

Synthesis and Characterization of Al-Doped ZnO as a Prospective High Adsorption Material

Haoyang Wu,[‡] Mingli Qin,^{†,‡} Dezhi Zhang,[§] Aimin Chu,[¶] Zhiqin Cao,^{‡,||} Baorui Jia,[‡] Pengqi Chen,[‡] Shidi Yang,[‡] Xiaoli Li,[‡] Xuanhui Qu,[‡] and Alex A. Volinsky^{‡‡}

[‡]Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China

[§]Aerospace Research Institute of Materials & Processing Technology, Beijing 100076, China

[¶]School of Electro-mechanism Engineering, Hunan University of Science and Technology, Xiangtan 411201, China

^{||}School of Resources and Environmental Engineering, Pan Zhihua University, Pan Zhihua 617000, China

^{‡‡}Department of Mechanical Engineering, University of South Florida, Tampa, Florida 33620

This work demonstrates Al-doped ZnO adsorbents successfully synthesized by glucose-assisted solution combustion. The addition of glucose results in nanocomposite powders with highly fluffy network, mesoporous structure, high specific surface area, and physical properties, which in turn improve the adsorption properties. The adsorption performance of the material was studied, and the influence of Al doping concentration, adsorbents and methyl orange concentration in the solution were investigated. The addition of glucose increased the adsorption capacity of methyl orange onto Al-doped ZnO by over 2 times. The adsorption followed the Langmuir isotherm, was spontaneous and exothermic. Kinetic calculations show that the adsorption followed the pseudo-second-order model with a multistep diffusion process. Thermodynamic parameters indicate that the adsorption is a feasible, spontaneous, and exothermic process.

Keywords: absorption/adsorbents; nanoparticles; zinc oxide; synthesis

I. Introduction

DISCHARGED wastewater produced by the textile industry always contains dyes and pigments without further treatment. This not only hampers the aesthetic quality of water, but also causes enormous damage to the aquatic ecosystem.^{1,2} Traditionally, many physicochemical methods have been utilized to remove these pollutants from waste water, including adsorption, coagulation-flocculation, biological treatment, and photocatalysis.^{3–6,27} Among all the approaches, adsorption has become the most popular technique for dye removal due to its effectiveness, operational simplicity, environmental friendliness, low cost, and energy consumption.^{1,7–10,21,22,28–30} Many conventional adsorbents have been used to remove pollutants from wastewater, such as activated carbon, layered double hydroxides, metal oxides, and bentonite.^{1,11–14,18,21,22} Most of them have high cost, low adsorption capability, or regeneration efficiency.^{11,15,16} Therefore, it is necessary to develop new materials with high capacity, low consumption, and high efficiency for use as adsorbents.

Zinc oxide (ZnO) is an interesting material for wastewater treatment, due to its cost effectiveness, nontoxicity, and structural stability. According to literature reports,^{26,31,32} when metal or nonmetal elements is doped into the ZnO nanostructures, it is expected that the dopants can modify the physical properties of ZnO to extend its practical applications. Among them, Al-doped ZnO is a solid solution consisting of ZnO and Al₂O₃, which both have hexagonal wurtzite structure. It has been widely studied for its potential applications in wastewater treatment, gas sensing, and thermoelectric materials.^{9–11,18,19,20,23} In the previous studies of wastewater treatment, apart from good photocatalytic performance, Al-doped ZnO also exhibited great adsorption properties.^{17,18} Actually, adsorption is more effective and simple than photocatalysis. However, the adsorption performance in these studies is still too low. Thus, adsorption properties enhancement techniques are required. Synthesis of adsorbents with high porosity and specific surface area is an effective method. In the paper, Al-doped ZnO with superior adsorption properties is synthesized via the glucose-assisted solution combustion method. Solution combustion synthesis (SCS)¹⁷ is instantaneous and self-sustainable reaction by the exothermal combustion process. Glucose addition can be an alternative to SCS for tuning combustion behavior, microstructure, and properties of the products. Generally, glucose has been considered as a good substance for producing transparent “gel” without any precipitation during combustion. Moreover, carbon derived from the decarburization of glucose could act as an excellent dispersing and pore-forming agent during heat treatment to synthesize the oxide. In this study Al-doped ZnO was synthesized by the glucose-assisted SCS method to significantly improve its adsorption properties. The adsorption mechanisms have also been investigated. This study suggests that it may be possible to utilize glucose-assisted SCS as a new strategy to design adsorbents with desired porosity and high specific surface area.

II. Experimental Procedure

(1) Synthesis

All reagents were of analytical grade and used as received without further purification. In a typical synthesis run, zinc nitrate (Zn(NO₃)₂·6H₂O), aluminum nitrate (Al(NO₃)₃·9H₂O), urea (CO(NH₂)₂), and glucose (C₆H₁₂O₆·H₂O) were dissolved in 150 mL of deionized water under stirring to obtain a homogeneous solution. In the solution, the amount of zinc nitrate was 0.05 M, and the molar ratio of urea to zinc nitrate was fixed at 4. The amount of added

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[†]Author to whom correspondence should be addressed; e-mail: qinml@mater.ustb.edu.cn

glucose was 0.015 M. The mixture was poured into a 500 mL glass, and heated in air in a temperature-controlled electrical furnace. The whole process only took several minutes finally resulting in a porous and foamy precursor. The Al-doped ZnO powder was obtained after calcination at 750°C in air for 1 h. For simplicity Al-doped ZnO samples prepared by conventional SCS and glucose-assisted SCS after calcination were named $\text{Zn}_{1-x}\text{Al}_x\text{O}$ and $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$, respectively, where x was 0, 0.01, 0.02, 0.04, 0.08, 0.16, and 0.32. For comparison, the industrial Al-doped ZnO (Beijing Xing Rong Yuan Technology Co., Ltd, Beijing, China) and activated carbon (Tianjin Fuchen Chemical Reagents Factory, Tianjin, China) have been used as adsorbents, identified as $\text{i-Zn}_{0.96}\text{Al}_{0.04}\text{O}$ and activated carbon, respectively.

