

出國報告 (出國類別: 國際會議)

4th European Chemistry Congress

服務機關：國立高雄應用科技大學 化材系

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摘要

This investigation employed the co-precipitation method to generate MgAl layered double hydroxides (LDHs). Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and alumina nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as precursors in the formation of Mg and Al, respectively, to generate MgAl LDHs. Samples with Mg/Al ratios of 1 and 2 are denoted as MgAl1 and MgAl2, respectively, and were used as adsorbents to decolorize C.I. Reactive Red 2 (RR2). The surface characteristics of MgAl LDHs were measured by specific surface area analysis and scanning electron microscopy. The effects of RR2 concentration, MgAl1 dose and pH on RR2 adsorption were elucidated. Kinetic analyses were performed using pseudo first- and second-order models and the intraparticle diffusion model. Equilibrium results were plotted using Langmuir, Freundlich and Temkin isotherms. The specific surface area, pore volume and pore width of MgAl1 were $43.7 \text{ m}^2/\text{g}$, $0.16 \text{ cm}^3/\text{g}$ and 36 nm , respectively; and those of MgAl2 were $6.5 \text{ m}^2/\text{g}$, $0.03 \text{ cm}^3/\text{g}$ and 53 nm , respectively. The regression results revealed that the adsorption kinetics were more accurately represented by a pseudo second-order model and the equilibrium results were most accurately fitted using the Temkin isotherm. The RR2 adsorption efficiency of MgAl1 exceeded that of MgAl2. Increasing the MgAl1 dosage increased RR2 adsorption, whereas increasing the RR2 concentration or pH reduced RR2 adsorption. The maximum RR2 adsorption capacity of MgAl1 at pH 3 was 153.9 mg/g .

目的

至 4th European Chemistry Congress，發表"Decolorization of azo dye wastewater by MgAl layered double hydroxides"一文。

過程

本次會議於西班牙巴塞隆納舉行(05/11/2017-05/13/2017)，本人於 05/09/2017 啟程，05/10/2017 於杜拜轉機，05/10/2017 抵達西班牙巴塞隆納，05/11/2017 報到並於 05/12/2017 進行論文發表，05/14/2017 啟程返台，於杜拜轉機後於 05/15/2017 抵台。本次 4th European Chemistry Congress 論文以口頭及海報兩種型態進行，大會邀請專家及學者參與，針對有機化學、無機化學、分析化學、綠色化學、物理化學、藥理生物化學、生物化學、環境化學、材料化學、理論化學、石油化學、聚合物化學、藥物化學、合成化學、和奈米科技及應用等 15 個議題進行報告，本人報告內容屬環境化學範圍。此次受邀之專題講者有 Dr. Janis Gravitis (Latvian State Institute of Wood Chemistry, Latvia)，Dr. Vakhtang Barbakadze (Tbilisi State Medical University, Georgia)，Dr. Daniel T Gryko (Polish Academy of Sciences, Poland)，Dr. Maia Merlani (Tbilisi State Medical University, Georgia)，Dr. Radovan Buffa (Contipro Pharma, Czech Republic)，Dr. Andreia Valente (Universidade de Lisboa, Portugal)，Dr. Halina Abramczyk (Lodz University of Technology, Poland)，Dr. Ionel I Mangalagiu (AlIcuza University of Iasi, Romania)，Dr. Changjian Feng (University of New Mexico, USA)，Dr. Marc Le Borgne (University of Lyon, France)，Dr. Linghai Xie (Nanjing University of Posts & Telecommunications, China)，Dr. Injae Shin (Yonsei University, Korea)，Dr. Luc Jaeger (University of California, USA)，Dr. Violina T Angelova (Medical University of Sofia, Bulgaria)，及 Dr. Silvia Antonia Brandan (Institute of Inorganic Chemistry, Argentina)共 15 位來自世界的專家學者，本次 4th European Chemistry Congress 會議共有 64 篇論文發表，參與人員來自新加坡、台灣、韓國、馬來西亞、澳洲、英國、印度、美國、印尼、西班牙、瑞士、俄羅斯、墨西哥、喬治亞、法國、威爾斯、南非、義大利、羅馬尼亞、厄瓜多、烏克蘭、德國、黎巴嫩、約旦、埃及、英國、科威特、日本、阿爾及利亞、委內瑞拉、剛果、土耳其、沙烏地阿拉伯、摩洛哥及泰國等三十五國，會議議程相當豐富。本人於此次大會發表"Decolorization of azo dye wastewater by MgAl layered

double hydroxides"一文，會後並與多名學者進行意見交流。

與會心得與建議事項

這次出國參加的會議是4th European Chemistry Congress，發表"Decolorization of azo dye wastewater by MgAl layered double hydroxides"一文。在會議的過程中不只聽到了一些與自己研究有相關的演講外，還可以聽到其他的研究以增加自己的知識。藉由參加這次研討會，不但增加了許多新知也得到許多的資訊，而這些資訊讓我可以了解各國實驗室的實驗進展，也可以督促自己研究之腳步。本次在研討會接觸到較多歐洲來之學者，本次我投稿論文之領域為環境化學，在會議上我亦特別關注此領域之研究。俄羅斯學者提出利用植物油從水溶液中提取稀土元素Ce的應用(Application of vegetable oils for extraction of rare-earth elements from water solutions)及將混合奈米催化劑表面(Nano- $\text{Al}_2\text{O}_3+\text{CuO}$)的一氧化碳轉化為二氧化碳的動力學，以減少車輛排放(The kinetics to conversion of carbon monoxide to carbon dioxide on the surface of mixed nano-catalyst for reduce the vehicles emissions)都是極為新穎之想法。土耳其學者建議二氧化碳是潛在的合適碳資源，可以在許多合成應用中部分替代石油和天然氣(CO_2 Utilisation: Waste or Resource for Chemical Industry)，阿爾及利亞學者發明一種膨潤土/聚丙烯酰胺微複合材料作為水處理新材料(Bentonite/polyacrylamide micro-composites - New materials for water treatment)，該材料第一次使用於水處理之浮除程序中。和本次投稿論文類似之吸附文章，約旦學者以一種特殊C-4-溴苯基鈣-[4]間苯二酚作為吸附劑(Adsorption studies of some heavy metal ions onto C-4-bromophenylcalix-[4]resorcinarene)，使用合成吸附劑(C-4-溴苯基鈣-[4]-間苯二酚)對重金屬(Pb(II), Co(II), Cu(II), Mn(II), Zn(II))進行吸附研究，結果指出擬二階模型得到的速率常數值大小順序為Co(II) > Cu(II) > Zn(II) > Mn(II) > Pb(II)。瑞典學者利用高度多孔的生物基奈米纖維氣凝膠去除水溶液中陽離子染料(Highly porous bio-based nanofibrous aerogels for removing cationic dyes from aqueous solutions)，會議內容極為豐富，最深之感受是歐洲學者在理學之研究，其深度及理論基礎扎實度，真是我需學習的方向。

