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Aerobic granular sludge-derived activated carbon: mineral acid modification and superior dye adsorption capacity

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A novel aerobic granular sludge-derived activated carbon (AC) was prepared by zinc chloride activation method and further modified by mineral acid (nitric acid (NA) and sulfuric acid (SA)). The morphology, physical structure and chemical properties of unmodified AC, NA-modified AC (AC-NA) and SA-modified AC (AC-SA) were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Boehm's titration, Fourier transform infrared spectroscopy (FTIR), Zeta potentials and N₂ adsorption-desorption isotherms. Batch experiments were conducted to study the sorption of malachite green (MG) onto three types of carbons from aqueous solution. The effects of sorption parameters including adsorbent dose, pH values and contact time were investigated by comparing adsorptive properties of the carbons toward MG. Data implied that the pseudo-second-order kinetic model and the Langmuir model could well explain the adsorption processes of MG onto the three carbons. Moreover, AC-NA and AC-SA exhibited a higher adsorption capacity (303.03 and 284.90 mg/g) than AC (269.54 mg/g). The reason may be attributed to the fact that the modified ACs exhibited more oxygenic functional groups through mineral acid modification, which played a more crucial role than pore structure to determine the adsorption capacity of MG.

1. Introduction

Dye has been widely applied in the textiles, paper, plastics and food industries etc.¹ Inevitably, the dye wastewater pollution is becoming a serious environmental problem. Therefore, it is necessary to remove dye from effluents to avoid discharging into natural water. Recently, various techniques for dye removal have been developed, including anaerobic microbial degradation, coagulation and chemical oxidation, membrane separation process, electrochemical, adsorption, filtration and reverse osmosis etc.^{2,3}

Among these methods, adsorption is one of the most competitive methods owing to its simple process, low cost and easy operating conditions. Activated carbon as a highly effective adsorbent has been used to remove pollutants from water due to its large surface area, micro-porous nature and high adsorption capacity. However, commercial activated carbon is relatively expensive and non-renewable, which is unjustified for most pollution control in real applications.^{4,5}

Excess activated sludge, a byproduct from numerous industrial WWTPs, has been recognized as an ecological burden for society. Considering the sludge as a carbon-rich material, it has been successfully prepared for the production of porous activated carbons for wastewater treatment.⁶ This mode would not only solve the disposal problem of sludge but also turn solid waste into useful material as efficient-adsorbent. Some researchers have focused on the potential of sludge-derived activated carbons for the removal of metals and dyes from aqueous media.⁷⁻¹⁰

Recently, aerobic granular sludge have been regarded as a novel biological nitrogen removal technology for the treatment of municipal and industrial wastewaters.¹¹ Compared with

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† Electronic Supplementary Information (ESI) available.

conventional activated sludge, aerobic granular sludge has the advantages of high surface area, excellent settle ability, dense and porous microbial structure. De Bruin et al. suggested that aerobic granular sludge could be considered as one of best alternatives to activated sludge.¹² Aerobic granular sludge technology has been applied for the treatment of various wastewaters, especially for the wastewater containing organic compound, nitrogen and phosphorus etc.¹³ Therefore, once this technology is largely applied in the future, it is expected the utilization of aerobic granular sludge as a potential carbon-rich precursor for preparing activated carbon.

The synthesis of activated carbon from sludge are influenced by many activation parameters, including activation type, activating agent, pyrolysis/activation temperature and impregnation ratio etc.¹⁴ The various activation parameters could affect the textural characteristics of the production of activated carbon, including surface area, pore volume, and pore size.¹⁵ Moreover, chemical surface modification, especially acid modification of activated carbon, has been recognized as an effective method to enhance the oxygen content on the surface of activated carbon.¹⁶ It is well been reported that the amount of oxygen containing surface functional groups could effectively improve the pollutant removal capacity.¹⁷

Based on the above discussion, a novel activated carbon (AC) was prepared from aerobic granular sludge by chemical activation with zinc chloride. The mineral acid modification (nitric acid and sulfuric acid) was used to improve the number of oxygen function groups on the surface of activated carbon. The application of unmodified AC, nitric acid-modified AC (AC-NA) and sulfuric acid-modified AC (AC-SA) were compared for dye removal. Malachite green (MG) was selected as a target pollutant to explore the adsorption performance of ACs. MG is extensively utilized as parasiticide, fungicide and bactericide in aquaculture industries world-wide.¹⁸⁻²¹ The effects of different parameters including adsorbent dose, pH value and contact time were studied to optimize the adsorption process. In order to further explore the interaction between activated carbon and MG, the kinetics, isotherm and mechanism were also studied.

