Effective Removal of Anionic Dye by Ni-Zn-Cr-Ldhs Prepared from Electroplating Wastewater via Accelerated Carbonation

Guoqing Zhang, Chong Liu, Jun Zhao, Ji Zhi Zhou, Guangren Qian,
Jianyong Liu, Yueying Wu*

School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, PR China

ABSTRACT

A novel Layered double hydroxide (LDH) was synthesized by accelerated carbonation in Ni-Zn-Cr-bearing wastewater for dye removal from aqueous solution. The obtained Ni-Zn-Cr-LDHs materials were characterized by XRD, FT-IR, SEM and BET surface area techniques. The removal of a dye, Acid Scarlet GR (GR), from aqueous solution onto the synthesized Ni-Zn-Cr-LDHs products was studied under varying conditions of pH, adsorbent dose and contact time. The maximum adsorption amount of GR was 122 mg/g LDH at 298 K and slight increased with temperature increasing. The adsorption isotherms were well fitted by the Langmuir equation, and the adsorption capacity increased with rising temperature. The adsorption kinetics of GR onto Ni-Zn-Cr-LDH could be described by the intra-particle diffusion model. The experimental results indicate that Ni-Zn-Cr-LDHs will be an efficient adsorbent for removing anionic dye wastewater.

Keywords：Ni-Zn-Cr-LDH; Acid Scarlet GR; Adsorption; Electroplating wastewater.

1. INTRODUCTION

Electroplating wastewaters contain a number of heavy metal cations, such as Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cr^{3+} (Ajmal et al., 2001), which are substantially toxic to human health and the environment. Even though, these cations can be transformed into valuable materials if suitably recovered (Cesteros et al., 2001; Yu et al., 2007; Silva et al., 2009).

Layered double hydroxides (LDHs), a class of anionic clays with a high anion exchange capacity and a large surface area, are well-known effective adsorbents for removing various anionic pollutants (Goh et al., 2008). The general formula of LDHs is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} is divalent metal (Mg^{2+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, and/or Cu^{2+}), M^{3+} is trivalent metal (Al^{3+}, Fe^{3+}, and/or Cr^{3+}), and A^{n-} is interlayer anions (Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-} and many others) (Evance and Duan, 2006). Coprecipitation is usually used for the preparation of pure LDH, in which solution containing metals is mixed with a basic solution (such as NaOH solution) and the LDH solid is obtained via separation and drying (Braterman et al., 2004). Therefore, such a LDH preparation in wastewater provides an efficient and facile strategy for the recovery of heavy metals in effluent from industrial processes such as electroplating treatment.

Accordingly, our laboratory (Wu et al., 2009) successfully removed heavy metal in CuZnCr-LDHs from simulated wastewaters

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* *Corresponding to*: wuyy@staff.shu.edu.cn

with an accelerated carbonation method. This treatment was also applied in the removal of heavy metal from a real electroplating wastewater containing Ni^{2+}, Zn^{2+}, and Cr^{3+} and allowed the formation of pure LDH material with 99% of heavy metal removed (Zhou et al., 2010). It indicates that electroplating wastewaters can be purified through the LDH formation with accelerated carbonation.

On the other hand, the positive charge of hydroxide layers in LDH has strong affinity to the aqueous negative anions (Xu et al., 2008). It makes LDH be a promising adsorbent for the removal of anionic pollutants (Cavani et al., 1991; Goh et al., 2008). In particular, LDH was also used in the decoloration of the effluent containing dye which is one of the most important pollutants in wastewater. Compared with other adsorption treatment (Auxilio et al., 2007; Marangoni et al., 2009; Saiah et al., 2009), LDH also exhibited its efficient removal capacity of anionic dye from industrial effluent due to its strong affinity of the positive LDH layer to negative group of dye (Setti et al., 2010). Therefore, the adsorption capacity of LDH gives a potential application of LDH prepared from wastewater. However, there is few research concerning the anionic dye removal on the various heavy metals containing LDHs obtained from wastewater (Zhou et al., 2010).

Herein, the objectives of the current work are (1) to prepare LDHs with the accelerated carbonation from Ni-Zn-Cr-bearing electroplating wastewater; (2) investigate the adsorption behaviors of Acid Scarlet GR from aqueous solution. Our work suggests a sustainable strategy to recover heavy metal from wastewater and reuse the heavy metal containing as-product in organic anions removal.