攜回資料名稱及內容

本次攜回會議的議程書，其內容包括會議期間的流程以及各演講者與題目。

Scientific Program

4th European Chemistry Congress, May 11-13, 2017 Barcelona, Spain

Theme: Exploring recent advances in chemistry, related fields and applications

Day 1 : May 11, 2017

Advancements of Organic Chemistry

Inorganic Chemistry

Analytical Chemistry

Green Chemistry: Green chemical principles

Medical Biochemistry

Physical Chemistry

Julissa Gonzalez Villegas, University of Puerto Rico, USA

Title: Surface derivatization of zirconium phosphate nanoplatelets: Potential nanocarrier of doxorubicin anticancer drug

Deswati, Andalas University, Indonesia

Title: Application response surface methodology for determination optimization of trace zinc in environmental samples by adsorptive stripping voltammetry

Manmohan L Satnami, Pt Ravishankar Shukla University, India

Title: Mn²⁺ Doped-CdTe/ZnS modified fluorescence nanosensor for detection of glucose

Hardy Castada, The Ohio State University, USA

Title: Characterization of lamb flavor using selected ion flow tube mass spectrometry (SIFT-MS)

Don Coltart, University of Houston, USA

Title: An umpolung approach to the asymmetric-alkylation of aldehydes and ketones

Amit Adhikary, Missouri University of Science and Technology, USA

Title: Unusual atmospheric water capture and reversible structural transformation of NaGaS₂

Ismael Zamora, Lead Molecular Design S.L, Spain

Title: De-novo structural elucidation from Mass/NMR Spectra

Hansjorg Grutzmacher, ETH Zurich, Switzerland

Title: Dehydrogenations catalyzed by metal amides

Irina P. Beletskaya, Moscow State University, Russian Federation

Title: Catalysis by copper derivatives in substitution and addition reactions

Irina P. Beletskaya, Moscow State University, Russian Federation

Title: Catalysis by copper derivatives in substitution and addition reactions

Rocio Gamez-Montano, University of Guanajuato, Mexico

Title: Synthesis of methane-linked bis-heterocycles containing the 1,5-disubstituted-tetrazole moiety via Ugi-azide based methodologies

Alexander O. Terentev, ZIOC RAS, Russia

Title: Oxidative cross-dehydrogenative coupling with selective C-O bond formation

Vakhtang Barbakadze, Tbilisi State Medical University Institute of Pharmacochimistry, Georgia

Title: Plant Macromolecule from different species of Boraginaceae family, its synthetic monomer and their anticancer efficacy

Eric Pasquinet, CEA, France

Title: A new Staudinger-diaza-Wittig tandem reaction and its application to the synthesis of 1H-indazoles, 1H-benzindazoles and 1H-azaindazoles from (het)aryl azides

Davide Motta, Cardiff University, Wales

Title: Hydrogen generation from hydrous hydrazine using Ir-based nanocatalysts

Peter I. Ejidike, University of Fort Hare, South Africa

Title: In vitro Antioxidant and Anticancer Studies of Heterocyclic Schiff base Ruthenium (III) complexes: Synthesis and Characterization

Antonio Bettero, University of Padova, Italy

Title: Tenskinmetry as a conceptually innovative Tensiometric Versus Skin pathway (TVS) for non-invasive evaluation of surface energy phenomena related to the epidermal functional state and its aging critical level

Denis Lutckii, Saint-Petersburg Mining University, Russia

Title: Application of vegetable oils for extraction of rare-earth elements from water solutions

Eugenia Fagadar-Cosma, Institute of Chemistry Timisoara of Romanian Academy, Romania

Title: Sensors based on biomimetic porphyrin derivatives & their hybrid combinations with photonic nanoparticles

Samar Gewily, Dubai Police Forensic Laboratory, UAE

Title: Physical and chemical characterisation of captagon tablets seized in Dubai in 2016

Hugo Romero B, Technical University of Machala, Ecuador

Title: Development and validation of a voltammetric method for the determination of antimony in aqueous medium

Marie Colmont, University of Lille, France

Title: Towards the synthesis of novel selenium based geoinspired materials

Geeta Verma, Chandra Shekhar Azad Govt Post Graduate Nodal College, India

Title: P-BGCE - Photoreduction of Benzophenone in Green chemistry using an Alternate Solvent Ethyl Alcohol

Harish Kumar, Ch. Devi Lal University, India

Title: Synthesis of Graphene for the fabrication of Electrochemical Biosensor for the Detection of Baccilus cerrus as Biological Warfare Agent

Hanan M.F.Elnagdy, University, Dibrugarh, India

Title: Recyclable claycop/ hydrazine hydrate catalytic system for 1,2,3 triazole derivative synthesis under solvents free condition

Day 2 : May 12, 2017

Physical Chemistry

Biological Chemistry

Environmental Chemistry

Theoretical Chemistry

Materials Chemistry

Victor V. Zhirnov, Institute of Bioorganic Chemistry and Petrochemistry, Ukraine

Title: Influence of low rate β -radiation ($^{90}\text{Sr}/^{90}\text{Y}$) on transmembrane electron transport in human erythrocytes