2. Materials and methods

2.1. Reagents

All chemicals were obtained from Sinopharm Chemical Reagent Beijing Co. Ltd., China and of analytical reagent grade without further purification. Ultrapure water (EASY-pure LF, Barnstead International, Dubuque, IA, USA) was used throughout the experiment.

2.2. Preparation and modification of AC

The aerobic granular sludge was obtained from a lab bioreactor by seeding activated sludge. The seeding activated sludge was with fluffy, irregular, loose morphology, while the formed aerobic granular sludge was with a regular round-shaped outer structure (Fig. S1 (ESI[†])). The aerobic granular sludge sample first was dried at 100 °C for 24 h to achieve constant weight,

and then crushed and activated by using zinc chloride. Next, the sample was carbonized at 650 °C in a tube furnace (OTL 1200, Nanjing) for 2 h under nitrogen atmosphere and then cooled to room temperature. Finally, the obtained AC was washed with hydrochloric acid, ultrapure water and dried at 103 °C for 12 h.

For modification process of AC-NA, 1 g AC was first impregnated with 20 mL nitric acid solution (2 mol/L) in 250 mL stoppered conical flask. Next, the modification reaction was continued in a water bath shaker for 3h at 60 °C. Then, the sample was heated up to 300 °C for 3 h in the muffle furnace. The sample was washed with ultrapure water until pH of the washed solution was steady. Finally, the sample was dried at 103 °C for 12 h. AC-SA was got with the same procedure except sulfuric acid instead of nitric acid.

2.3. Characterization methods

The Brunauer-Emmett-Teller (BET) surface area and pore size distribution of activated carbons were characterized with an automated gas sorption apparatus (Micromeritics ASAP 2020 system, USA). The surface morphology of activated carbon was observed by using a scanning electron microscopy (SEM) (JEOL JSM-6700F microscope, Japan). The surface functional groups of activated carbon were analyzed by the Fourier transforms infrared (FTIR) spectroscopy (VERTEX70 spectrometer, Bruker Co. Ger). X-ray powder diffraction (XRD) patterns were gathered from a Bruker D8 Focus diffractometer (Germany) using CuK α radiation (40 kV, 30 mA) of wavelength 0.154 nm to confirm the structure of materials. Zeta potential was measured by a Malvern zetameter (Zetasizer 2000). Boehm titration method was used to determine the amount of the surface groups. More detailed, basic groups were determined adding 50 mL of 0.05 mol/L HCl solution on 0.1g samples in stoppered conical flask. Same procedure was repeated with 50 mL of 0.05 mol/L NaHCO₃, Na₂CO₃, and NaOH solution in order to determine surface acidic groups. The NaHCO₃ neutralizes carboxylic groups, Na₂CO₃ neutralizes carboxylic and lactonic groups, and NaOH neutralizes carboxylic, lactonic and phenolic groups.

2.4. Adsorption studies

The dye stock solution (1000 mg/L) of MG was prepared by dissolving 1 g of the MG in 1000 mL ultrapure water. All working solutions with desired concentration were prepared by diluting the dye stock solution with ultrapure water. The adsorption studies were conducted by mixing 0.012 g of activated carbon and 40 mL of MG solution under mechanical shaking in oscillator. The concentrations of MG were analyzed by absorbance measurements using a spectrophotometer (722, Shanghai spectrum) at 618 nm. The pH value was adjusted using HCl or NaOH (1 mol/L) and was measured by pH meter (Model PB-10, Shanghai).

