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Microwave regeneration of spent activated carbon for the treatment of ester-containing wastewater†

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In this study, an integrated granular activated carbon (GAC) adsorption/microwave (MW) irradiation process was used for the treatment of ester-containing wastewater from a lithium-ion battery (LIB) factory. Firstly, ester-containing organic matter was adsorbed onto GAC, then the pollutants were decomposed. The GAC was then regenerated by MW irradiation. The efficacy of this procedure was analyzed by determining adsorption effectiveness, adsorption kinetics and the textural properties of GAC in successive GAC adsorption/MW cycles. The mechanism of MW regeneration was investigated by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric (TG) analysis. The results show that the adsorption isotherms and kinetics for the adsorption of ester contaminants are in accordance with Langmuir isotherm and pseudo second-order kinetic models. It was also found that though the adsorption rate constant (k_2) of GAC increased with the adsorption/MW regeneration cycles, the adsorption capacity (q_m) decreased where the q_m of GAC at the 5th regeneration cycle had a 20.4% reduction in comparison to the determined original GAC, which could be explained by changes in the GAC's textural properties. The GAC adsorption/MW process mainly occurred at the peak of 1117 cm^{-1} by FTIR. Through TG and differential thermogravimetric (DTG) analyses, the weight loss of saturated GAC took place between $120\text{ }^\circ\text{C}$ and $260\text{ }^\circ\text{C}$, caused by the decomposition of ester organic molecules.

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1 Introduction

Lithium-ion batteries (LIBs), which are light weight, energy dense, and have a long storage life, have been increasingly produced since industrialization in the 1990s, largely for applications in the portable electronics industry.^{1,2} The disposal of spent LIBs has attracted much attention from environmental scientists^{3,4} due to the latent environmental risks caused by the use of a wide variety of complex solvents and heavy metals.⁵ In the past decades, research has focused on the recovery of valuable metals from spent LIBs^{6–8} and on the removal of heavy metals from landfills containing spent LIBs, as heavy metals have been known to leach into surrounding soils.^{9–11} However, the reclamation of wastewater generated by the LIB

manufacturing processes has not yet been investigated. LIB manufacturing wastewater contains a significant amount of organics and inorganics such as dimethyl carbonate (DMC), carbonic acid ethyl methylester (CEM), diethyl carbonate (DC), ethylene carbonate (EC), *N*-methylpyrrolidone (NMP) and lithium hexafluoro phosphate (LiPF_6). Biodegradation is not an efficient treatment of the wastewater as it contains complicated components with high levels of chemical oxygen demand (COD) and low levels of biodegradability.¹²

Activated carbon (AC) adsorption may be one of the most effective technologies for the pretreatment of highly concentrated and refractory organic wastewater.^{13,14} The application of AC adsorption allow the effect of toxic pollutants on microbes to be alleviated, which is conducive to a stable and cost effective treatment process.¹⁴ The economics of the adsorption process depends on the potential reuse of AC. There are several well-established methods for the regeneration of exhausted AC, including thermal, chemical and biological regeneration.¹⁵ Thermal regeneration is the most widely used regeneration technology, however, it requires an extremely high temperature environment (above 1100 K) and its application is limited due to the significant energy demand.¹⁶ Chemical regeneration involves desorption of adsorbates with specific solvents or by decomposition of adsorbed species using oxidizing chemical agents under subcritical/supercritical conditions.^{15,17} The requirement of further purification and the necessity of harmful solvents increases disposal costs.¹⁸ As a result of the long

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reaction time and the limitations of biodegradable adsorbed substances, no efficient biological regeneration protocol has yet been found.^{15,19}