2.   EXPERIMENTAL

2.1   Preparation and Characterization of Ldhs

Ni-Zn-Cr-LDH was prepared with the accelerated carbonation (Wu et al., 2009) in electroplating wastewater. Typically, wastewaters were mixed in the same way reported in previous work (Zhou et al., 2010). The mixture solution containing 0.075 M Ni^{2+}, 0.075 M Zn^{2+} and 0.05 M Cr^{3+} (Ni/Zn/Cr = 3:3:2). Stoichiometric quantities of 2 M sodium hydroxide and the mixed wastewater were simultaneously added by two constant-flow pumps separately into a 500 ml beaker under vigorous mechanical stirring. CO_2 was bubbled into the mixed solution at a constant rate at 353 K and pH of 8 in the precipitation process. After ageing for 4 hrs at this temperature, the mixture was cooled down to room temperature, and then the precipitate was filtered, washed several times with deionised water and dried at 373 K overnight. The as-prepared LDH was named as LDH-CO_2.

In comparison, the conventional co-precipitation with Na_2CO_3 mixing in NaOH solution (Sharma et al., 2008) was also performed similarly, and the LDH was denoted as LDH-Na_2CO_3.

2.2   Adsorption Experiments

To estimate the feasibility of as-prepared Ni-Zn-Cr-LDH as the adsorbent for dye wastewater treatment, Acid Scarlet GR was used as the adsorbate in this research. The basic information of GR was listed in Table 1.

Solutions with different initial GR concentrations ranging from 25 to 400 mg/L were prepared. Known amount of LDH was placed into a 100 mL conical flask and 50 mL of the synthetic dye solution was added, and then the flask was shaken in a mechanical shaker at a speed of 150 rpm at temperature of 303 K. At the end of the adsorption, the adsorbed product was collected by filtration and drying for further characterization. The concentration of GR before and after the adsorption experiment

was determined on a UV/Vis spectrophotometer at 510 nm.

For investigating the effect of initial solution pH, the initial pH was adjusted with dilute HNO_3 or NaOH. The total aqueous volume added for pH adjustment never exceeded 1% of the total volume.

2.3 Chemical and Physical Characterizations

The inductively coupled plasma-atomic emission spectrometry (ICP-AES, LEEMAN Prodigy) was used to determine the concentration of heavy metals in solution. For the component in solid sample, the precipitate was dissolved in 0.1M HNO_3 solution before the ICP-AES analysis.

The powder X-ray diffraction (XRD) was recorded on a D/max RB diffractometer (Rigaku Co.) with Cu Kα radiation at 45 kV and 40 mA. Fourier transform infrared (FTIR) spectrum was collected on a Perkin-Elmer 2000 FTIR in the range of 4000–400 cm^{-1} with resolution of 4 cm^{-1} using the KBr pellet technique. The morphology of solid samples was performed on a scanning electron microscope (SEM, JSM-6360). The specific surface area was derived using Brunner-Emmett -Teller (BET) method to analyze the low temperature N_2 adsorption isotherm on a Quantachrome NOVA-1200 gas absorption analyzer.

3. Results and Discussion

3.1 Characteristics of Ni-Zn-Cr-LDH

The XRD patterns of two samples are shown in Fig. 1a. Both of the patterns exhibit the characteristic reflections of LDHs materials, consisting of three intense lines at low 2θ angles corresponding to planes (003), (006), and (012), and the peak at about 62º (2θ) attributed to (110) plan (Xu and Zeng, 2001). The interlayer distance (d_{003}) of LDH-CO_2 is 0.75 nm, and LDH-Na_2CO_3 0.77 nm. It is noting that the peak intensities of LDH-CO_2 are higher and shaper than those of LDH-Na_2CO_3, indicating a better crystallinity. The XRD patterns illustrate that a hydrotalcite-like compound synthesized by the accelerated carbonation with a better crystallinity than that prepared by the conventional co-precipitation.

The FTIR spectra of two samples are shown in Fig. 1b. Obviously, the spectra are similar to that of hydrotalcite-like compounds (Zhang et al., 2004) in which the typical vibrations at 3424 cm^{-1} (v_{OH}), 1640 cm^{-1} δ (H_2O) and 760 and 517 cm^{-1} (M-O bond stretching vibration) were recorded. In particular, two adsorption bands observed at 1360 and 1477-1480 cm^{-1} are assigned to the a split asymmetric stretching modes of the interlayer carbonate (v_3) while the band at 1384 cm^{-1} indicated a bit NO_3^- residue with the LDH (Frost et al., 2003).