The removal efficiency and the amount of MG adsorbed q_t (mg/g) were given according to the following Eq (1) and Eq (2):

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where C_t (mg/L) is the concentration of adsorbate at time t (min), V (L) is the volume of adsorbate solution, W (g) is the mass of adsorbents, q_t (mg/g) is the adsorbed amount at time t (min).

3. Results and discussion

3.1. Characterization of AC, AC-NA and AC-SA

The surface morphology of different activated carbons was characterized by SEM. As shown in Fig. 1, all the surface of activated carbons are loose and multi hole. These holes resulted from the evaporation of impregnates ZnCl₂ derived compounds, leaving the space previously occupied by the reagent.²² It could be seen that both AC-NA and AC-SA had more smooth surface structure than that of AC, which could be attributed to the interaction of nitric acid, sulfuric acid and AC.²³ The structure of carbonized products could obtain more surface area available, which is beneficial for surface adsorption.²⁴

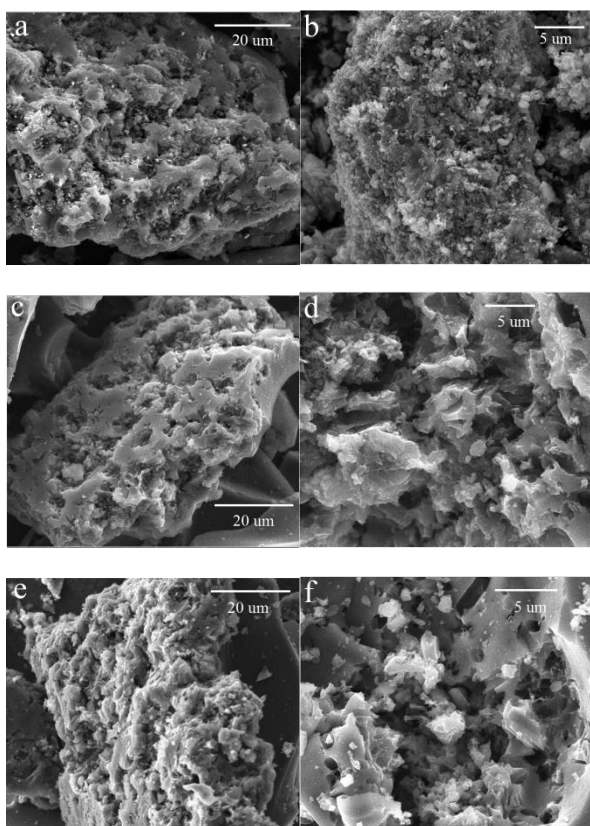


Fig.1 SEM of AC (a, b), AC-NA (c, d) and AC-SA (e, f).

The N₂ adsorption/desorption isotherms (inset) and pore size distributions for AC, AC-NA, AC-SA were shown in Fig.2. The N₂ adsorption/desorption isotherms of the three carbons were a mixture of types IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification, with a wider hysteresis loop, indicating that AC, AC-NA and AC-SA have mesoporous structures. The textural properties of carbonized product were presented in Table 1. Compared with the surface area of AC (1003.8 m²/g), the surface area of AC-NA and AC-SA had a lower value of 838.3 m²/g and 960 m²/g, respectively. The decrease of the surface area in mineral acid modification process is mainly caused by the decrease in the micropore volume. The result was constant with the literature reported by Huang et al., in which the activated carbon was modified with nitric acid and applied for Cr(VI) sorption.²⁵ However, the surface area of activated carbons in this work were larger than that of other reported sludge adsorbents (Table 1). Moreover, the total pore volumes (V_{tot}) of AC-NA and AC-SA decrease to 0.498 and 0.531 cm³/g compared with AC (0.594 cm³/g), respectively. However, the average pore diameters (D_p) of the three activated carbons have no significant different (2.37, 2.37, 2.38 nm for AC, AC-NA, AC-SA, respectively).