Simon Korte, Munster University of Applied Sciences, Germany

Title: Phosphor solutions for the reduction of the time dependant intensity variation of AC LEDs

Pierre Karam, American University of Beirut, Lebanon

Title: Turning the heat on conjugated polyelectrolytes: A ratiometric nanothermometer for solution and hydrogel samples

Mohamad Hmadeh, American University of Beirut, Lebanon

Title: Synthesis and structural evolution of MOFs and ZIFs via a reaction diffusion process at room temperature

Mike Broxtermann, Munster University of Applied Sciences, Germany

Title: On the VUV luminescence and degradation of UV-C emitting phosphors

Hasanov Sadig Huseyn, Institute of Radiation Problems of National Academy Sciences of Azerbaijan, Russia

Title: The kinetics to convertation of carbon monoxide to carbon dioxide on the surface of mixed nano-catalyst for reduce the vehicles emissions

Ozge Yuksel Orhan, Hacettepe University, Turkey

Title: CO₂ Utilisation: Waste or Resource for Chemical Industry

Koo Thai Hau, Form 6 centre of SMK Taman Johor Jaya 1, Malasiya

Title: Allium cepa. L As Acid-Base indicator

Batric Pesic, University of Idaho, USA

Title: Electrodeposition of nickel on glassy carbon electrode – The rotating disk study

Solhe F. Alshahateet, Aqaba University of Technology, Jordan

Title: Adsorption studies of some heavy metal ions onto C-4-bromophenylcalix-[4]resorcinarene

Lars Baltzer, Uppsala University, Sweden

Title: Increasing affinity and selectivity for target proteins by peptide conjugation to small molecule ligands – extending interactions “just” outside of the binding pocket

Serag Ahmed Farag, National Centre for Radiation Research & Technology, Egypt

Title: Mitigation strategies of furan in coffee beans by irradiation process

Hathaikarn Manuspiya, Chulalongkorn University, Thailand

Title: Cellulose based separator membrane in Li-ion battery device

Hwan Kyu Kim, Korea University, Korea

Title: Organic semiconductor materials for high efficiency dye-sensitized solar cells

Cheolmin Park, Yonsei University, Korea

Title: Self-assembled nanomaterials for flexible photo-electronic polymer devices

Eunkyoung Kim, Yonsei University, South Korea

Title: Photothermal thin films from conductive polymers for programmable bilayers

Reem AlBilali, Cardiff University, UK

Title: Transfer dehydrogenation of 1-phenylethanol over supported palladium nanoparticles under mild conditions

Felipe Sánchez, Cardiff University, UK

Title: CNFs-supported Pd series catalysts comparison for hydrogen evolution from additive-free formic acid decomposition

Nevin Kaniskan, Anadolu University, Turkey

Title: Modelling of low band gap polymers

Rochd Sanaa, Hassan II University, Morocco

Title: Influence of different parameter in air gap membrane distillation for seawater desalination

Buhani, University of Lampung, Indonesia

Title: Synthesis of algae-silica hybrid material from Nitzschia sp. biomass through silica coating technique with magnetite nanoparticles as Pb(II) ion adsorbent in solution

Hyunwook Jung, Yonsei University, Korea

Title: First principles study on the reaction mechanisms of hydrolysis reaction of PCl_3 and POCl_3

David L Officer, University of Wollongong, Australia

Title: Moving microdroplets in 3D using photochemopropulsion

Diana Ciuculescu-Pradines, University of Toulouse, France

Title: Evaluation of the coordination of a phosphonic acid-based ligand to the surface of zerovalent iron nanoparticles

Chung-Hsin Wu, National Kaohsiung University of Applied Sciences, Taiwan

Title: Decolorization of azo dye wastewater by MgAl layered double hydroxides

Pavel Sorokin, National University of Science and Technology MISiS, Russian Federation

Title: The features of diamond nucleation on nanolevel. Prediction of diamondization of multilayered graphene

Ozge Yuksel Orhan, Hacettepe University, Turkey

Title: CO₂ utilisation: Waste or resource for chemical industry

Byunghan Han, Yonsei University, Korea

Title: Understanding underlying chemistry for renewable energy materials and environmental remedies using first principles-based computational modelings

Sara Mousavi, ZHAW Life Sciences and Facility Management, Switzerland

Title: Highly porous bio-based nanofibrous aerogels for removing cationic dyes from aqueous solutions

Zahoor Ahmad, Kuwait University, Kuwait

Title: In-situ preparation of aramid-MWCNTs nano-composites: morphology and thermal-mechanical properties

Day 3 : May 13, 2017

Petro Chemicals

Polymer Chemistry

Medicinal Chemistry

Pharmaceutical Chemistry

Nanotechnology and Applications

Synthetic Chemistry

Jung-Mi Hah, Hanyang University, Republic of Korea

Title: Targeting CNS Protein kinase as therapeutics for neurodegenerative diseases

Jae-Sang Ryu, Ewha Womans University, Republic of Korea

Title: Synthesis of 1,2,3-Triazole-linked salicylamide analogs as potent aurora kinase inhibitors

Abdeldayem R A, Mansoura University, Egypt

Title: Water, Iron and Liver Cihrrrosis

Vikrant A Adsool, ASTAR, Singapore

Title: Synthesis and biological evaluation of BCP derivatives: A steadfast effort towards introducing a contemporary lead optimization tool

Yutaka Moritomo, University of Tsukuba, Japan

Title: Prussian blue analogues as battery materials for energy science

Ali Mansri, University of Tlemcen, Algeria

Title: Bentonite/polyacrylamide micro-composites – New materials for water treatment

Fernando Ruette, Venezuelan Institute of Scientific Research, Venezuela

Title: Multidisciplinary theoretical studies of small nanostructures of carbon compounds for multiple purposes

Jean-Christophe Carry, Sanofi, France

Title: SAR156497 an exquisitely selective inhibitor of Aurora kinases

Koane Jean-Noel, Marien-Ngouabi University, Brazzaville

Title: Phytochimic and pharmacological studies of some central african medicinal plants with antidiabetic properties