Microwave (MW) regeneration is a promising method of AC regeneration because of its short regeneration time, high regeneration efficiency, less regeneration loss and significant energy savings.^{20–22} Presently, new-type carbon materials called magnetoresistive polyaniline–magnetite nanocomposites have been explored with microwave absorption applications, which possess stabilized magnetic properties, oxidative resistance and indissolvable potential under acidic condition.^{23,24} However, the adsorption and regeneration mechanism of the MW regeneration for spent AC needs to be comprehensively understood under different reaction conditions. Ania *et al.*²⁵ reported the regeneration of AC spent with salicylic acid having regeneration efficiencies of up to 99% after six cycles with MW irradiation at 2450 MHz. Liu *et al.*²⁶ regenerated GAC that had been spent with 2,4,5-trichlorobiphenyl in a simulated soil-washing solution in a quartz reactor with 2450 MHz MW irradiation for 5 min, with a regeneration yield after five adsorption/regeneration cycles of up to 163%. Mao *et al.*²⁷ also examined the microwave-assistant irradiation restored the original adsorption capacity of the spent activated carbon prepared with pine and wheat activated carbon, when the microwave regeneration was conducted at a constant power of 600 W for irradiation times of 3 min (toluene) and 1 min (acetone), the results showed that the regeneration efficiencies after the initial cycle of microwave irradiation were 97.0–98.4% during the five adsorption/regeneration cycles. Deng *et al.*²⁸ showed that the prepared functional fibrous fibers still retained more than 85% of the original adsorption capacity for the heavy metal ions from wastewater, which indicated that there was no appreciable loss in capacities during the five MW regeneration cycles. Liu *et al.*²⁹ derived that the regenerated efficiency of exhausted GAC was 97.6% of its original adsorption when the microwave power, radiation time and the GAC amount were 400 W, 3 min, and 10 g respectively. The regenerated efficiency maintained a stable performance in the first few repetitions, but a decrease was observed after further repetitions. Despite the availability of several studies, the mechanisms of successive AC adsorption/MW regeneration had never being observed during the ester-containing wastewater treatment. In our previous study,¹² optimal parameters for GAC adsorption and MW regeneration were determined for the pretreatment of ester-containing wastewater from a LIB factory. However, the inherent mechanism including adsorption equilibrium isotherms, adsorption kinetics, and MW regeneration were not determined.

In this study, a GAC adsorption/MW irradiation process was used in the treatment of ester-containing wastewater from a LIB factory. Adsorption efficiency, regeneration efficiency, and the regeneration loss rate were analyzed in successive adsorption/MW regeneration cycles under optimal operation conditions. The adsorption equilibrium isotherms and adsorption kinetics of the GAC were also investigated. The mechanisms of MW regeneration were also explored, based on Brunauer–Emmett–Teller (BET) theory, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric (TG) analysis.

2 Materials and methods

2.1 Wastewater

The experimental wastewater was ester-containing wastewater generated by a LIB factory in Northern China. The wastewater was a mixture of the wastewater from the cleaning of the surface of LIBs after the secondary seal producing processes and the condensate water of a vacuum pump involved in the liquid injection process. The wastewater was stored at 4 °C. The physical and chemical properties of the wastewater are shown in Table 1. This wastewater is characterized by high levels of chemical oxygen demand (COD) and low biodegradability, and contains ester organic pollutants such as dimethyl carbonate, diethyl carbonate, and methyl ethyl carbonate. The main composition of pollutants in the ester-containing wastewater is shown in Table S1.†

2.2 Experimental procedure

2.2.1 GAC adsorption. Treatment of ester-containing wastewater with the activated carbon adsorption method was investigated. 100 mL of wastewater and the original GAC (OAC) were added into a 250 mL Erlenmeyer flask which was placed on a shaking table. The rotation speed and temperature were 150 rpm and 20 °C respectively. This adsorption experiment was conducted under conditions of pH 3.0–5.0 and a GAC dosage of 10 g L^{−1}.¹²

2.2.2 MW regeneration. The saturated GAC (SAC) was regenerated by MW. Under the conditions of a MW power of 420 W and irradiation time of 6 min per cycle,¹² the regeneration efficiency and regeneration loss of the regeneration cycles were investigated.

The regeneration efficiency (R_E) and regeneration loss (R_S) were calculated with the following equations:

$$R_E = \frac{\text{COD}_{\text{cr}} \text{ removal of OAC (\%)}}{\text{COD}_{\text{cr}} \text{ removal of RAC (\%)}} \times 100\% \quad (1)$$

$$R_S = \frac{\text{OAC weight (g)} - \text{RAC weight (g)}}{\text{OAC weight (g)}} \times 100\% \quad (2)$$

where OAC represents the original granular activated carbon before adsorption and RAC is the regenerated GAC that was the product of MW regeneration of SAC.