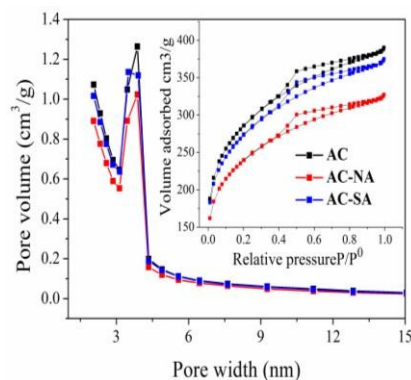


Fig.2 Pore size distributions (N₂ adsorption/desorption isotherms (inset)) of the activated carbons.

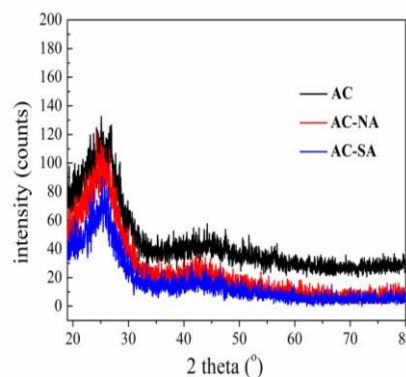


Fig.3 The X-ray powder diffraction patterns of the activated carbons.

Table 1. Comparison of the textural properties of raw sludge and the carbonized product.

samples	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	$S_{\text{mic}}/S_{\text{BET}}$ (%)	V_{mic} (cm^3/g)	V_{tot} (cm^3/g)	D_p (nm)	Refs.
AC	1003.8	360.7	643.1	35.9	0.159	0.594	2.37	this work
AC-NA	838.3	298.0	540.3	35.5	0.133	0.498	2.37	this work
AC-SA	960.0	328.3	631.7	34.2	0.145	0.531	2.38	this work
AC-1	472.0	-	-	-	0.010	0.320	-	27
AC-2	29.2	-	-	-	-	0.052	7.10	28
AC-3	202.0	-	-	-	-	0.240	0.340	29

BET surface area (S_{BET}), external surface area (S_{ext}), micropore surface area (S_{mic}), micropore volume (V_{mic}), total pore volume (V_{tot}), and average pore diameter (D_p)

Fig. 3 shows the XRD patterns of the three activated carbons. Similar broad peaks at $2\theta = 25.5^\circ$ and 44° were observed, indicating the presence of large amounts of amorphous carbon nanoparticles. Kadirova et al. also reported the similar XRD results of granular activated carbons prepared from commercial activated carbon by heat treatment.²⁶

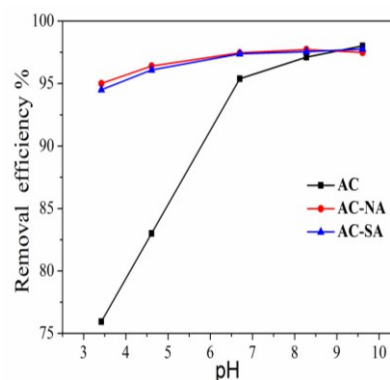
The results of Boehm titrations were given in Table 2. The AC-NA and AC-SA contained more acidic groups than that of AC, indicating the mineral acid modification obviously enhanced the surface acidity of activated carbon. The total surface acidity of the carbons is higher than basicity. The amounts of acidic groups on the three activated carbons' surfaces were as follows: phenolic > carboxylic > lactonic.

3.2 Effect of adsorbent dose

The effect of adsorbent dose on MG removal by AC, AC-NA and AC-SA were shown in Fig. S2 (ESI†). The dose of adsorbents varied from 3 to 18 mg in a 40 mL MG solution (30 mg/L). It can be seen that the removal percentage of MG increased with the increasing activated carbon doses. The reason may due to the increasing sorbent surface area and availability of more adsorption sites.³⁰ However, the dye removal percentages could not be significantly improved when the doses of AC, AC-NA and AC-SA increased to 12 mg. This may be due to an insufficient number of MG in the solution overlapping or aggregating of adsorption sites.³¹ Considering the removal efficiency and practicality, 12 mg was selected as the optimum adsorbent dose in the following study.