Fatih Sirindil, University of Strasbourg, France

Title: Palladium tandem catalyzed 1,5-sulfonyl migration / suzuki-miyaura cross coupling reactions

Decolorization of azo dye wastewater by MgAl layered double hydroxides

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ABSTRACT

This investigation employed the co-precipitation method to generate MgAl layered double hydroxides (LDHs). Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and alumina nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as precursors in the formation of Mg and Al, respectively, to generate MgAl LDHs. Samples with Mg/Al ratios of 1 and 2 are denoted as MgAl1 and MgAl2, respectively, and were used as adsorbents to decolorize C.I. Reactive Red 2 (RR2). The surface characteristics of MgAl LDHs were measured by specific surface area analysis and scanning electron microscopy. The effects of RR2 concentration, MgAl1 dose and pH on RR2 adsorption were elucidated. Kinetic analyses were performed using pseudo first- and second-order models and the intraparticle diffusion model. Equilibrium results were plotted using Langmuir, Freundlich and Temkin isotherms. The specific surface area, pore volume and pore width of MgAl1 were $43.7 \text{ m}^2/\text{g}$, $0.16 \text{ cm}^3/\text{g}$ and 36 nm , respectively; and those of MgAl2 were $6.5 \text{ m}^2/\text{g}$, $0.03 \text{ cm}^3/\text{g}$ and 53 nm , respectively. The regression results revealed that the adsorption kinetics were more accurately represented by a pseudo second-order model and the equilibrium results were most accurately fitted using the Temkin isotherm. The RR2 adsorption efficiency of MgAl1 exceeded that of MgAl2. Increasing the MgAl1 dosage increased RR2 adsorption, whereas increasing the RR2 concentration or pH reduced RR2 adsorption. The maximum RR2 adsorption capacity of MgAl1 at pH 3 was 153.9 mg/g .

Key words: Decolorization; Layered Double Hydroxides; Isotherm; Kinetics

1. INTRODUCTION

The general formula of layered double hydroxides (LDHs) is $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot \text{H}_2\text{O}$, where M(II) is a divalent metal cation; M(III) is a trivalent metal cation, and A^{n-} is the interlayer anion. LDHs are a family of synthetic anionic clays [1]. The hydrotalcite type LDHs comprise positively charged hydroxide layers, which are separated by anions and water molecules, of which the interlayer anions can be exchanged. The anions in the interlayers of LDHs can be exchanged with other anions by an ion exchange mechanism [2]; therefore, LDHs are suitable for use as adsorbents to remove anionic pollutants from wastewater. Zhang *et al.* [2] used ZnAl LDHs to take up and degrade Orange II. Zhang *et al.* [3] coated Zn-LDHs (FeZn, CoZn or AlZn LDHs) on the surface of the natural bio-ceramic and compared its phosphorus removal efficiency with these Zn-LDHs. Their experimental results revealed that AlZn LDHs had the highest total phosphorus removal efficiency among these Zn-LDHs. Zhou *et al.* [4] found that the

maximum adsorption capacity of Reactive Orange 5 by MgAl LDHs was 53.8 mg/g. C.I. Reactive Red 2 (RR2), an azo dye with the most commonly used anchor - the dichlorotriazine group; therefore, in this study MgAl LDHs were used as adsorbents to decolorize RR2.

An understanding of adsorption kinetics and equilibrium is critical in supplying the basic information that is required for the design and operation of adsorption equipment. The adsorption rates were determined quantitatively and those obtained using the pseudo first- and second-order models and the intraparticle diffusion model were compared. The Langmuir, Freundlich and Temkin isotherms were fitted to the equilibrium data. The objectives of this study were (i) to evaluate the effects of the Mg/Al ratio on the decolorization of RR2 during the preparation of MgAl LDHs; (ii) to determine the effects of RR2 concentration, adsorbent dosage, and pH on the adsorption of RR2; (iii) to assess adsorption rates using various kinetic models and (iv) to measure the coefficients of the Langmuir, Freundlich, and Temkin isotherms.

2. MATERIALS AND METHODS

2.1. Materials

Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and alumina nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as precursors in the formation of Mg and Al, respectively, to generate MgZn LDHs (Merck, USA). The RR2 ($\text{C}_{19}\text{H}_{10}\text{Cl}_2\text{N}_6\text{Na}_2\text{O}_7\text{S}_2$) was purchased from Sigma Aldrich (USA). The solution pH was controlled by adding HNO_3 or NaOH during the reaction, and both reagents were purchased from Merck (USA). All chemicals were used without further purification.

2.2. Preparation of MgAl LDHs

MgAl LDHs was prepared by the co-precipitation method at pH 10. Eighty mL of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.25 or 0.5 M) and 80 mL $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.25 M) were mixed to form solution A. Then, 80 mL NaCl (0.2 M) was added dropwise to solution A. Finally, the mixture was adjusted to pH 10 by adding NaOH (5 M) under vigorous stirring (600 rpm) for 2 h. The resultant slurries were sealed in a Teflon-lined stainless steel autoclave and heated at 353K for 24 h. The precipitates were collected by filtration and washed with 200 mL D.I. water three times to remove any residual ions. The samples were finally dried in air at 333K for 12 h. Samples with Mg/Al ratios of 1 and 2 denoted as MgAl1 and MgAl2, respectively.

2.3. Characterization of the adsorbents

The MgAl LDHs were examined by scanning electron microscopy (SEM) to determine their size and morphology (JEOL JSM-6500F, Japan), and their specific surface areas were determined by BET method using a surface area analyzer (ASAP 2010; Micromeritics, USA).