Table 1 Textual property of Acid Scarlet GR

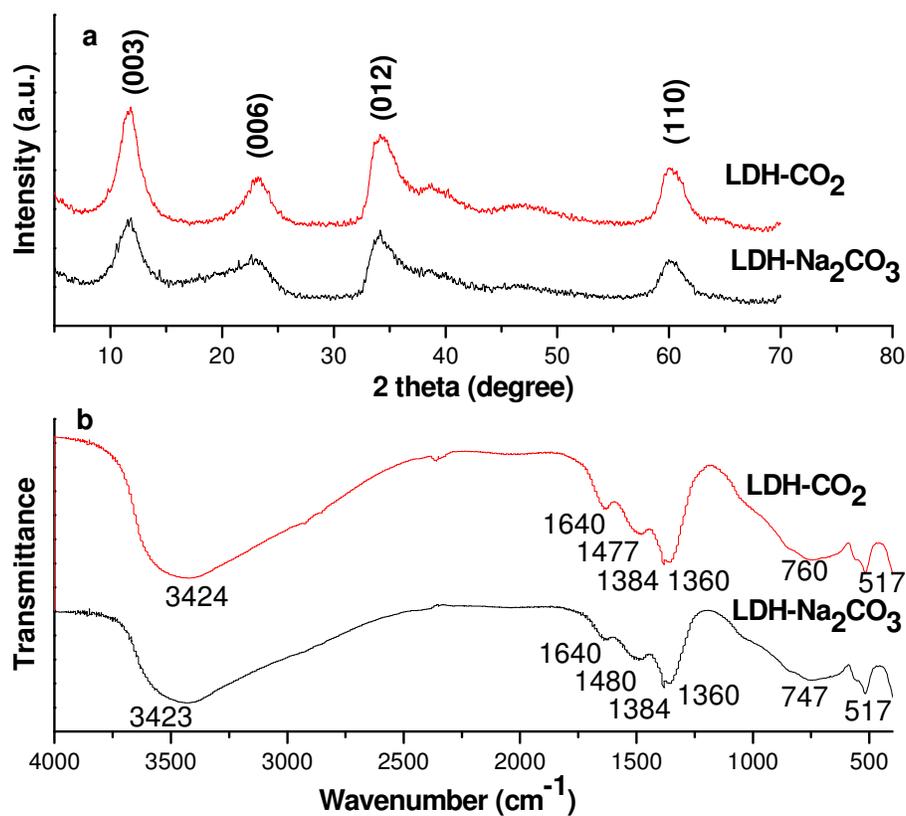| Color Index Name	Color Index No.	M_w	Maximum wavelength (λ_{max})	Chemical structure
Acid Red 73	27290	556.5	510 nm	

Figure 1 XRD patterns (a) and FTIR spectra (b) of LDH-CO$_2$ compared with those of LDH-Na$_2$CO$_3$
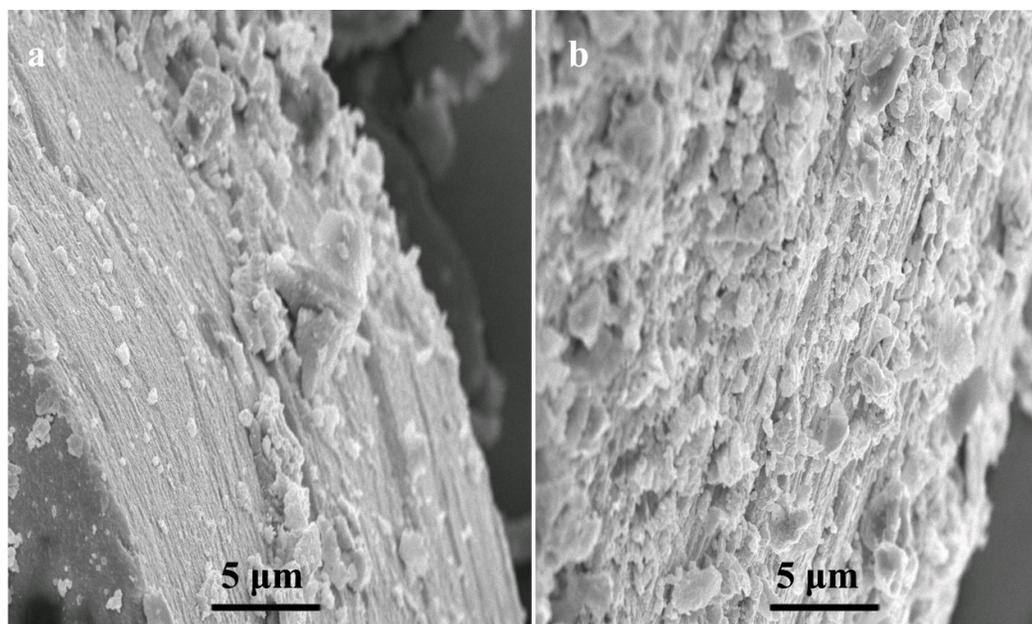
Figure 2 Scanning electron micrographs of (a) LDH-CO$_2$ and (b) LDH-Na$_2$CO$_3$