(2) Characterization

The crystal structures of the calcined powders were investigated by X-ray diffraction (XRD, MXP21VAHF) at room temperature, using a $\text{CuK}\alpha$ radiation ($\lambda = 0.15409$ nm), with a scanning speed of 1 min^{-1} for 2θ in the range from 20° to 90° . Morphology of the calcined powders was characterized by scanning electron microscopy (SEM, JSM-6510; JEOL Co., Ltd, Tokyo, Japan) and transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN, FEI, Hillsboro, OR). Nitrogen adsorption and desorption isotherms of the calcined samples were collected using the NOVA1000e surface area analyzer (Quantachrome Instruments Co., Boynton Beach, FL). The specific surface area (SSA) of the calcined samples was determined by the Brunauer–Emmett–Teller (BET) method using an Automated Surface Area & Pore Size Analyzer (QUADRASORB SI-MP, Quantachrome Instruments, Boynton Beach, FL). Pore diameter and pore volumes of the calcined samples were calculated from the desorption branch of the Barret–Joyner–Halenda (BJH) model. The residual contents of carbon in Al-doped ZnO samples after calcination were measured by Carbon Sulfur Determinator Analyzer (LECO CS844; Leco, San Jose, MO).

(3) MO Adsorption

All adsorption experiments were carried out at room temperature. To investigate organic pollutants adsorption of the Al-doped ZnO materials, methylene orange (MO) was selected as a model contaminant. For the adsorption experiments, 100 mL of solution with known dye concentration and 0.1 g of Al-doped ZnO adsorbents were added into 250 mL glass flasks and then shook at room temperature. During the adsorption experiment, the MO solution was sampled (3 mL), centrifuged at a speed of 6000 rpm for 10 min and then filtered. The measurements of MO concentration were carried out using a UV-visible spectrophotometer (UV-Vis spectrophotometer, Varian Cary 5000; Varian Co., Palo Alto, CA). The MO concentration was determined by measuring the solution absorbance at 466 nm. The concentration retained in the adsorbent phase (q_t , mg/g) was calculated as:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 (mg/L) is the initial MO concentration and C_t (mg/L) is the MO concentration at time t (min), V (L) is the volume of the solution, and W (g) is the weight of the dry adsorbent.

III. Results and Discussion

(1) Synthesis and Characterization of the Products

In a typical synthesis run, 0.05 mol zinc nitrate, 0.2 mol urea, 0.015 mol glucose, and some aluminum nitrate were dissolved in 150 mL of deionized water under stirring to

obtain a homogeneous solution. The solution was heated in air in a furnace at 300°C (shown in Fig. S1). Upon heating, the solution evaporated and formed a gelatinous mass in several minutes. Then this gelatinous mass swelled, leaving highly fluffy precursor with a quite large volume [shown in Fig. S2(b)]. On the contrary, the conventional SCS procedure was coupled with flame, resulting in precursor with remarkably smaller volume [shown in Fig. S2(a)]. The differences in the two combustion behaviors may be attributed to the glucose additives acting as a complex agent, resulting in large gas flow rate and relatively low combustion temperature. Finally, the Al-doped ZnO powder was obtained after calcination at 750°C in air for 1 h. The residual contents of carbon in Al-doped ZnO samples after calcination have been listed in Table SI.

Figure 1 shows the XRD patterns of the $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ samples. For Al doping content varied from 1 to 4 at.%, all diffraction peaks are in good agreement with those of the hexagonal wurtzite structure ZnO with lattice constants $a = 0.3248$ nm and $c = 0.5204$ nm, which is in agreement with the literature values (JCPD No. 36-1451), and no characteristic peaks of other impurities are observed. The results show that the three samples are crystalline-phase ZnO. In addition, inset in Fig. 1 shows that the major diffraction peaks intensity is decreased and peaks position shifted slightly towards higher angle with increasing the Al concentration. The lattice constant c calculated from the XRD patterns (Table SII) decreases from 0.5204 nm in pure ZnO to 0.5202, 0.5199, and 0.5194 nm in $\text{g-Zn}_{0.99}\text{Al}_{0.01}\text{O}$, $\text{g-Zn}_{0.98}\text{Al}_{0.02}\text{O}$, and $\text{g-Zn}_{0.96}\text{Al}_{0.04}\text{O}$. The decreased lattice parameters suggest that Al^{3+} has been incorporated into the ZnO lattice and effectively replaced the Zn^{2+} sites.¹⁸ EDS analysis [Fig. 1(c)] indicates the presence of Zn, O and Al. As Al doping content increased to 8 at.%, new peaks, characteristic of the spinel ZnAl_2O_4 phase were observed, and higher content lead to increased peaks intensity. The formation of ZnAl_2O_4 is due to the limited solubility of Al in ZnO. However, from Fig. 1(b), it is evident that the $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ sample contains the ZnAl_2O_4 secondary phase. The higher solid solubility of $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ may be due to the increased contact area between Al and ZnO, consistent with the higher specific surface.

