values after sorption experiments using CLDHs is also shown in Fig. 5. It could be seen that the final pH values were significantly enhanced when the initial pH values are at <8.0. For example, the final pH was enhanced to 10.6 when the initial pH was 3.7. When initial pH was higher than 11.0, differences disappeared between the initial and final pH values. Generally, when initial pH values are lower than 10.0, final pH values can be enhanced and finally stabilized within a narrow alkaline range of 10.6–10.8. A similar phenomenon was reported by You et al. [14]. This is environmentally meaningful for precipitation or co-precipitation of some co-existing metal cations like Ca<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup>, which are attracting attention of environmental scientists [27–29]. The increase in the final pH could be explained by structural reconstruction by which OH<sup>-</sup> ions were released.

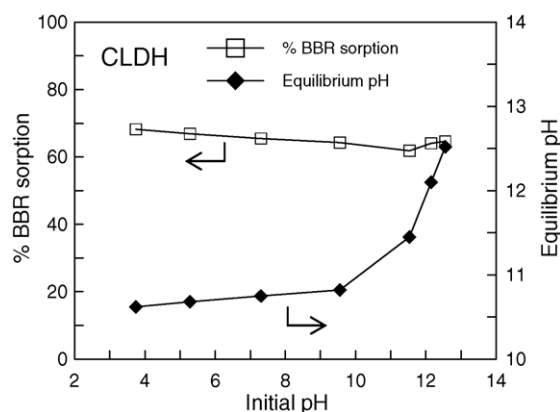


Fig. 5. Effect of initial pH on Brilliant Blue R (BBR) sorption by calcined layered double hydroxides (CLDHs) and on equilibrium pH.



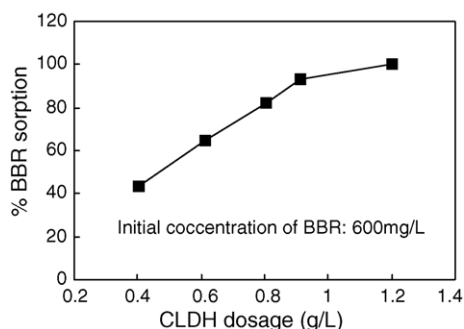


Fig. 6. Effect of calcined layered double hydroxides (CLDHs) dose on Brilliant Blue R (BBR) sorption.

### 3.5. Effect of adsorbent dosage

Effect of CLDH dosage on BBR sorption is shown in Fig. 6. Percentage BBR sorbed increased almost linearly with increasing dosage of CLDHs before a complete removal of BBR, probably implying that the amount of sorption sites also increased linearly with increasing dosage of CLDHs during structural reconstruction. When a 600 mg/L BBR solution was treated using 0.9 g/L CLDHs, the % BBR sorbed reached 93%, while BBR was completely sorbed using 1.2 g/L CLDHs. These results suggest that CLDHs are very efficient sorbents for anionic dyes and are particularly suitable to remove anionic dyes of relatively high concentrations. Compared with data reported previously (Table 3), chitosan products and cation surfactant-modified clays are generally highly effective adsorbents for dyes. Efficiency of CLDHs for anionic dye removal is much higher than that of most low-cost solid waste adsorbents and is somewhat higher than that of much more expensive activated carbon adsorbents produced from agricultural waste products. Efficiency of LDHs is equivalent to that of some low-cost ad-

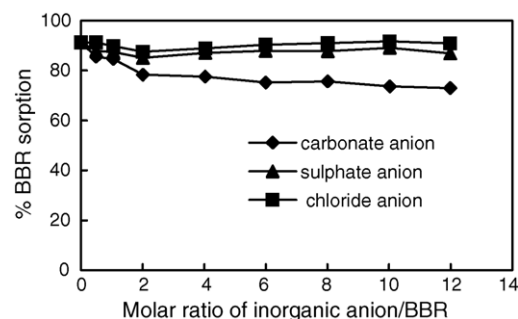


Fig. 7. Effect of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  on Brilliant Blue R (BBR) sorption.

sorbents. Unfortunately, a direct comparison of the sorption capacities between our data and those previously reported by other authors is unreasonable due to different structures and molecular sizes of the dyes studied.