Table 2   Textual property of LDH-Na$_2$CO$_3$ and LDH-CO$_2$

Sample	Ni/Zn/Cr (theoretical)	Ni/Zn/Cr (EDX)	SSA (m^2/g)	Pore diameter (nm)	Pore Volume (cm^3/g)
LDH-Na$_2$CO$_3$	3:3:2	2.7:2.9:2	98	2.499	0.117
LDH-CO$_2$	3:3:2	2.6:2.7:2	123	2.200	0.139
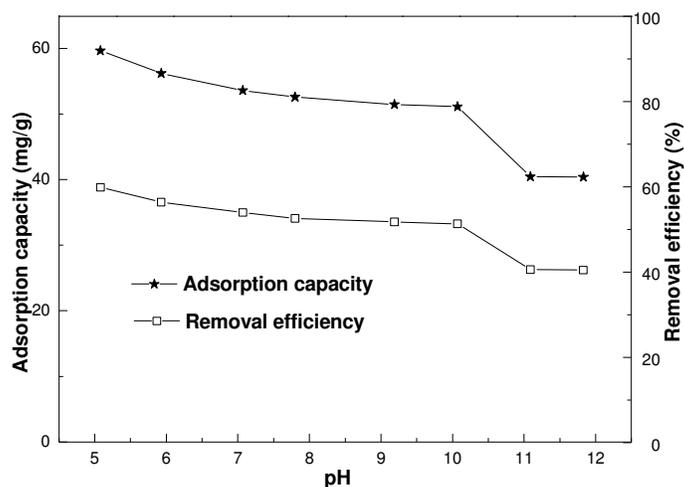
(a)
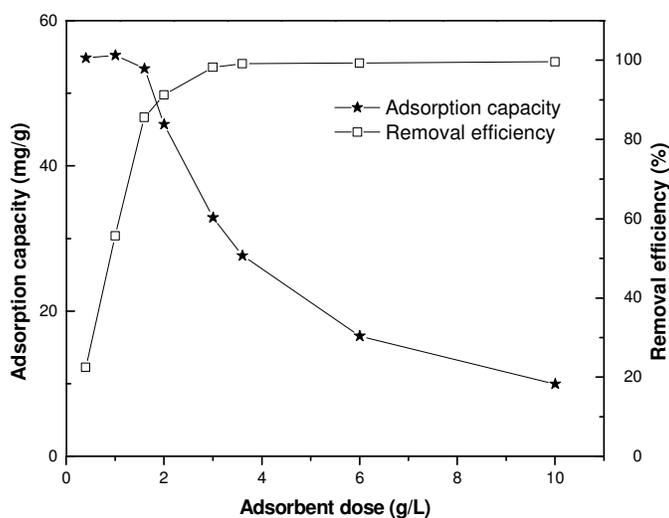
(b)

Figure 3   Effect of pH (a) and adsorbent dose (b) on the removal of GR by LDH

The SEM images (Fig. 2) show that as-prepared LDH-CO$_2$ and LDH-Na$_2$CO$_3$ have a similar layered structure made of a stacking of slices with the typical layered structure. LDH-CO$_2$ has more uniform slices, probably due to CO$_2$ bubbling that makes the precipitation to smoothly take place. The Ni/Zn/Cr values (by EDX) of LDH-Na$_2$CO$_3$ and LDH-CO$_2$ are approximate to the theoretical values (Table 2), indicating a high removal efficiency of heavy metal ions. In addition, LDH-CO$_2$ has a larger specific area

and pore volume and a smaller pore diameter (Table 2). In this connection, LDH-CO$_2$ was chosen as the adsorbent for GR removal from aqueous solution in the following studies.