As shown in Fig. S3(a), the g-ZnO sample mainly has a highly fluffy network structure. When Al is doped into the ZnO, SEM images [Fig. 2(b)] show that the $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ renders the highly fluffy network structure, different from the tight three-dimensional flakes of the $\text{Zn}_{1-x}\text{Al}_x\text{O}$ sample [shown in Fig. 2(a)]. EDS line scans for the $\text{g-Zn}_{0.96}\text{Al}_{0.04}\text{O}$ sample (Fig. S4) clearly reveal that the elements Zn, O and Al are evenly distributed throughout the powder. TEM results in Figs. 2(d)–(f) and Fig. S3(b) show that the particles sizes of the $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ samples are highly dependent on the ZnO:Al ratio. The g-ZnO sample prepared by glucose-assisted SCS after calcination is composed of 60 nm nanoparticles. With the Al doping content increase, the particles size initially becomes smaller, reaching the minimum at 4 at.% Al doping (20–30 nm), and then becomes larger. Compared with $\text{Zn}_{1-x}\text{Al}_x\text{O}$ [shown in Fig. 2(c)], the $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ samples have smaller and well-distributed particles. This may be ascribed to decarburization during calcination, resulting in the inhibition of particles growth and dispersed particles. Combining the highly fluffy and porous structure with the dramatically reduced particle size, the $\text{g-Zn}_{0.96}\text{Al}_{0.04}\text{O}$ sample has high specific surface area of $29.5 \text{ m}^2/\text{g}$, which is nearly six times of that obtained by conventional SCS ($5.1 \text{ m}^2/\text{g}$), as demonstrated in Table SIII. Dramatic increase in the specific surface area should be ascribed to the added glucose and its multiple roles during combustion and heat treatment.

Nitrogen adsorption isotherms of the $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ samples are shown in Fig. 3(a). The shapes of these isotherms agree with the type IV isotherm characteristics with the H3