2.4. Adsorption experiments

All adsorption experiments were performed in a closed, pyramidal, glass bottle with a volume of 250 mL. Adsorption kinetics were measured over 2 h. An initial pH of 3.0 was used in all RR2 adsorption experiments, except for the experiments with variable pH in which the effect of pH on RR2 removal was studied. In adsorption experiments, 0.1 g of adsorbent was placed in a bottle that contained 200 mL of an RR2 solution with a concentration of 20 mg/L and shaken at 100 rpm. The effect of RR2 concentration on removal by MgAl1 was investigated using [RR2] values of 20 and 40 mg/L with $[\text{MgAl1}] = 0.5 \text{ g/L}$. The

effect of adsorbent concentration on removal by MgAl1 was examined using [MgAl1] values of 0.3 and 0.5 g/L at [RR2] = 20 mg/L. The effect of pH on removal by MgAl1 was studied using initial pH values of 3 and 9 at [RR2] = 20 mg/L and [MgAl1] = 0.5 g/L. To obtain the equilibrium parameters, adsorption experiments were conducted at 298K over 24 h. Suspended particles were separated by filtering through a 0.22 μm filter (Millipore). The RR2 concentration was measured using a spectrophotometer (Hitachi U-2001) at 538 nm. Decolorization efficiency was obtained from the difference between RR2 concentrations before and after experiments. Most experiments were performed in duplicate, and values shown are averages.

3. RESULTS AND DISCUSSION

3.1. Surface characteristics of MgAl LDHs

SEM was utilized to characterize the surface structure and morphology of MgAl LDHs, and to determine their shape and pore structures in particular. The surface of MgAl LDHs comprised overlapping crystals in the form of stacked layers (Fig. 1). MgAl samples exhibited the typical platelike morphology of LDHs with a lamellar structure. The specific surface area, pore volume and pore width of MgAl1 were 43.7 m^2/g , 0.16 cm^3/g and 36 nm, respectively; and those of MgAl2 were 6.5 m^2/g , 0.03 cm^3/g and 53 nm, respectively.

3.2. Effects of Mg/Al ratio, RR2 concentration, adsorbent dose, and pH on RR2 removal

Figure 2 plots the effects of Mg/Al ratio in the preparation of MgAl LDHs on RR2 removal. After the reaction had proceeded for 30 min, the percentages of RR2 adsorbed onto MgAl1 and MgAl2 were 100% and 75%, respectively. The adsorption process was rapid for the first 10 min, after which time its rate gradually decreased until equilibrium was reached. Initially, all surface sites on the adsorbent were vacant and the RR2 concentration gradient was relatively high, so the initial adsorption rate was high. This initial phase may be explained by passive uptake via physical adsorption or ion exchange at the surface [5]. Of the samples, MgAl1 exhibited the highest adsorption efficiency for RR2, so MgAl1 was used as the model adsorbent to analyze kinetics and equilibrium.

Figure 3 plots the effects of adsorbent dose, RR2 concentration and pH on the adsorption of RR2 by MgAl1. Increasing the MgAl1 dosage increased RR2 adsorption, mainly because of the increase in adsorptive surface area and availability of adsorption sites on ZnAl3. However, the amount of RR2 adsorbed per unit mass of MgAl1 declined as the MgAl1 dose increased (Table 1). The decrease in unit adsorption as the MgAl1 dose increased follows from the fact that adsorption sites remain unsaturated during the adsorption process and, possibly from the fact that adsorption sites overlap because of MgAl1 particle overcrowding. Several studies have also determined that unit adsorption capacity declines as the adsorbent dosage increases [6, 7].

The RR2 removal percentage declined as the initial RR2 concentration increased, even though the amount of RR2 adsorbed per unit mass of MgAl1 increased with the initial RR2 concentration (Table 1). This increase is caused by an increase in the driving force of the concentration gradient as the initial RR2 concentration increases. Various studies have found that adsorption capacity increases with the dye concentration [6-8].

Solution pH is an important adsorption parameter because pH depends on complex reactions or electrostatic interactions in physisorption processes at the adsorption surface. Reducing pH increased the adsorption of RR2 onto MgAl1. At a lower solution pH, more H^+ causes more hydroxyl groups to become

protonated (-OH₂⁺) on the surface of MgAl1, promoting the electrostatic attraction between the surface of MgAl1 and the -SO₃⁻ group in RR2. At a higher solution pH, the surfaces of MgAl1 are more negatively charged, causing a stronger electrostatic repulsion between negatively charged surface sites and the -SO₃⁻ groups of RR2.

The adsorption kinetics of an adsorbent determines the rate of the adsorption process. The pseudo first-order model [9], pseudo second-order model [9, 10], and intraparticle diffusion model [11] were used to fit the experimental data and determine the adsorption kinetics. Equation (1) is the pseudo first-order model.

$$\ln(q_e - q) = \ln(q_e) - k_1 t \quad (1)$$

where q_e and q (mg/g) are the amounts of RR2 that are adsorbed on the adsorbent at equilibrium and at time t , respectively, and k_1 (min⁻¹) is the rate constant of the pseudo first-order model. Equation (2) is the pseudo second-order model.

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

where q_e and q (mg/g) are as defined for the pseudo first-order model, and k_2 (g/mg · min) is the rate constant of the pseudo second-order model. Since neither model yielded a potential diffusion mechanism, kinetic results were analyzed using the intraparticle diffusion model. In the intraparticle diffusion model, film diffusion was negligible and intraparticle diffusion was the only rate-controlling step. Equation (3) is the intraparticle diffusion model.

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

where C (mg/g) is the intercept value and k_i (mg/g · min^{0.5}) is the intraparticle diffusion rate constant.

Table 1 presents the kinetic parameters of RR2 removal by MgAl LDHs. The q values ($q_{e, \text{cal}}$) that were calculated using the pseudo second-order model were more consistent with the experimental q values ($q_{e, \text{exp}}$) than those calculated using the pseudo first-order model. Therefore, this study suggests that the pseudo second-order model more accurately represents the adsorption kinetics. When the regression of q as a function of $t^{1/2}$ is linear and passes through the origin, intraparticle diffusion is the only rate-limiting step [8]. Although the regression was linear, the plot did not pass through the origin (Table 1), suggesting that adsorption involved intraparticle diffusion, but that it was not the only rate-controlling step. Other kinetic mechanisms probably controlled the adsorption rate, which finding is consistent with one obtained by other adsorption studies [12, 13]. Akkaya *et al.* [14] suggested that pore diffusion and surface diffusion occur simultaneously within the adsorbent particle.