3.2   Effect of pH on the Adsorption Process

Generally, pH is considered to be an important parameter that controls the adsorption at water-adsorbent interfaces. It is known that LDH is not so stable and the quick dissolution is obvious at lower pH (pH below 5.0) (Musumeci et al., 2010). Therefore, the adsorption of GR (100 mg/L) by LDH was studied at a pH range from 5.0 to 12.0 at 303 K (Fig. 3a).

Obviously, the adsorption capacity and removal efficiency decreased slightly at pH from 5.0 to pH 10.0. With the further increasing in pH, an apparent fall in the adsorption capacity and removal efficiency was observed. This is consistent with the results reported in other adsorption studies (Özcan and Özcan, 2004; Das et al., 2006). It was due to the competition of anion with OH$^-$. As pH increases, there were more hydroxyl ions, which competed with the dye anions to occupy the adsorption sites. It resulted to a lower adsorption amount of dye. The results showed that aqueous dye could be effectively removed over a wide pH range (pH = 5.0-12.0) with as-prepared LDHs. In addition, the variation of removal efficiency at pH 5.0-10.0 was not remarkable, so in the following experiments the initial pH of GR solution (6.4) was not adjusted anymore. After the treatment of the colorful water at various pH, the concentrations of Cr in the filtration conducted by ICP-AES were all below 0.3 mg/L (0.28, 0.22, 0.20, 0.19, 0.18, 0.15, 0.14, 0.12 mg/L for pHs of 5.0-12.0). This indicates the concentrations of Cr in the treated water can meet the Integrated Wastewater Discharge Standard (GB 8978-1996).

3.3   Effect of Adsorbent Dose

The effect of adsorbent dose on the extent of removal of GR (100 mg/L) at 303 K for 24 h is shown in Fig. 3b. An increase in the solid content generally resulted in an increase in the removal efficiency, while the adsorption capacity with respect to GR dye decreased. The influence of increasing adsorbent dose was mainly related to the resulting increased in surface area, which lead to higher numbers of adsorption sites and an increasing in removal efficiency. However, while the adsorbent dose (3.6 g/L) was excess in comparison with adsorbate, further raising the adsorbent dose has little effect on increasing the removal efficiency.

On the other hand, a higher adsorbent dose resulted in a lower adsorption capacity at a fixed GR concentration (100 mg/L), as shown in Fig. 3b. This illustrates that the surface sites of the adsorbent are heterogeneous (Catts and Langmuir, 1986). According to the surface site heterogeneity model, the adsorbent surface is composed of sites with a wide spectrum of binding energies. At lower adsorbent dose, all types of sites are used to adsorb, showing a higher adsorption capacity. Whereas at a higher adsorbent dose, only the fraction of lower energy sites is occupied, resulting in a lower adsorption capacity (Liao and Shi, 2005).

3.4   Adsorption Isotherms

The adsorption isotherms of GR on LDH-CO$_2$ were taken by adding 0.10 g LDH into 50 ml GR solution (100 mg/L) with a contact time of 24 h at various temperatures. The results are shown in Fig. 4a.

The pattern of four curves is similar and the adsorption capacity increased with rising temperature and increasing equilibrium concentration of GR. The data were further analyzed by the Langmuir and Freundlich equations, and Langmuir equation (Eq. 1)

(Langmuir, 1916) gave a more satisfactory fitting to the adsorption isotherms:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \qquad (1)$$

where C_e is equilibrium concentration (mg/L); Q_e is adsorption capacity (mg/g); Q_m is theoretical adsorption capacity (mg/g); K_L is the Langmuir adsorption constant (L/mg).

The fitted Langmuir parameters, Q_m and K_L (Table 3), increased with the temperature increasing. A higher reaction temperature could provide the dye a higher chance being adsorbed onto the adsorbent with an enhanced adsorption capacity (Sohn and Kim, 2005). The fitted results demonstrated that the chemical adsorption mechanism might be involved in the adsorption process and the adsorption process might be monolayer.