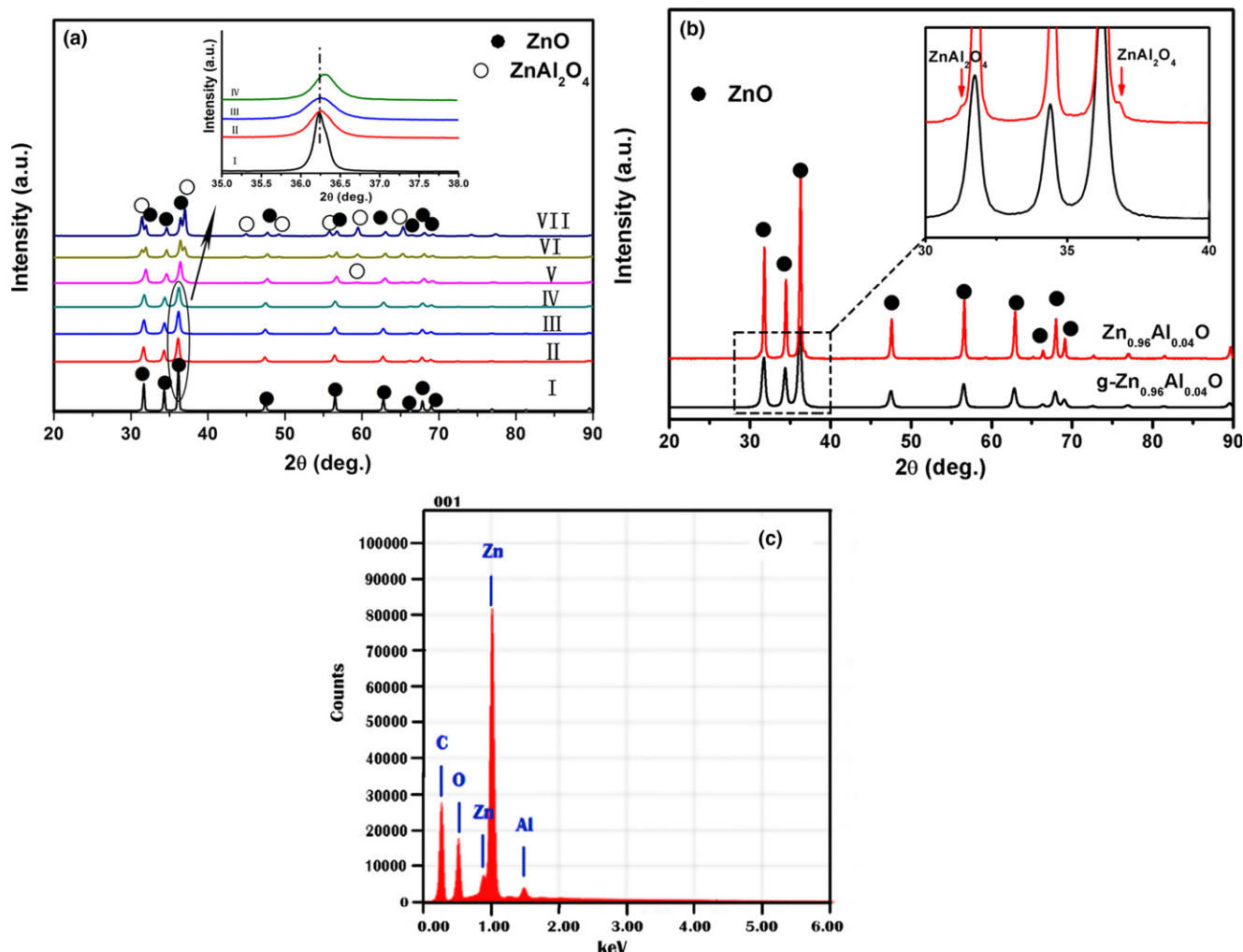


Fig. 1. (a) XRD patterns of g- $\text{Zn}_{1-x}\text{Al}_x\text{O}$ samples after calcination: (I) g- ZnO , (II) g- $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$, (III) g- $\text{Zn}_{0.98}\text{Al}_{0.02}\text{O}$, (IV) g- $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$, (V) g- $\text{Zn}_{0.92}\text{Al}_{0.08}\text{O}$, (VI) g- $\text{Zn}_{0.84}\text{Al}_{0.16}\text{O}$, (VII) g- $\text{Zn}_{0.68}\text{Al}_{0.32}\text{O}$; (b) XRD patterns of g- $\text{Zn}_{0.98}\text{Al}_{0.02}\text{O}$ and ZnAl_2O_4 samples after calcination; (c) EDX spectra of g- $\text{Zn}_{0.98}\text{Al}_{0.02}\text{O}$ samples after calcination.

hysteresis (cylindrical shape), indicating the presence of mesoporous structure. With an increase in Al doping content to 4 at.%, the slope of the hysteresis loop increased and the end of the hysteresis loop shifted toward lower relative pressure (P/P_0), representing superior physical properties. However, with further increase in Al doping content, it is evident that the slope of the hysteresis loop decreased, indicating poor physical properties. As shown in Table SIII, derived from the desorption data, the pore size of the g- $\text{Zn}_{1-x}\text{Al}_x\text{O}$ samples is between 20 and 30 nm. Compared with the $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ sample, the g- $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ sample has larger pore diameter and higher pore volume with steeper hysteresis loop. Thus, it is evident from the above observations that the glucose-assisted combustion synthesis results in the formation of nanostructured samples with superior physical properties.

(2) Other Factors Affecting MO Adsorption

Figure 3(b) shows adsorption capacity (q_t) plots of MO onto g- $\text{Zn}_{1-x}\text{Al}_x\text{O}$ versus contact time for different Al doping concentrations. It is obvious that the ratio of ZnO to Al has an effect on the MO percentage removal and related adsorption equilibrium time. After 30 min of adsorption, pure ZnO exhibits low adsorption equilibrium capacity (q_e) (0.40 mg/g), in agreement with other studies.^{1,24} For the g- $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$ sample, the q_e reached 9.26 mg/g after 20 min. This appreciable result in improving adsorption capacity was attributed to increasing the number of active sites in ZnO, the presence of mesoporous structure and superior physical properties. By

increasing the Al content to 4 at.% (g- $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ sample), the q_e reached 9.89 mg/g in 3 min, which is better compared with other research reports.¹⁷ The Fig. S5 shows a series of color changes of the MO solution with the g- $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ for different time durations. It can be seen that the color of the solution gradually changed from intense yellow to colorless in 3 min. However, with the further increase in Al content, the q_e became lower. This may be attributed to relatively poor physical properties and spinel ZnAl_2O_4 phase with further increase in Al doping content. The pure alumina sample prepared by glucose-assisted SCS does not show any dye removal. This is because the alumina surface with negative charge cannot adsorb the MO ions, as reported by other researchers.¹⁷

Figure 3(c) shows the effects of different adsorbents on the MO adsorption. Four types of adsorbents: g- $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$, activated carbon and i- $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ were used. After 100 min of adsorption time, adsorption capacity (q_t) of MO onto g- $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ reached 98.65 mg/g, higher than the other three samples (46.21, 41.04, and 14.65 mg/g, respectively), indicating that the g- $\text{Zn}_{1-x}\text{Al}_x\text{O}$ samples show better adsorption properties. These excellent adsorption properties can be attributed to several factors: (1) highly fluffy network structure; (2) mesoporous structure; (3) superior physical properties and high specific surface area increasing the amount of reactive sites for adsorption.

Figure 3(d) shows plots of adsorption capacity (q_t) of MO onto g- $\text{Zn}_{1-x}\text{Al}_x\text{O}$ samples (taking g- $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ sample as an example) versus contact time for different initial MO concentrations. It can be concluded that the initial concentration