Table 2. Concentrations of surface functional groups of the carbons.

Samples	carboxylic	lactonic	Phenolic	Total acidic	Basic
	(mmol/g)	(mmol/g)	(mmol/g)		
AC	0.296	0.104	1.301	1.701	0.308
AC-NA	1.02	0.206	2.064	3.290	0.208
AC-SA	0.96	0.224	2.148	3.332	0.116

**Fig. 4** Effect of initial pH values on the adsorption of MG onto carbons

3.3. Effect of initial pH

In order to explore the effect of pH value on MG removal, experiment were conducted at various pH values for activated carbons. The initial pH values of MG solutions were controlled in the range of 3.5 to 9.5, and the results were shown in Fig. 4. Data implied that MG removal efficiency gradually increased with increasing pH values for all three kinds of carbons. The maximum adsorption efficiency could reach above 95 % when the pH value at 9.5. More detailed, for AC, pH values could affect the MG removal efficiency (76 and 95 % for pH at 3.5 and 9.5, respectively). A good adsorption performance was observed at a pH range from 6.5 to 9.5. However, The removal efficiency of MG was always above 94 % at various pH values for AC-NA and AC-SA.

At low pH values, the high concentration of H^+ ions accelerated the protonation of the functional groups easily, thereby the adsorbent became more positively charged.³² There is a repulsion force between the MG molecules and the

adsorbent surface. Furthermore, excessive H^+ ions would compete with positively charged MG molecules for the adsorption sites, so the adsorption of MG decreased greatly at low solution pH values. However, with the increase of pH values, this competition receded and dye cations bound to the adsorbent surface more easily. Therefore, the removal efficiency of MG increased at high pH values.³³

3.4 Adsorption kinetics

Adsorption is a time-dependent process, and it is important to predict the removal rate of contaminants from aqueous solution for the design and optimization of a wastewater treatment plant. Fig. 5(a) shows the effect of contact time on the MG adsorption by the activated carbons. The adsorption efficiencies of MG onto three carbons increased rapidly in the first 60 min and thereafter gradually increased till it reached equilibrium at 240 min. The fast adsorption during the initial stage may be due to the fact that the higher driving force made fast transfer of MG to the surface of adsorbent particles. After a period of time, the adsorption became difficult because the number of vacant sites decreased and a repulsive force formed between the solute molecules on solid surface and the bulk phase.³⁴ Furthermore, it could be observed that the modified activated carbons had higher MG removal efficiencies than the unmodified carbon.

Pseudo-first-order and pseudo-second-order kinetic models were used to evaluate adsorption kinetics of MG onto carbons (Fig. 5 (b) and (c)).

Pseudo-first-order kinetic equation (Eq (3)):³⁵

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Pseudo-second-order kinetic equation (Eq (4)):³⁶

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_t and q_e (mg/g) refer to the amount that adsorbed at time t and at equilibrium, k_1 (min^{-1}) is the pseudo-first-order rate constant for the adsorption process and k_2 (g/mg min) is the pseudo-second-order rate constant.

The parameters obtained from models were presented in Table S1(ESI†). The correlation coefficients (R^2) value for pseudo-second-order model was higher than that of pseudo-first-order model. Moreover, the values of the calculated q_e are very close to the experimental data according to pseudo-second-order kinetic model, while the calculated q_e value differed a lot from pseudo-first-order equation. Therefore, the adsorption of MG onto activated carbon can be well described by the pseudo-second-order model and supported the assumption for the model that the adsorption is caused by the chemisorptions.³⁷