3.3. Adsorption isotherms

The equation parameters and thermodynamic assumptions that underlie these equilibrium isotherms commonly provide insights into the adsorption mechanisms, surface properties and affinities of the adsorbent. Langmuir [15], Freundlich [16], and Temkin [17] isotherms were used herein to describe the

observed adsorption equilibrium. The Langmuir isotherm assumes monolayer coverage of the adsorption surface and no subsequent interaction among adsorbed molecules. Therefore, the adsorption saturates, and then no further adsorption can occur. Equation (4) describes the Langmuir isotherm.

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \quad (4)$$

where q_e is the mass of RR2 that is adsorbed per unit mass of MgAl1 (mg/g) at equilibrium; C_e is the aqueous concentration of RR2 (mg/L) at equilibrium; K_L is the Langmuir constant (L/mg) that is related to the affinity of binding sites, and q_m is the maximum adsorption capacity (mg/g). Parameters q_m and K_L are obtained from the intercept and slope of the best linear fit of $1/q_e$ as a function of $1/C_e$.

The Freundlich isotherm is an empirical relationship that describes multilayer adsorption on heterogeneous surface sites, and is given by Eq. (5):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

where q_e and C_e are as defined as above and K_F and n are Freundlich constants that specify the adsorption capacity and adsorption strength, respectively. Parameters K_F and $1/n$ are obtained from the intercept and slope of the best linear fit of $\ln(q_e)$ as a function of $\ln(C_e)$.

The Temkin model assumes that the heat of adsorption of all molecules in a layer declines linearly as surface coverage increases owing to adsorbent-adsorbate interactions. Adsorption is characterized by a uniform distribution of binding energies up to a maximum value. The Temkin isotherm describes the behavior of adsorption systems on a heterogeneous surface. Equation (6) gives the linear form of the Temkin isotherm.

$$q_e = B_1 \ln(K_t) + B_1 \ln(C_e) \quad (6)$$

where B_1 is a constant that is related to heat of adsorption and K_t is the equilibrium binding constant (L/mol) that corresponds to the maximum binding energy. A plot of q_e as a function of $\ln(C_e)$ yields constants of the isotherm.

Figure 4 displays different isotherms at various temperatures for the adsorption of RR2 on MgAl1. The adsorption capacities increased with concentration, up to a plateau, which represents the maximum adsorption capacity. Table 2 presents the isotherm parameters for the RR2 removal by MgAl1. The high correlation coefficient of the Temkin isotherm reveals that it accurately describes the adsorption process, suggesting that the adsorption system was on a heterogeneous surface. The value of $1/n$ in the Freundlich model is significantly less than one in this study, revealing a favorable adsorption system. If n is below unity, then the adsorption is chemical; otherwise, the adsorption is physical [18]. The value of n exceeds three, suggesting that the adsorption of RR2 on MgAl1 is physical.

4. CONCLUSIONS

In this investigation, co-precipitation was used to synthesize MgAl LDHs as an adsorbent to remove

RR2. The RR2 adsorption efficiency of MgAl1 was higher than MgAl2. Increasing the MgAl1 dosage increased RR2 adsorption, whereas increasing the RR2 concentration or pH reduced RR2 adsorption. According to kinetic analyses, the adsorption involved intraparticle diffusion, but this was not the only rate-controlling step. Equilibrium isotherm analyses suggested that RR2 was adsorbed onto a heterogeneous surface.

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REFERENCES

- [1] X. Wen, Z. Yang, X. Xie, Z. Feng, and J. Huang, The effects of element Cu on the electrochemical performances of Zinc-Aluminum-hydroxalcalites in Zinc/Nickel secondary battery, *Electrochim. Acta*, 180 (2015) 451–459.
- [2] L. Zhang, Z. Xiong, L. Li, R. Burt, and X.S. Zhao, Uptake and degradation of Orange II by zinc aluminum layered double oxides, *J. Colloid Interf. Sci.*, 469 (2016) 224–230.
- [3] X. Zhang, L. Guo, H. Huang, Y. Jiang, M. Li, and Y. Leng, Removal of phosphorus by the core-shell bio-ceramic/Zn-layered double hydroxides (LDHs) composites for municipal wastewater treatment in constructed rapid infiltration system, *Water Res.*, 96 (2016) 280–291.
- [4] Q. Zhou, F. Chen, W. Wu, R. Bu, W. Li, and F. Yang, Reactive orange 5 removal from aqueous solution using hydroxyl ammonium ionic liquids/layered double hydroxides intercalation composites, *Chem. Eng. J.*, 285 (2016) 198–206.
- [5] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, and W. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, *Colloids Surf. A Physicochem. Eng. Asp.*, 317 (2008) 512–521.
- [6] V. Ponnusami, S. Vikram, and S.N. Srivastava, Guava (*Psidium guajava*) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions, *J. Hazard. Mater.*, 152 (2008) 276–286.
- [7] W.T. Tsai, K.J. Hsien, H.C. Hsu, C.M. Lin, K.Y. Lin, and C.H. Chiu, Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution, *Bioresour. Technol.*, 99 (2008) 1623–1629.
- [8] I.D. Mall, V.C. Srivastava, and N.K. Agarwal, Removal of orange-G and methyl violet dyes by adsorption onto bagasse fly ash - kinetic study and equilibrium isotherm analyses, *Dyes Pigm.*, 69 (2006) 210–223.
- [9] Y.S. Ho, and G. McKay, Sorption of dye from aqueous solution by pit, *Chem. Eng. J.*, 70 (1998) 115–124.
- [10] G. Blanchard, M. Maunaye, and G. Martin, Removal of heavy metals from waters by means of natural zeolites, *Water Res.*, 18 (1984) 1501–1507.
- [11] Jr.W.J. Weber, and J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. ASCE*, 89 (1963) 31–60.
- [12] C.H. Wu, Adsorption of reactive dye onto carbon nanotubes: Equilibrium, kinetics and thermodynamics, *J. Hazard. Mater.*, 144 (2007) 93–100.
- [13] C.H. Wu, C.Y. Kuo, C.H. Yeh, and M.J. Chen, Adsorption of C.I. Reactive Red 2 from aqueous

solutions by chitin: An insight into kinetics, equilibrium, and thermodynamics, *Water Sci. Technol.*, 65 (2012) 490–495.