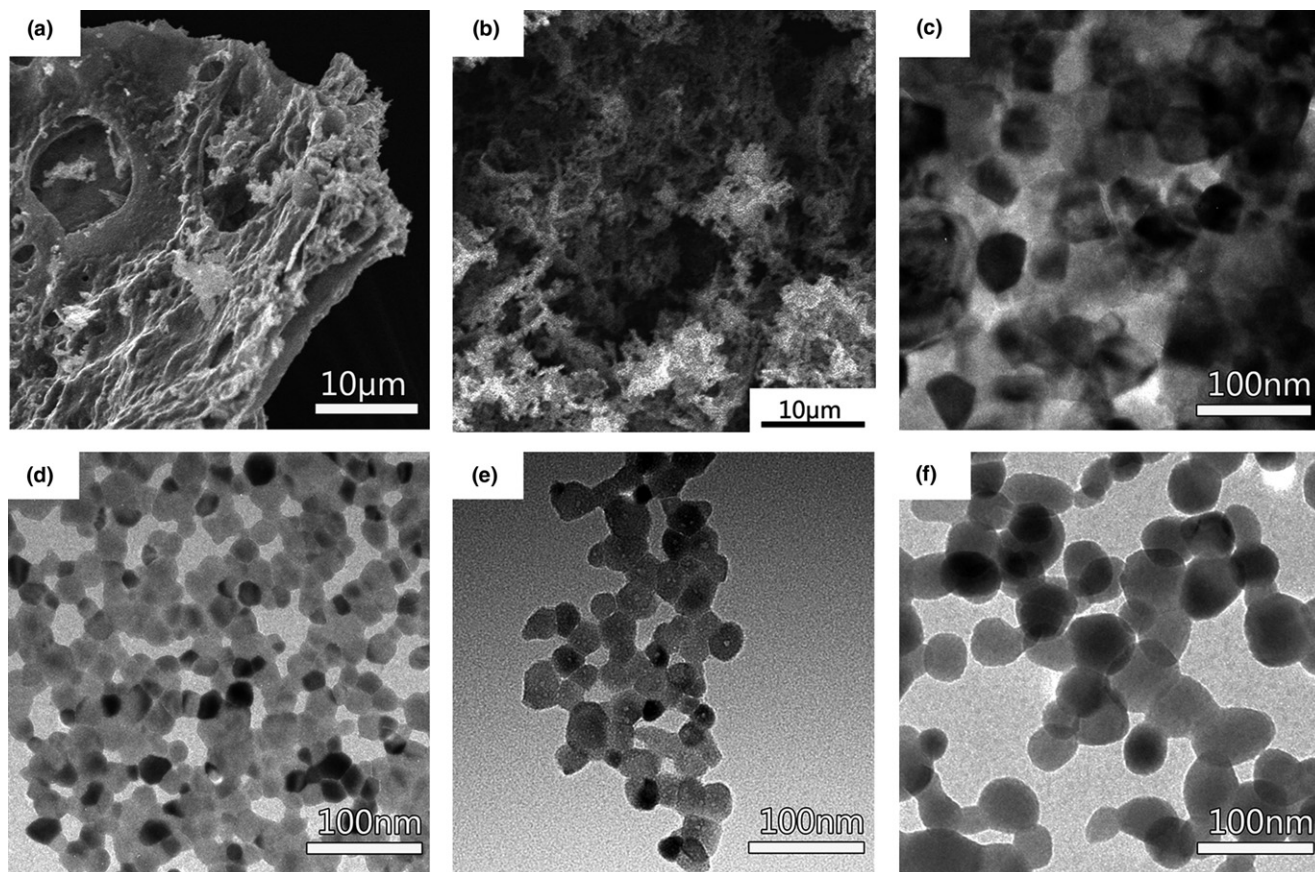


Fig. 2. SEM and TEM images of the Al-doped ZnO samples after calcination: (a) $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$; (b) $\text{g-Zn}_{0.96}\text{Al}_{0.04}\text{O}$; (c) $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$; (d) $\text{g-Zn}_{0.96}\text{Al}_{0.04}\text{O}$; (e) $\text{g-Zn}_{0.98}\text{Al}_{0.02}\text{O}$; and (f) $\text{g-Zn}_{0.92}\text{Al}_{0.08}\text{O}$.

played an important role in the adsorption capacity of MO on the $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ samples. After 30 min of adsorption time, the q_t value increased from 9.89 to 69.74 mg/g with the increase in initial concentration from 10 to 70 mg/g. Higher initial dye concentration led to an increase in the adsorption capacity, which then functions as a driving force for the transfer of dye molecules from bulk solution to the $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ surface.¹ However, further increase in the initial concentration up to 100 mg/g led to the adsorption equilibrium time increase to 90 min. Obviously, a certain amount of $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ samples could only provide a certain amount of reactive sites for the adsorption of MO with the increasing concentration.

(3) Evaluation of Adsorption Kinetics

To investigate the potential application of the synthesized $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ in water purification, the adsorption mechanisms for MO were tested (taking $\text{g-Zn}_{0.96}\text{Al}_{0.04}\text{O}$ sample as an example). In this study, the Lagergren first-order equation [Eq. (2)], the pseudo-second-order equation [Eq. (3)] and the intraparticle diffusion model [Eq. (4)] were considered to investigate the kinetics.^{1,21}

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

$$q_t = k_{id} t^{1/2} + c \quad (4)$$

Here, q_e (mg/g) and q_t (mg/g) are the amounts of MO adsorbed at time t (min) in equilibrium, respectively, and k_1

(min^{-1}), k_2 (g/mg/min) and k_{id} ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$) are the rate constants of the Lagergren first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model, respectively. Different kinetic parameters are shown in Table I. Plots of the Lagergren first-order and pseudo-second-order kinetic models are shown in Figs. 4(a) and (b) for the effect of the initial MO concentration. The highest values of R^2 were observed with the pseudo-second-order model ($R^2 > 0.999$ for all concentrations), and the theoretical q_e values obtained from this model were also closer to the experimental $q_{e,\text{exp}}$ values at different initial MO concentrations. It could be found that the pseudo-second-order kinetic model is more appropriate to describe the adsorption behavior of MO onto the $\text{g-Zn}_{1-x}\text{Al}_x\text{O}$ samples, indicating that the adsorption might be a chemical adsorption process. It is likely that the adsorption behavior may involve valence forces by sharing electrons between anions and adsorbent.²¹