2.3 Analytical methods

Most of the wastewater quality parameters were measured according to The Water and Wastewater Monitoring and Analysis Method (4th Edition).³⁰ In addition, COD_{cr}, BOD₅, and TOC were respectively measured by a COD rapid digestion apparatus (DIS-1A, Shenzhen Changhong Instrument, Co., Ltd., China), OxiTop system (OxiTop, WTW, Germany), and vario TOC analyzer (vario TOC, Elementar, Germany). The pH was determined with an automatic potentiometric titrator meter (ZD-2, LEICI, China) at 20 °C.

The surface area and pore characteristics of GAC were analyzed using a gas adsorption apparatus (QuadraSorb SI, Quantachrome Instruments, USA). A BET equation was used to

Table 1 Characteristics of the ester-containing LIB factory wastewater. Data generated from 107 samples of COD_{cr} and pH and 53 samples of BOD₅, NH₃-N and BOD₅/COD_{cr}^a

Parameter	COD _{cr} (mg L ⁻¹)	BOD ₅ (mg L ⁻¹)	NH ₃ -N (mg L ⁻¹)	BOD ₅ /COD _{cr}	pH
Range of values	1800–3000	120–360	0.3–1.0	0.05–0.12	3.0–5.0
Mean ± S.D.	2316 ± 130	147 ± 48	0.48 ± 0.08	0.06 ± 0.008	3.5 ± 0.8

^a S.D. is the abbreviation of standard deviation.

calculate the total surface area and average pore diameter. The total pore volume was calculated from a single N₂ adsorbance point at a relative pressure of 0.99. Density functional theory (DFT) was used to analyze the successive pore size distribution curve from micropores to mesopores. The micropore and mesopore size distributions were deduced using the Horvath-Kawazoe (HK) and Barrett-Joyner-Halenda (BJH) methods.

The chemical functional groups in the samples were investigated by FTIR (Nicolet 6700, Thermo Fisher Scientific, USA). Thin disc samples with a diameter of approximately 10 mm and a thickness of 1 mm were made from a homogeneous mixture of GAC samples and a certain amount of potassium bromate (KBr). Each sample was then scanned at wavenumbers from a range of 4000 to 400 cm⁻¹. The quantities of surface functional groups were measured with the Boehm iodometric method.³¹

TG and derivative thermogravimetric (DTG) analysis was carried out with a thermogravimetric analyzer (TG/DTA6300, SEIKO, Japan). To investigate the pyrolysis behaviors of the original, saturated, and regenerated activated carbon, approximately 5 to 10 mg of each sample was pyrolysed under 200 cm³ min⁻¹ N₂ (99.995%) flow at a heating rate of 10 °C min⁻¹ from room temperature to 900 °C. Before the TG-DTG analysis, the saturated GAC was dried in an oven at 80 °C for 3 h.

COD_{cr} *etc.* means were calculated from three independent runs of the reactor, with values given as mean ± standard deviation throughout the text.

2.4 Adsorption studies

2.4.1 Adsorption isotherms. Equilibrium sorption studies were conducted in a set of 250 mL Erlenmeyer flasks each containing 100 mL ester-containing wastewater and 0.2, 0.4, 0.6,

0.8, 1.0, 1.5, 2.0, 3.0, and 5.0 g OAC or RAC with a corresponding initial AC amount (2, 4, 6, 8, 10, 15, 20, 30 and 50 g L⁻¹, respectively). The flasks were agitated in a shaker at 150 rpm and 20 °C for 2 h to reach equilibrium. Samples were taken at regular time intervals and the concentrations of COD_{cr} were measured. The COD_{cr} uptake per unit mass of adsorbent at equilibrium, q_e (mg g⁻¹), was calculated by eqn (3):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where C_0 and C_e (mg L⁻¹) are the initial and equilibrium liquid-phase concentrations of COD_{cr}, V (L) is the volume of the wastewater, and m (g) is the mass of OAC or RAC used. The equilibrium data were modeled using the Langmuir, Freundlich and Temkin isotherm models, and the model equations are shown in Table 2.^{32,33}

2.4.2 Adsorption kinetics. The experiment was performed at 20 °C using 1.0 g of OAC or RAC with 100 mL of wastewater in a 250 mL Erlenmeyer flask. The amount of COD_{cr} adsorbed by carbon at time t , q_t (mg g⁻¹), was calculated by eqn (4):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (4)$$

where C_t (mg L⁻¹) is the liquid-phase concentration of COD_{cr} at time t . Three widely used kinetic models, including pseudo-first-order, pseudo-second-order and Elovich kinetic models (Table 3),³⁴ were used to characterize the adsorption process of GAC during the adsorption/MW irradiation process.