- [14] G. Akkaya, I. Uzun, and F. Guzel, Kinetics of the adsorption of reactive dyes by chitin, *Dyes Pigm.*, 73 (2007) 168–177.
- [15] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.*, 38 (1916) 2221–2295.
- [16] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.*, 57 (1906) 385–470.
- [17] M.I. Temkin, and V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalyst, *Acta Phys. Chim. USSR*, 12 (1940) 217–222.
- [18] J.Q. Jiang, C. Cooper, and S. Ouki, Comparison of modified montmorillonite adsorbents. Part I. Preparation, characterization and phenol adsorption, *Chemosphere*, 47 (2002) 711–716.

Table 1 Kinetic parameters for the removal of RR2 by MgAl

pseudo first-order model	$q_{e, \text{exp.}}$ (mg/g)	k_1 (min ⁻¹)	$q_{e, \text{cal.}}$ (mg/g)	R^2
[RR2] = 20 mg/L, [MgAl1] = 0.5 g/L, pH 3	40.0	0.419	27.3	0.992
[RR2] = 20 mg/L, [MgAl2] = 0.5 g/L, pH 3	33.8	0.034	25.2	0.965
[RR2] = 20 mg/L, [MgAl1] = 0.3 g/L, pH 3	60.0	0.044	46.7	0.963
[RR2] = 40 mg/L, [MgAl1] = 0.5 g/L, pH 3	63.0	0.042	60.8	0.995
[RR2] = 20 mg/L, [MgAl1] = 0.5 g/L, pH 9	16.0	0.011	35.1	0.903
pseudo second-order model	$q_{e, \text{cal.}}$ (mg/g)	k_2 (g/mg/min)	R^2	
[RR2] = 20 mg/L, [MgAl1] = 0.5 g/L, pH 3	41.2	0.0347	0.999	
[RR2] = 20 mg/L, [MgAl2] = 0.5 g/L, pH 3	32.4	0.0102	0.991	
[RR2] = 20 mg/L, [MgAl1] = 0.3 g/L, pH 3	64.1	0.0030	0.996	
[RR2] = 40 mg/L, [MgAl1] = 0.5 g/L, pH 3	68.5	0.0029	0.993	
[RR2] = 20 mg/L, [MgAl1] = 0.5 g/L, pH 9	17.5	0.0083	0.994	
intraparticle diffusion model	k_i (mg/g/min ^{0.5})	C (mg/g)	R^2	
[RR2] = 20 mg/L, [MgAl1] = 0.5 g/L, pH 3	8.909	14.21	0.878	
[RR2] = 20 mg/L, [MgAl2] = 0.5 g/L, pH 3	3.897	9.908	0.978	
[RR2] = 20 mg/L, [MgAl1] = 0.3 g/L, pH 3	8.294	10.64	0.968	
[RR2] = 40 mg/L, [MgAl1] = 0.5 g/L, pH 3	9.730	9.633	0.997	
[RR2] = 20 mg/L, [MgAl1] = 0.5 g/L, pH 9	2.334	1.739	0.973	

Table 2 Isotherm parameters for the removal of RR2 by MgAl1 at 298 K (pH = 3)

Langmuir constants	K_L (L/mg)	q_m (mg/g)	R^2
	0.631	153.9	0.905
Freundlich constants	K_F	n	R^2
	51.6	3.26	0.769
Temkin constants	B_1	K_t (L/mol)	R^2
	19.2	21.5	0.909

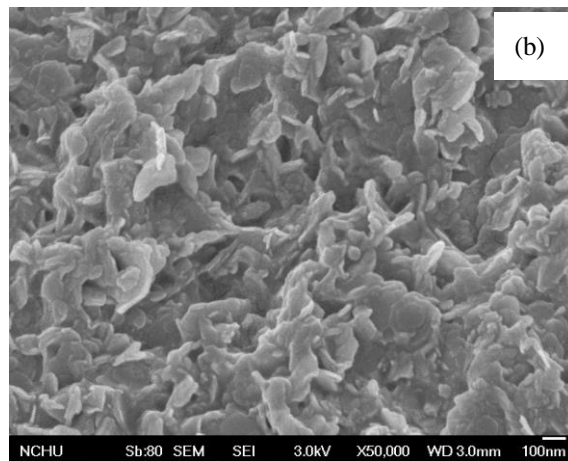
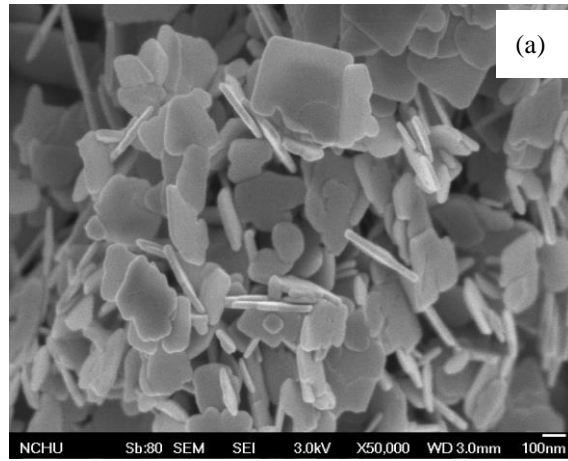