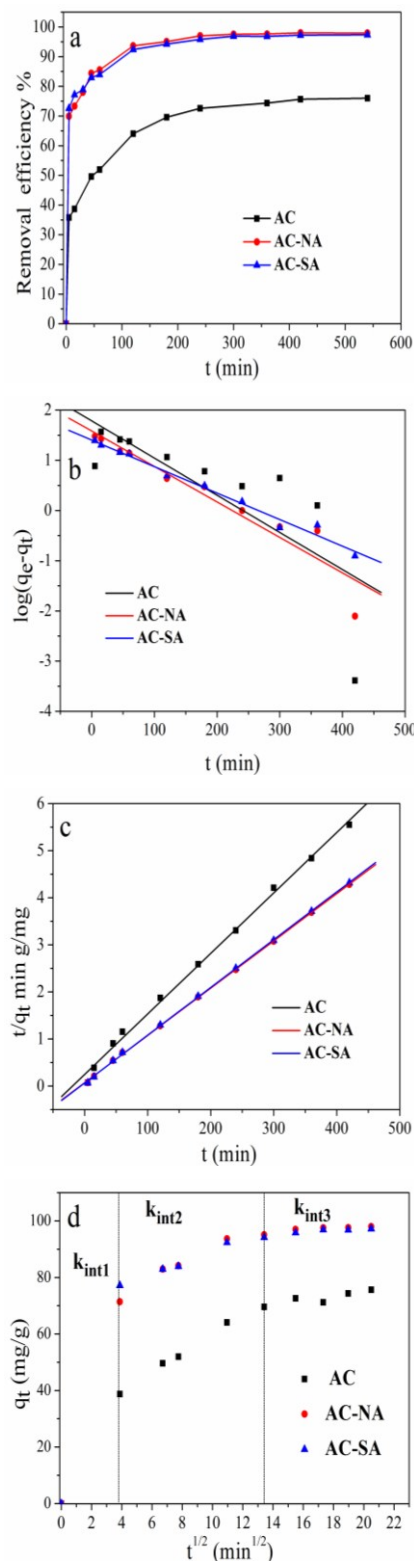


Fig. 5. (a) Effect of contact time, (b) Pseudo-first-order kinetics plots, (c) Pseudo-second-order kinetics plots (d) Intra-particle diffusion plots for MG onto activated carbon.

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Table 3. Isotherm parameters for adsorption of MG onto activated carbons.

	Samples		
	AC	AC-NA	AC-SA
		Freundlich	
K_F	24.45	88.52	78.00
$1/n$	0.4251	0.2280	0.2434
R^2	0.9255	0.8648	0.9183
		Langmuir	
q_m (mg/g)	269.54	303.03	284.90
K_L (l/mg)	0.0203	0.0585	0.0626
R^2	0.9843	0.9974	0.9996
R_L	0.1593-0.4509	0.0617-0.2217	0.0579-0.2103

The intra-particle diffusion model was applied in order to elucidate the diffusion mechanism and investigate whether intra-particle diffusion is the rate-limiting step in the adsorption process. The intra-particle diffusion can be expressed in the following way (Eq (5)):³⁸

$$q_t = k_{int} t^{1/2} + C \quad (5)$$

The k_{int} is the intra-particle diffusion rate constant (mg/g min^{1/2}), where C is the intercept that reflects the boundary layer effect; the larger the C value is, the greater the contribution of the surface sorption in the rate-controlling step will be.

Fig.5(d) shows the intra-particle plot for MG onto the activated carbon. It was evident that the adsorption process follows three steps which indicated the multi-stage adsorption processes.³⁹ The diffusion parameters of each region are shown in Table S2 (ESI†). Each step is able to be identified by a change in the slope of the linear line which is used to fit the experimental data. These results could be illustrated as follows: the first region was very sharp and indicated rapid attachment of MG molecules to the external surface of the activated carbon. The second linear region was the gradual adsorption stage in which the intra-particle diffusion was the rate-limiting step. The third region showed the final equilibrium stage where MG diffusion was very slow due to its low concentration.⁴⁰ It can be seen that the linear lines of the second and the third stage did not pass through the origin. Therefore, intra-particle diffusion was not the only rate limiting-step and the main chemisorption or physisorption may be involved in the process.⁴¹

3.5 Adsorption isotherms

The adsorption equilibrium data were analyzed using the Freundlich and Langmuir isotherms. The linear form of Freundlich isotherm equation (Eq (6)) is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

The linear form of Langmuir isotherm equation (Eq (7)) is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (7)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_e (mg/L) is the equilibrium dye concentration in solution, K_F is the Freundlich constant and $1/n$ is the heterogeneity factor, respectively. Where q_m (mg/g) is monolayer adsorption capacity, K_L (L/mg) is Langmuir isotherm constant.