It was reported that the adsorption amount of GR by sludge-based activated carbon and modified bentonite was 14.6 and 42.2 mg/g (Wang et al. 2008; Li et al. 2010), respectively. In comparison, the LDH adsorbent in current work showed a higher adsorption capacity of GR as more than 122 mg/g of GR removed (Table 3). This difference provides a promising application of prepared LDH in anionic dye removal.
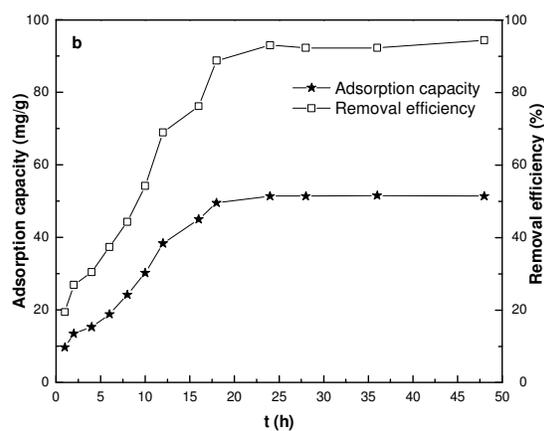
3.5 Adsorption Kinetic

The adsorption kinetic experiments were carried out for a contact time ranging from 1 to 48 h at 303 K with the GR concentration of 100 mg/L. The data are presented in Fig. 4b.

Table 3   Parameters of Langmuir adsorption models at various temperatures

Temperature (K)	K_L (L/mg)	Q_m(mg/g)	r^2
298	0.057	122.5	0.973
303	0.096	123.3	0.979
313	0.135	124.5	0.982
323	0.137	128.5	0.989
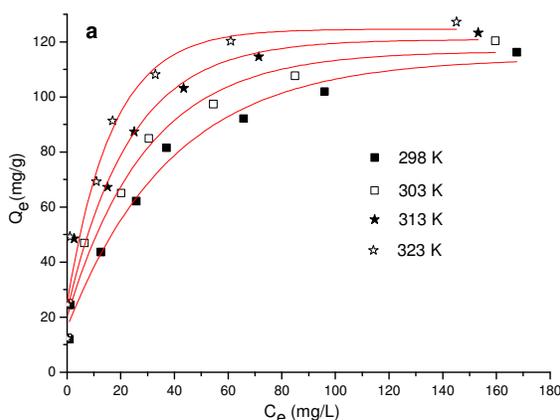
(a)   (b)

Figure 4   Adsorption isotherms (a) and kinetics (b) of GR on LDH

Table 4 Kinetic parameters and correlation coefficients (R^2) for the four common kinetic models in the adsorption process

Kinetic models	Parameter equations	Fitting parameters
Pseudo-first order (Lagergren, 1898)	$\dfrac{1}{Q_t} = (\dfrac{K_1}{Q_{m1}})(\dfrac{1}{t}) + \dfrac{1}{Q_{m1}}$	**R^2 = 0.933** K_1^w=2.947 Q_{m1}^x = 34.97
Pseudo-second order (Ho and Mckay, 1998)	$\dfrac{t}{Q_t} = \dfrac{1}{K_2 Q_{m2}^2} + \dfrac{1}{Q_{m2}}t$	**R^2=0.916** K_2^w =0.0014 Q_{m2}^x=65.06
Elovich (Goh et al., 2009)	$Q_t = (\dfrac{1}{b})\ln(ab) + (\dfrac{1}{b})\ln t$	**R^2=0.926** a^y =15.91 b^y = 0.0829
Intra-particle diffusion (Satterfield et al., 1973)	$Q_t = K_p t^{1/2} + C$	**R^2=0.979** K_p^w =10.28 C^z = -3.32

Note: [w] rate constant of kinetic process; [x] the maximum adsorption capacity; [y] Elovich constant, where *a* is related to the sorption rate while b is related to the surface coverage. [z] intercept of the kinetic equation

The adsorption capacity and removal efficiency increased with the contact time and then attained an adsorption equilibrium plateau. Specifically, the adsorption capacity was enhanced by five times from 9.7 mg/g at 1 h to 47.2 mg/g at 24 h. Further extension of the contact time did not further increase the adsorption capacity and removal efficiency.