Fig. 1 SEM micrographs of MgAl LDHs (a) MgAl1 (b) MgAl2

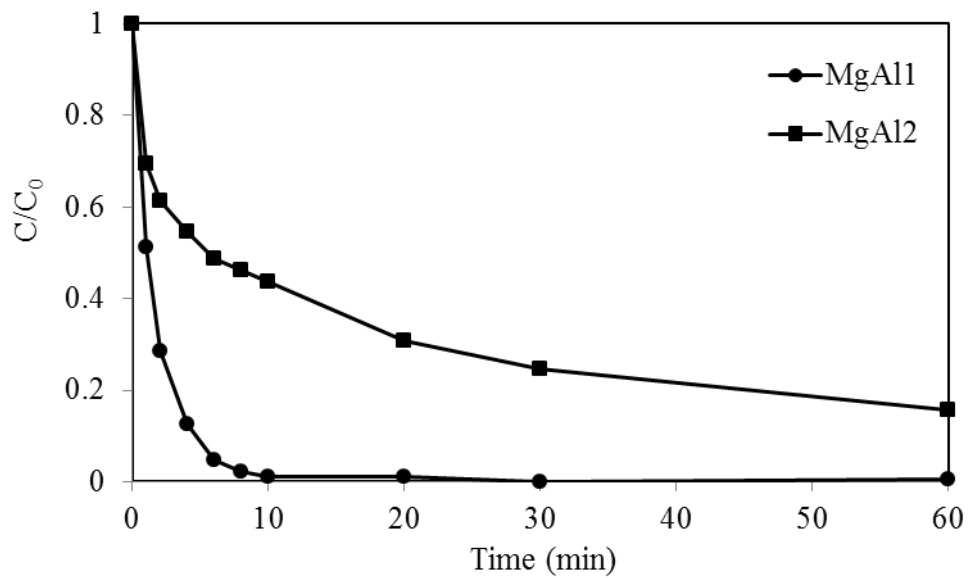


Fig. 2 Effect of Mg/Al ratio in preparation of MgAl LDHs on RR2 adsorption ([RR2] = 20 mg/L, [adsorbent] = 0.5 g/L, pH = 3, and T = 298K)

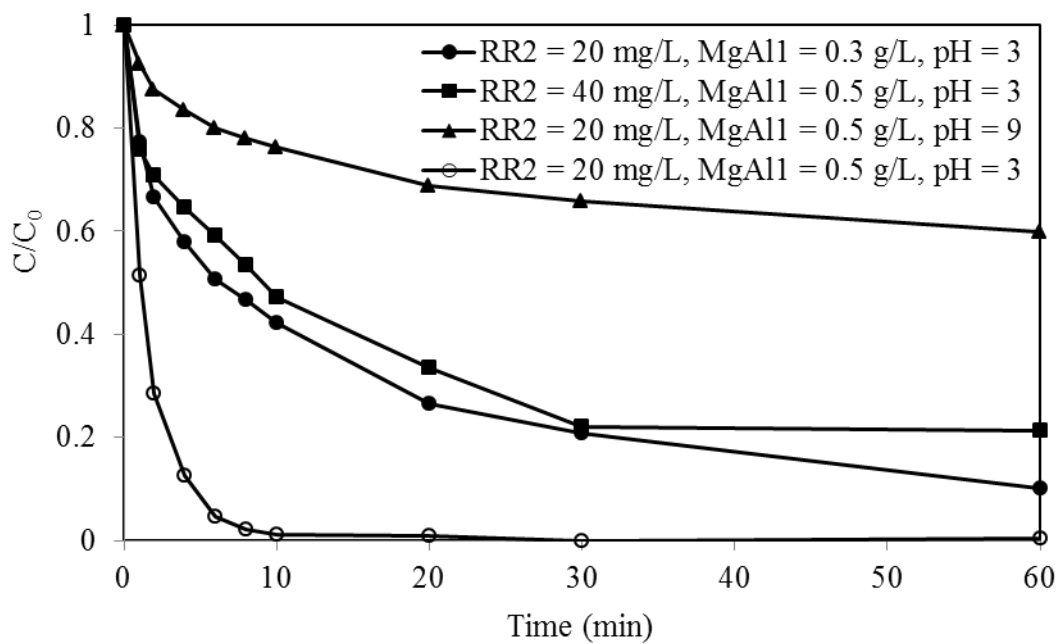


Fig. 3 Effects of adsorbent dose, RR2 concentration and pH on adsorption of RR2 by MgAl1

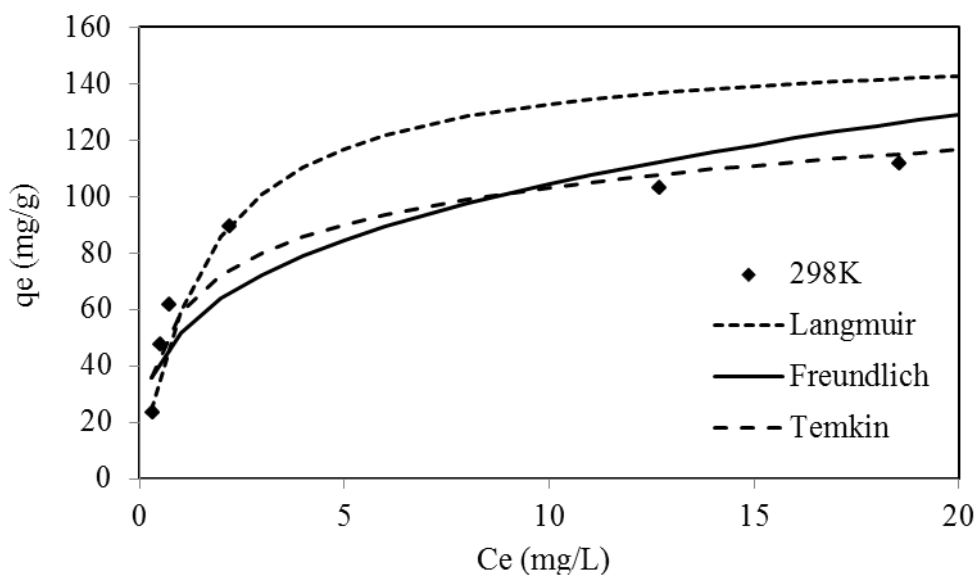


Fig. 4 Isotherms fitting for the adsorption of RR2 on MgAl1 at 298K