For the intraparticle diffusion model, a plot of q_t versus the square root of time ($t^{1/2}$) should be linear, and if these lines pass through the origin, then the intraparticle diffusion is the only rate-controlling step. However, as shown in Fig. 4(c), the plots are not linear over the whole time range and, instead, can be separated into multilinear curves, indicating that intraparticle diffusion was not the only rate-controlling step and multiple stages were involved in the adsorption process.^{1,25} The first sharper line represents surface adsorption, whereas the second line corresponds to the intraparticle diffusion and the third line indicates the final equilibrium stage of adsorption.

(4) Evaluation of Equilibrium Adsorption Isotherm

In this study, two commonly used models, the Langmuir [Eq. (5)] and the Freundlich [Eq. (6)] isotherms were applied to investigate the equilibrium adsorption isotherm.^{1,21}

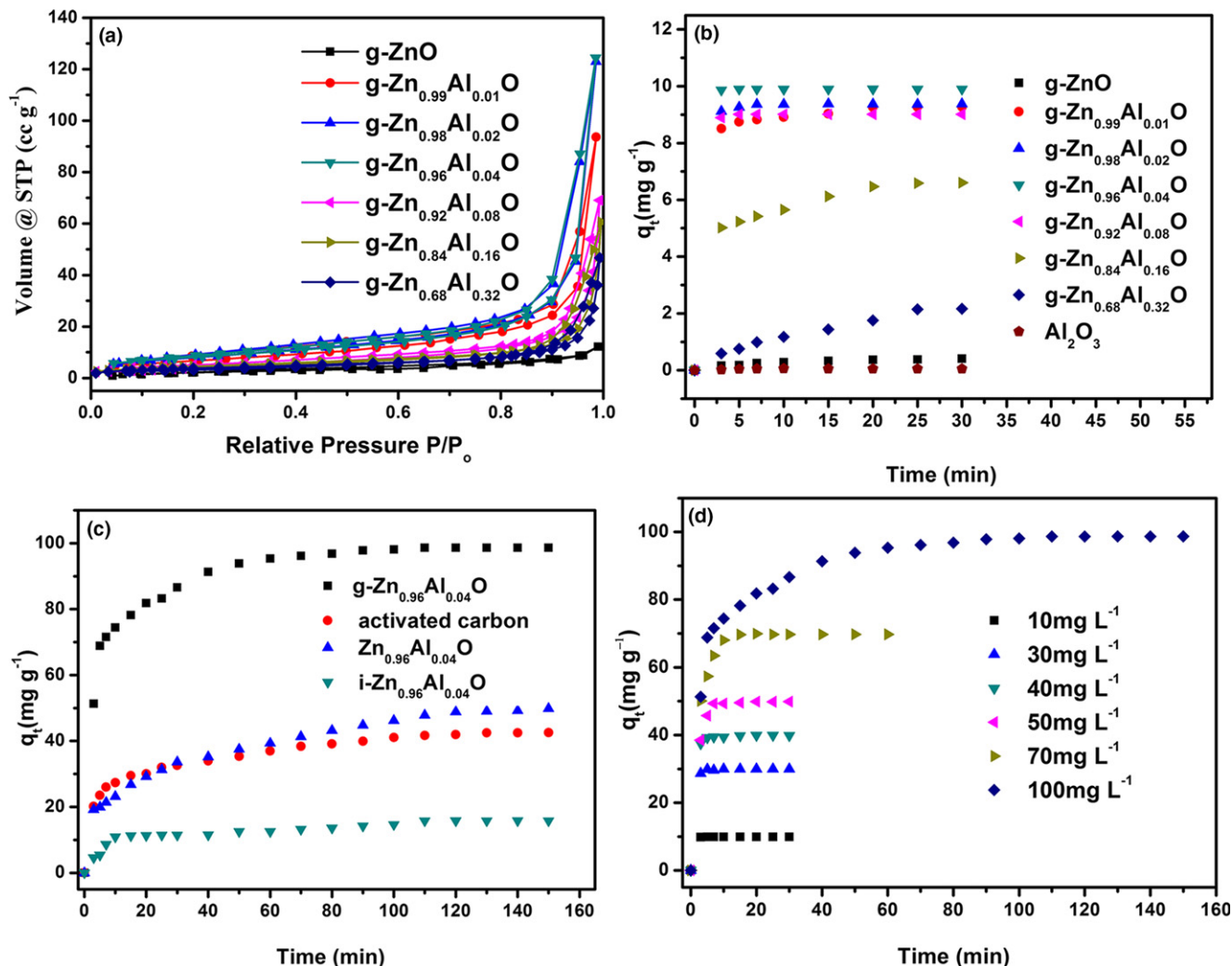


Fig. 3. (a) N₂ adsorption-desorption isotherm of the g-Zn_{1-x}Al_xO samples after calcination; (b–d) Effects of key factors on MO adsorption: (b) Al doping concentration (initial concentration 10 mg/L, adsorbent dosage 1 g/L); (c) Different adsorbents (initial concentration 100 mg/L, adsorbent dosage 1 g/L) and (d) initial MO concentrations (adsorbent dosage 1 g/L).