Kinetic models can estimate the adsorption rate, obtain the suitable rate expression and reveal the possible reaction mechanism. The equilibrium data of Fig. 4b (the data in 1-24 h) were fitted by four common kinetic models. To quantity the applicability of each model, the kinetic parameters and correlation coefficients (R^2) were calculated, as listed in Table 4. The correlation coefficient (R^2) for the intra-particle diffusion model is the highest (R^2 = 0.979), indicating that the intra-particle diffusion model, which is the generally rate-limiting step for the systems with high concentration of the adsorbate, good mixing, large particle size of adsorbent and low affinity towards adsorbent is the most suitable model to describe the adsorption kinetics of GR on LDH-CO_2.

CONCLUSIONS

Ni-Zn-Cr-LDH was successfully synthesized from simulated Ni-Zn-Cr-bearing wastewater in the accelerated carbonation, and showed the effective adsorption of GR from aqueous solutions. The adsorption capacity was slightly dependent on the solution pH, but highly dependent on the adsorbent dose. The adsorption isotherms implied that GR were adsorbed in the form of monolayer. The kinetics study indicated the intra-particle diffusion model better described the adsorption process of GR onto Ni-Zn-Cr-LDH. The results showed that Ni-Zn-Cr-LDH is a promising material for dye wastewater treatment and this method will explore a new way for electroplating wastewaters and anionic dye wastewater treatment.

Shanghai University (Shanghai, P.R. China) for XRD and SEM characterizations.

REFERENCES

Ajmal, M., Rao, R.A.K., Ahmad, R., Ahmad, J., Rao, L.A.K. (2001). Removal and recovery of heavy metals from electroplating wastewater by using Kyanite as an adsorbent. *J. Hazard. Mater.*, B 87, 127-137.

Auxilio, A.R., Andrew, P.C., Junk, P.C., Spiccia, L., Neumann, D., Raverty, W., Vanderhoek, N. (2007). Adsorption and intercalation of Acid Blue 9 on Mg-Al layered double hydroxides of variable metal composition. *Polyhedron*, 26, 3479-3490.

Braterman, P.S., Xu, Z.P. and Yarberry, F. (2004). Layered Double Hydroxides(LDHs). In: S.M. Auerbach, K.A. Carrado and P.K. Dutta (Editors), Handbook of Layered Materials. Marcel Dekker, New York, pp. 373.

Catts, J.G., Langmuir, D. (1986). Adsorption of Cu, Pb and Zn by δMnO2: applicability of the site binding-surface complexation model. *Appl. Geochem.*, 1, 255-264.

Cavani, F., Trifirò, F. and Vaccari, A. (1991). Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catal. Today*, 11: 173-301.

Cesteros, Y., Salagre, P., Medina, F., Sueiras, J.E., Tichit, D., Coq, B. (2001). Hydrodechlorination of 1,2,4-trichlorobenzene on nickel-based catalysts prepared from several Ni/Mg/Al hydrotalcite-like precursors. *Appl. Catal. B Appl. Catal.*, B32, 25-35.

Das, J., Patra, B.S., Baliarsingh, N., Parida, K.M. (2006). Adsorption of phosphate by layered double hydroxides in aqueous solutions. *Appl. Clay Sci.*, 32, 252-260.

Evance, D.G., Duan, X. (2006). Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine. *Chem. Comm.*, 2006(5), 485-496.

Frost, R.L., Weier, M.L., Clissold, M.E., Williams, P.A. (2003). Infrared spectroscopic study of natural hydrotalcites carrboydite and hydrohonessite. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 59, 3313-3319.

Goh, K.H., Lim, T.T., Dong, Z.L. (2008). Application of layered double hydroxides for removal of oxyanions: A review. *Water Res.*, 42, 1343-1368.

Goh, K.H., Lim, T.T. and Dong, Z.L. (2009). Enhanced Arsenic Removal by Hydrothermally Treated Nanocrystalline Mg/Al Layered Double Hydroxide with Nitrate Intercalation. *Environ. Sci. Technol.*, 43: 2537-2543.

Ho, Y.S., Mckay, G. (1998). Sorption of dye from aqueous solution by peat. *Chem. Eng. J.*, 70, 115-124.

Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *K. Sven. Vetenskapsakad. Handl.*, Band 24, 1-39.

Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. part i. solids. *J. Am. Chem. Soc.*, 38, 2221-2295.