The essential feature of a Langmuir isotherm can be expressed in accordance with a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined by (Eq (8)):

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

where C_0 (mg/L) is the initial dye concentration and K_L (L/mg) is Langmuir isotherm constant. The R_L values indicate the type of the isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), irreversible ($R_L = 0$).

The adsorption parameters of Langmuir and Freundlich isotherm were summarized in Table 3. Compared with Freundlich isotherm model, the Langmuir isotherm model had a higher correlation coefficient (R^2), which indicated that the sorptions MG onto ACs were monolayer uniform adsorption. Zhang et al. also reported the sorption of MG onto carbon prepared from *Arundo donax* root, in which the equilibrium experimental data were better fitted to Langmuir isotherm.³¹

Table.4 Comparison of the maximum adsorption capacities of MG onto various adsorbents.

Precursor	Chemical activation	q_{\max} (mg/g)	Refs.
Aerobic granular sludge	ZnCl ₂	269.54	this work
Rice husk	NaOH	24.92	32
Rambutan peel	KOH	25.26	41
Lignite	KOH	200.00	42
Ricinus communis	H ₂ SO ₄	27.78	43

Moreover, the values of R_L were between 0 and 1, indicating the adsorption processes were very favorable.⁴⁴

Table 4 shows the comparison of the maximum adsorption capacities of MG onto various adsorbents. Although the published values were obtained under different experimental conditions, they may be useful as a criterion for comparing the adsorption capacities. It can be seen that the adsorption capacity of MG in this work was larger than other biological adsorbents.

3.6 Adsorption mechanism

The surface functional groups of AC, AC-NA and AC-SA were investigated by using FTIR spectroscopy in the range of 4000-450 cm⁻¹ (Fig. 6 (a)). After dye adsorption, the functional

groups of ACs were also measured and compared. The peaks for the three kinds of activated carbons were very similar, indicating that the samples have similar functional groups. The peaks at 3435 cm⁻¹ and 2927 cm⁻¹ represented the stretching frequency of the hydroxyl group and C-H vibration.⁴⁵ The band at 1621 cm⁻¹ may be attributed to asymmetric stretching vibration of -COO.⁴⁶ The band at 1379 cm⁻¹, 1113 cm⁻¹ and 618 cm⁻¹ corresponded to aromatic C=C stretching vibration, C-OH and C-O-H twist bending vibration.⁴⁷ After adsorption of MG, some new absorption bands were occurred on dye-loaded the activated carbon (Fig.6 (b)). The band at 1569 cm⁻¹ corresponded to aromatic ring⁴⁸. The band at 876 cm⁻¹ and 1040 cm⁻¹ were corresponded to N-O⁴⁹, indicating that MG was adsorbed onto activated carbons by chemisorption.

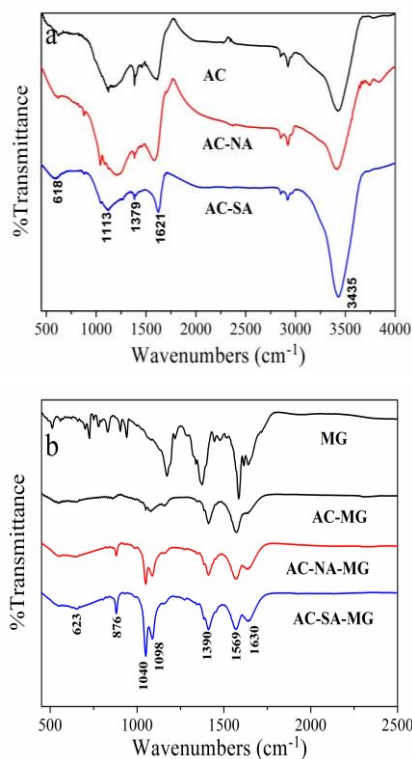


Fig.6 (a) The infrared spectrum of the activated carbon, (b) The infrared spectrum of the activated carbon after adsorption of MG