Table I. Kinetic Parameters of MO Adsorption onto g-Zn_{0.96}Al_{0.04}O for Different Initial Dye Concentrations

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Lagergren first-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e,cal}$ (mg/g)	k_1 (min ⁻¹)	R^2	$q_{e,cal}$ (mg/g)	k_2 [g·(mg·min) ⁻¹]	R^2
10	9.91	9.36	1.8460	0.99860	9.91	1.2283	0.99997
30	29.85	21.07	0.8497	0.83144	29.92	0.3892	0.99998
40	39.81	27.54	0.4412	0.86450	40.05	0.2327	0.99996
50	49.96	46.79	0.4134	0.95629	50.63	0.0529	0.99927
70	69.75	60.56	0.39741	0.98174	70.67	0.0250	0.99958
100	98.79	70.36	0.0546	0.97036	101.11	0.0029	0.99948

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \quad (5)$$

$$\ln q_e = \ln K + \frac{1}{n} \ln c_e \quad (6)$$

In these equations, q_e (mg/g) is the amount of MO adsorbed in equilibrium, q_m (mg/g) is the theoretical maximum monolayer adsorption capacity, c_e (mg/L) is the equilibrium concentration of MO in solution, and b (L/mg), n and K (mg^{1-(1/n)}L^{1/n}g⁻¹) are empirical constants.

The theoretical parameters of adsorption isotherms along with regression coefficients (R^2) are summarized in Table II.

The R^2 values of the Langmuir isotherms (0.95) were the closest to 1, indicating that the equilibrium sorption data can be best fitted with the Langmuir isotherm. These data confirm that the adsorption of MO on g-Zn_{1-x}Al_xO occurs as a monolayer coverage process. The essential features of the Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called the separation factor or equilibrium parameter (R_L), which is defined by the following relationship²⁶:

$$R_L = \frac{1}{1 + bC_0}, \quad (7)$$

where b is the Langmuir constant and C_0 (mg/L) is the highest dye concentration. The value of R_L indicates the type of