### 3.6. Effect of inorganic anion competition

Competition by inorganic anions  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  on BBR sorption is shown in Fig. 7. The effects of both  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  on BBR sorption were minimal. For example, the reductions in % BBR sorption was less than 7% when BBR concentration was 380 mg/L and the molar ratios of  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  to BBR were up to 12. With increasing molar ratios from 0 to 2.0, the % sorption decreased slightly and reached a minimum. With a further increase in molar ratio, the % sorbed increased slightly. When the molar ratios of  $\text{Cl}^-$  to BBR increased up to about 8.0, the % sorbed was equivalent to that in the absence of  $\text{Cl}^-$ ; with further increase in the ratios up to 12.0, the % sorbed was even slightly higher than that in the absence of  $\text{Cl}^-$ , which was probably caused by a salting out effect. A similar phenomenon was observed by Janoš et al. [11], who attributed a slight increase in anionic

Table 3

Comparison of the maximum monolayer adsorption capacities of some dyes on various adsorbents

Dyes	Sorbents	Maximum monolayer sorption Capacities (g/kg)	References
BBR	CLDHs	~615	This study
BBR	LDHs	~55	This study
BR 18	Activated sludge	180–285	[1]
BR 9	Activated sludge	170–256	[1]
Acid Red 57	Acid-activated bentonite	~642	[24]
AB 294	Acid-activated bentonite	~118	[24]
RR 189	Chitosan bead	1189–1930	[30]
RY 2	Activated sludge	333	[30] and therein
RB 2	Activated sludge	250	[30] and therein
RB 2	Rice husk	130	[30] and therein
Acid Blue 29	Peat, fly ash	14, 15	[30] and therein
Basic Blue 29	Peat, fly ash	46, 54	[30] and therein
Acid Orange 10	Activated carbon	2.3–5.8	[2]
Deorlene Yellow	Activated carbon	~200	[30] and therein
Telon Blue	Activated carbon	~160	[30] and therein
RR 222	Activated carbon	~50	[30] and therein
Acid Blue 80	Activated carbon	170–385	[31]
Acid Blue 193	Na–bentonite	242–308	[32]
Acid Blue 193	Surfactant-modified bentonite	1635–2011	[32]

dye sorption by fly ashes in the presence of  $\text{CaCl}_2$  due to the salting out effect. The % sorbed was always lower in the presence of  $\text{SO}_4^{2-}$  than in the absence of  $\text{SO}_4^{2-}$ , indicating  $\text{SO}_4^{2-}$  always suppressed BBR sorption in the present study.

Unlike the case of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , presence of  $\text{CO}_3^{2-}$  with increasing concentrations markedly and progressively suppressed BBR sorption by CLDH (Fig. 7). Percent BBR sorbed decreased rapidly from 91 to 78% when the molar ratios of  $\text{CO}_3^{2-}$  to BBR increased from 0 to 2.0, followed by a slow and progressive reduction in the % sorbed with a further increase in the ratio. The total reduction in % sorption was about 18% (from 91 to 73%) when the ratios increased up to 12. It has been demonstrated that the previously existing interlayer  $\text{CO}_3^{2-}$  ions in LDHs are difficult to be exchanged by other anions [16–18]. Our result suggests that the presence of  $\text{CO}_3^{2-}$  may suppress CLDHs ability to sorb BBR to some extent, whereas CLDHs still demonstrated a high sorption capacity even at a high molar ratio of  $\text{CO}_3^{2-}$  to BBR. Thus, the presence of  $\text{CO}_3^{2-}$  in aquatic solutions was not a critical limiting factor in the application of CLDHs as sorbents, but the effect of  $\text{CO}_3^{2-}$  should be considered in some cases.

### 3.7. Regeneration of CLDHs

As an adsorbent, re-use is economically important. Ulibarri et al. [12] proposed that both CLDHs and LDHs are capable of being regenerated based on the “memory effect” of CLDHs. By combustion at 450–500 °C, adsorbed organic pollutants can be almost completely eliminated and used LDH or CLDH sorbents reconverted into CLDH-like materials for re-use. These authors reported that after one cycle of trinitrophenol/trichlorophenol adsorption and combustion of LDHs, the thermally treated materials exhibited almost the same sorption capacity as the original LDH. Orthman et al. [15] reported that after one cycle of thermal regeneration of spent LDHs at 723 K, the calcined solid demonstrated shorter equilibrium time and better ability to remove anionic synthetic dyes Acid Blue 29 and Eosin B than the original LDHs. Crepaldi et al. [13] also reported that combustion is feasible for CLDH/LDH regeneration af-

ter sorption of terephthalate with only small and progressive reduction (10%) in sorption capacity up to five times of thermal recycling. But Shin et al. [25] observed extensive loss of adsorption capacity for phosphorus compounds after the fifth thermal cycle of LDHs, compared with the original one.