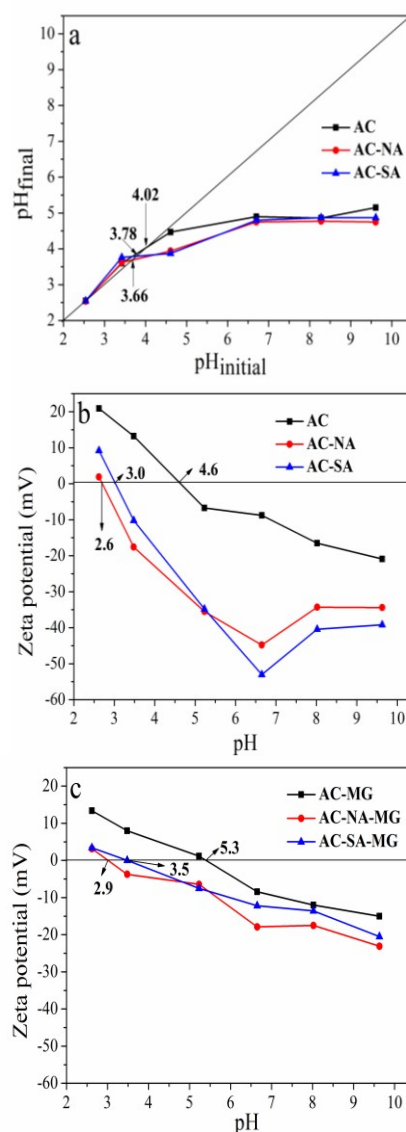


Fig.7 (a) The change of pH values after adsorption of MG, (b) Zeta potential of activated carbons, (c) Zeta potential of activated carbon after adsorption of MG.

The pH values of solution after the sorption experiments were shown in Fig. 7 (a). The final equilibrium pH values became lower after the adsorption of MG. Furthermore, the final pH values of AC-NA and AC-SA were lower than that of AC. One possible reason maybe acidic functional groups on the carbons surface could release H⁺ into solution. A similar phenomena has been reported by Mall et al., in which the presence of acidic functional groups on the surface was likely to give considerable cation exchange capacity to the adsorbents.
50

The zeta potentials of activated carbons before MG adsorption were shown in Fig. 7 (b). The modified activated carbons (AC-NA, AC-SA) have a relatively smaller isoelectric point and zeta potential than that of AC, indicating that positively charged pollutants (MG) may be more easily absorbed. After MG adsorption, the zeta potentials of carbons were significantly increased at the same pH values (Fig.7.(c)). Therefore, it could be speculated that the electrostatic attraction plays a certain role in adsorption process.

From Table 1 and 2, the S_{BET} , V_{mic} and V_{tol} of AC were higher than those of AC-NA and AC-SA, while AC showed less acidic groups. However, AC showed lower MG adsorption capacity (269.54 mg/g) than that of AC-NA (303.03 mg/g) and AC-SA (284.90 mg/g). Therefore, it could be concluded that surface functionality rather than pore structure played a more crucial role to determine the adsorption capacity of MG. Liu et al. also reported the adsorption mechanisms of Pb(II) onto activated carbons prepared from lotus stalks (LS), implying that higher content of O-containing functional groups could adsorb more Pb (II) species by electrostatic attraction, cation exchange and surface complexation.⁴⁶

4. Conclusion

In this study, AC, prepared from aerobic granular sludge, was successfully prepared by zinc chloride activation and used for MG adsorption. The prepared AC exhibited high specific surface area. The modified activated carbons with nitric acid and sulfuric acid showed lower surface area, and more surface oxygen functional groups compared with untreated activated carbon. The adsorption capacities are significantly influenced by the contact time, pH value and sorbent dose. Adsorption kinetic was found to follow the pseudo-second-order kinetic model for the activated carbons. The adsorption equilibrium data were better fitted with the Langmuir model.

5. Acknowledgements

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