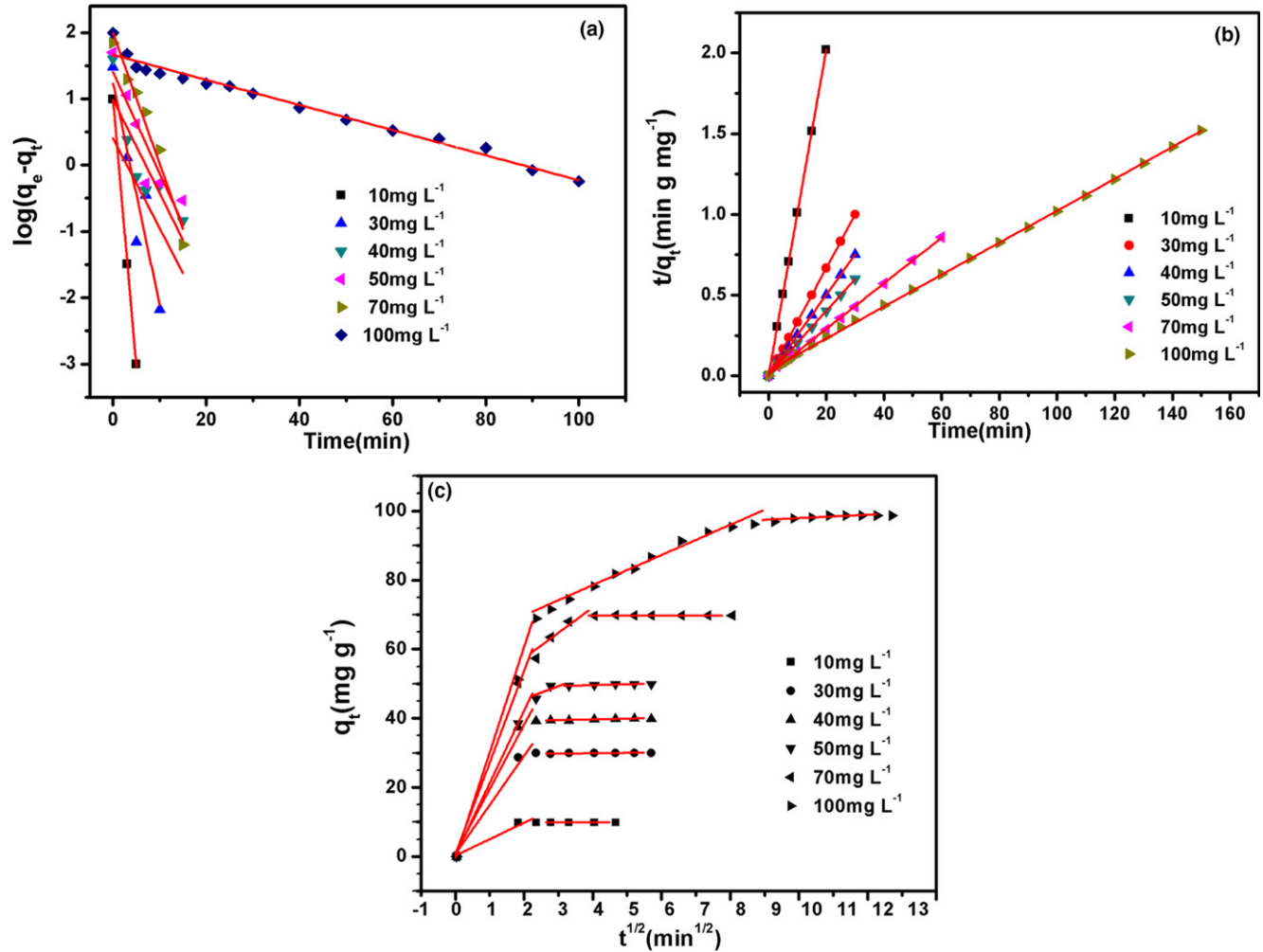


Fig. 4. Plots of (a) the Lagergren first-order, (b) pseudo-second-order and (c) intraparticle diffusion model of MO adsorption onto g-Zn_{0.96}Al_{0.04}O for different initial concentrations.

the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). As shown in Table II, the calculated values of R_L are between 0 and 1. This implies that the adsorption of the investigated dye on the g-Zn_{1-x}Al_xO samples from aqueous solutions is favorable under the conditions used in this study.

In the Freundlich isotherm equation, n gives an indication of how favorable the adsorption process is. The values of n in the 2–10 range represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics. The studied materials are good adsorbents for MO below 326 K ($n > 2$). It can be concluded that an increase in temperature resulted in a corresponding decrease in adsorption capacity of MO, which showed that the adsorption of MO onto g-Zn_{1-x}Al_xO was an exothermic process.

(5) Evaluation of Adsorption Thermodynamics

Thermodynamic parameters, such as the changes in the standard free energy [ΔG° (kJ/mol)], enthalpy [ΔH° (kJ/mol)], and entropy [ΔS° (kJ·mol⁻¹·K⁻¹)] can be calculated using the following equations:^{1,21}

$$\Delta G^\circ = -RT \ln K_c \quad (8)$$

$$\ln K_c = -\frac{1}{RT} + \frac{\Delta S^\circ}{R}, \quad (9)$$

where K_c is the ratio of MO concentration on adsorbent at equilibrium (q_e) to the remaining MO concentration in the solution at equilibrium (C_e).

Table II. Isotherm Model Constants and Regression Coefficients for MO Adsorption onto g-Zn_{0.96}Al_{0.04}O

T(K)	Langmuir isotherm constants				Freundlich isotherm constants		
	q_m (mg/g)	b	R^2	R_L	$K' \text{ (mg}^{1-(1/n)} \text{ L}^{1/n} \text{ g}^{-1})$	n	R^2
298	127.22	1.28	0.994	0.025	80.87	2.499375	0.922
312	119.33	0.09	0.958	0.27	29.99	2.109438	0.877
326	97.08	0.04	0.950	0.45	13.59	1.580153	0.837

Table III shows the enthalpy (ΔH°) and entropy (ΔS°) of adsorption of -96.45 kJ/mol and -0.28 kJ·mol⁻¹·K⁻¹, respectively. The negative value of ΔH° indicates the exothermic nature of adsorption. It is evident that the adsorption is favored at lower temperature. The negative values (-12.71 , -7.43 , and -5.23 kJ/mol) of ΔG° reflect the spontaneous process of MO adsorption at 298, 312, and 326 K.

Table III. Thermodynamic Parameters for MO Adsorption onto g-Zn_{0.96}Al_{0.04}O

T(K)	Thermodynamic parameters		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° [kJ·mol ⁻¹ ·K ⁻¹]
298	-12.71		
312	-7.43	-96.45	-0.28
326	-5.23		

IV. Conclusions

In the study, Al-doped ZnO sample was prepared by the glucose-assisted SCS method. The addition of glucose resulted in g-Zn_{1-x}Al_xO nanocomposite powders with highly fluffy network, mesoporous structure and improved specific surface area (29.5 m²/g). The adsorption of methyl orange onto g-Zn_{1-x}Al_xO was investigated with respect to different adsorbents, initial methyl orange, and contact time. Results of characterization indicated that the addition of glucose could obviously increase the adsorption capacity of methyl orange onto Al-doped ZnO by 2.1 times. The adsorption of MO onto the g-Zn_{1-x}Al_xO sample followed the pseudo-second order model with a multistep diffusion process, and was spontaneous and exothermic in nature. The efficient and fast adsorption process makes this material particularly promising for the removal of organic dyes in wastewater treatment. Moreover, this study suggests that it may be possible that glucose-assisted SCS can be used as a new strategy to design materials with desired porosity and high specific surface area, used as adsorbents.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Fig. S1. Schematic diagram of the experimental apparatus.

Fig. S2. Original appearances of the precursors: (a) Zn_{0.96}Al_{0.04}O and (b) g-Zn_{0.96}Al_{0.04}O.

Fig. S3. SEM (a) and TEM (b) images of the ZnO samples prepared by glucose-assisted SCS after calcination.

Fig. S4. EDS line scans for the g-Zn_{0.96}Al_{0.04}O sample.

Fig. S5. Change in the absorption of the MO solutions (10 mg/L) in the presence of the g-Zn_{0.96}Al_{0.04}O sample.

Table S1. The residual contents of carbon in Al-doped ZnO samples after calcination.

Table S2. Lattice Parameters of Al-doped ZnO samples after calcination.

Table S3. Physical Properties of Al-doped ZnO samples after calcination.

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