Sorption of BBR using the regenerated CLDHs as sorbents after three times of thermal recycling is shown in Fig. 8. After the first-cycle regeneration, % BBR sorbed and CLDH sorption capacities decreased by 69% (from 78 to 9%) and 88% (from 505 to 59 mg/g), respectively, compared with the original CLDHs. The progressive reduction after the second-cycle regeneration was small, only from 9 to 7.5%. The total reduction in BBR sorption capacity was relatively large (70.5%).

The % sorbed and sorption capacity of the regenerated materials was larger than those of the original LDHs after the first thermal cycle, whereas the % sorption after the third cycle significantly decreased compared with the original LDHs (Fig. 8b). This indicates that thermal regeneration of the used LDHs/CLDHs for re-use is feasible only within the first two cycles, after which the regenerated materials will suffer from a large loss in their sorption capacities. The large loss is probably due to progressively decreasing crystallinity of the LDH-like materials in structural reconstruction after each thermal regeneration. Ulibarri et al. [22] have proposed that poor crystallinity is one of important factors reducing sorption capacity of LDHs. Similarly, the poor crystallinity of regenerated LDH-like materials is expect to reduce their sorption capacities. It should be pointed out that certain amounts of thermally decomposed compounds of BBR were probably incorporated into the mixing metal oxides after the second and third thermal regenerations, because the color of the heated materials became pale yellow compared with pure white color of the original LDHs or CLDHs. Incorporation of BBR probably disturbed the structural reconstruction of the heated materials and thus decreased their crystallinity and sorption capacities. The reasons for the different thermal recyclability of CLDHs between our study and other authors are not known, but it is worthy to point out that varying chemical compounds of adsorbed inorganic/organic anions are probably one of the im-

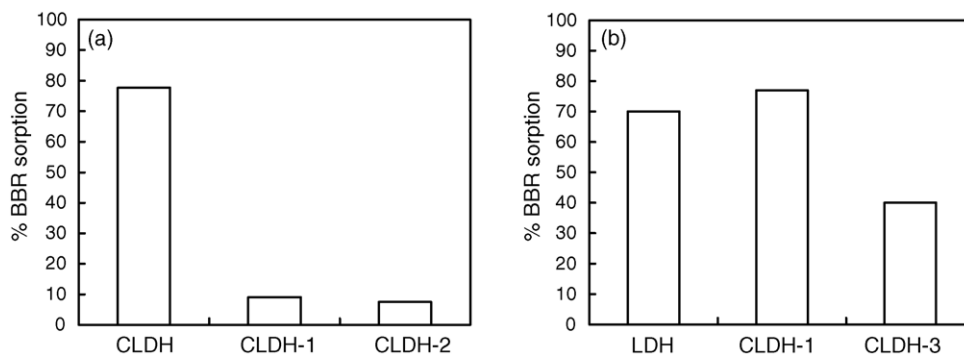


Fig. 8. Comparison of BBR sorption between original LDHs/CLDHs and thermally regenerated materials from used CLDHs. (a) Initial BBR concentration is 1000 mg/L; (b) initial BBR concentration is 130 mg/L. CLDH-1, CLDH-2 and CLDH-3 are the products after the first-, second- and third-cycle thermal regenerations of CLDH, respectively. BBR: Brilliant Blue R; LDHs: layered double hydroxides; CLDHs: calcined LDHs.

portant factors affecting LDH/CLDH thermal regeneration, for which a further study is needed.

#### 4. Conclusion

In batch sorption studies, equilibrium time required for BBR sorption by CLDHs was much shorter than those by LDHs. Sorption capacities of CLDHs were much higher than that of LDHs. CLDHs could possibly be used to remove anionic dyes of relatively high concentrations, whereas LDHs may only be used to remove anionic dyes of low concentrations.

Sorption isotherms for BBR retention by CLDHs and LDHs were well described using the Freundlich and Langmuir equations, respectively. When initial pH of BBR solutions was lower than 8.0, final pH after adsorption equilibrium ranged between 10.6 and 10.8, and the effect of initial pH (<8.0) on BBR sorption was minimal. When molar ratios of inorganic anions to BBR vary from 0 to 12, both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  had a minor impact on BBR sorption by CLDH, but in the presence of  $\text{CO}_3^{2-}$  there was a remarked reduction in BBR sorption. This effect should be considered in the application of CLDHs as sorbents.

Thermal regeneration for re-use of LDHs/CLDHs after BBR sorption was feasible only within the first two cycles, after which the regenerated materials suffered from a dramatic loss in their sorption capacities.

#### Acknowledgements

Financial support from the National Natural Science Foundation of China (Project 49904005) is gratefully acknowledged. The authors also thank Prof. Wen-Zheng Wang for his help in X-ray diffraction analysis.

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