Liao, X.P., Shi, B. (2005). Adsorption of Fluoride on Zirconium (IV)-Impregnated Collagen Fiber. *Environ. Sci. Technol.*, 39, 4628-4632.

Li, Q., Yue, Q., Su,Y., Gao, B., Sun, H. (2010). Equilibrium, thermodynamics and process design to minimize adsorbent amount for the adsorption of acid dyes onto cationic polymer-loaded bentonite. *Chem. Eng. J.*, 158, 489-497

Marangoni, R., Bouhent, M., Guého, C.T., Wypych, F., Leroux, F. (2009). Zn$_2$Al layered double hydroxides intercalated and adsorbed with anionic blue dyes: A physico-chemical characterization. *J. Colloid Interface Sci.*, 333, 120-127.

Musumeci, A.W. et al. (2010). Synthesis and characterization of dual radiolabeled lay-

ered double hydroxide nanoparticles for use in In-vitro and In-vivo nanotoxicology studies. *J. Phys. Chem. C*, 114(2): 734-740.

Özcan, A.S., Özcan, A. (2004). Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite. *J. Colloid Interface Sci.*, 276, 39-46.

Satterfield, C. N.; Colton, C. K.; Pitcher, W. H., Jr. (1973). Restricted diffusion in liquids within fine pores. *AIChE J.*, 19, 628-635.

Saiah, F.B.D., Su, B.L., Bettahar, N. (2009). Nickel-iron layered double hydroxide (LDH): Textural properties upon hydrothermal treatments and application on dye sorption. *J. Hazard. Mater.*, 165, 206-217.

Setti, N.D., Jouini, N. and Derriche, Z. (2010). Sorption study of an anionic dye - benzopurpurine 4B-on calcined and uncalcined Mg-Al layered double hydroxides. *J. Phys. Chem. Solids*, 71, 556-559.

Sharma, U., Tyagi, B., Jasra, R.V. (2008). Synthesis and Characterization of Mg-Al-CO_3 Layered Double Hydroxide for CO_2 Adsorption. *Ind. Eng. Chem. Res.*, 47, 9588-9595.

Silva, C.G., Bouizi, Y., Fornes, V., Garcia, H. (2009). Layered double hydroxides as highly efficient photocatalysts for visible light oxygen generation from water. *J. Am. Chem. Soc.*, 131, 13833–13839.

Sohn, S., Kim, D. (2005). Modification of Langmuir isotherm in solution systems-definition and utilization of concentration dependent factor. *Chemosphere*, 58, 115-123.

Wang, X., Zhu, N., Yin, B. (2008). Preparation of sludge-based activated carbon and its application in dye wastewater treatment. *J. Hazard. Mater.*, 153, 22-27

Wu, Y.Y., Bai, H.M., Zhou, J.Z., Chen, C.X., Xu, X., Xu, Y.F., Qian, G.R. (2009). Thermal and chemical stability of Cu-Zn-Cr-LDHs prepared by accelerated carbonation. *Appl. Clay Sci.*, 42, 591-596.

Xu, Z.P., Zeng, H.C. (2001). Abrupt Structural Transformation in Hydrotalcite-like Compounds $Mg_{1-x}Al_x(OH)_2(NO_3)_x \cdot nH_2O$ as a Continuous Function of Nitrate Anions. *J. Phys. Chem.*, B 105, 1743-1749.

Xu, Z.P., Jin, Y.G., Liu, S.M., Hao, Z.P. and Lu, G.Q. (2008). Surface charging of layered double hydroxides during dynamic interactions of anions at the interfaces. *J. Colloid Interface Sci.*, 326, 522-529.

Yu, J.J., Tao, Y.X., Liu, C.C., Hao, Z.P., Xu, Z.P. (2007). Novel NO trapping catalysts derived from Co-Mg/X-Al (X = Fe, Mn, Zr, La) hydrotalcite-like compounds. *Environ. Sci. Technol.*, 41, 1399-1404.

Zhang, L.H., Li, F., Evans, D.G, Duan, X. (2004). Structure and surface characteristics of Cu-based composite metal oxides derived from layered double hydroxides. *Mater. Chem. Phys.*, 87, 402-410.

Zhou, J.Z. et al. (2010). Effective Self-Purification of Polynary Metal Electroplating Wastewaters through Formation of Layered Double Hydroxides. *Environ. Sci. Technol.*, 44, 8884-8890.