2.4.3 Adsorption mechanism. The adsorption process is not only confined to interactions between solutes on the surface of the adsorbents but also the mechanisms by which solutes diffuse into the pores of the adsorbent. In order to examine the

Table 2 Linear and non-linear forms of Langmuir, Freundlich, and Temkin isotherm models^a

Model	Non-linear form	Linear form	Plot
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$	$\frac{C_e}{q_e}$ versus C_e
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$	$\ln q_e$ versus $\ln C_e$
Temkin	$q_e = B \ln(K_T C_e)$	$q_e = \frac{RT}{b} \ln C_e + \frac{RT}{b} \ln K_T$	q_e versus $\ln C_e$

^a q_m (mg g⁻¹) is the maximum monolayer adsorption capacity of the sorbent, K_L (L mg⁻¹) is the Langmuir constant related to the free energy of the sorption, and K_F (mg g⁻¹) (L mg⁻¹)^{1/n} and $1/n$ are the Freundlich adsorption constant and a measure of adsorption intensity; K_T (L mg⁻¹) is the Temkin equilibrium binding constant, and $B = RT/b$, with R (8.314 J mol⁻¹ K⁻¹), T (K), and b (J mol⁻¹), are the Temkin constant that refer to the gas constant, absolute temperature, and heat of sorption, respectively.

Table 3 Linear and non-linear forms of pseudo-first-order, pseudo-second-order and Elovich kinetic models^a

Model	Non-linear form	Linear form	Plot
Pseudo-first-order	$q_t = q_e[1 - \exp(-k_1 t)]$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ versus t
Pseudo-second-order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2}$	$\frac{t}{q_t}$ versus t
Elovich	$q_t = b \ln(abt)$	$q_t = \frac{1}{b} \ln t + \frac{1}{b} \ln(ab)$	q_t versus $\ln t$

^a k_1 (min^{-1}), k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the adsorption rate constants of the pseudo-first-order equation and pseudo-second-order equations, respectively. a ($\text{mg g}^{-1} \text{min}^{-1}$) is the initial sorption rate and b (g mg^{-1}) is related to the extent of surface coverage and activation energy for chemisorption. The value of $(1/b)$ is indicative of the available number of sites for adsorption while $(1/b) \ln(ab)$ is the adsorption quantity when $\ln t = 0$.

diffusion mechanism of the adsorption process, the Weber and Morris intraparticle diffusion model (IPD)³⁵ was applied to analyze the kinetic results:

$$q_t = k_{\text{di}} t^{0.5} + C_{\text{di}} \quad (5)$$

where k_{di} ($\text{g mg}^{-1} \text{min}^{-0.5}$) is the diffusion rate constant and C_{di} reflects the boundary layer effect. If intraparticle diffusion is involved, the plot q_t versus $t^{0.5}$ gives a straight line with slope, k_{di} and intercept, C_{di} . If intraparticle diffusion is the only rate-limiting step, the plot passes through the origin. Alternatively, both external diffusion and intraparticle diffusion contribute to the adsorption process when the straight line deviates from the origin. The larger C_{di} indicates the greater effect of the boundary layer on diffusion.

3 Results and discussion

3.1 The GAC adsorption under various MW regeneration cycles

3.1.1 GAC adsorption and MW regeneration effectiveness. Variation in adsorption efficiency, regeneration efficiency, and the regeneration loss rate were investigated under the optimal operation conditions (shown in Section 2.2), with the results shown in Fig. 1.

Fig. 1a shows a reduction in the COD_{cr} of the wastewater during the GAC adsorption for 30 min, and then a stable level for the remaining 90 min. The COD_{cr} removal efficiency of GAC was 67.5% at the adsorption time of 30 min, corresponding to an improved biodegradability from 0.06 to 0.25. The COD_{cr} removal rate decreased in further MW regeneration cycles, which might have been caused by a change in the textural structure of GAC, *i.e.* the oxidation of interior specific area and the obstruction of mesopores. When the SAC was regenerated at the first cycle, the R_E was 98.7%, corresponding to a 5.2% R_S , which suggests that MW is efficient in the regeneration of saturated activated carbon (shown in Fig. 1b). After 5 MW regeneration cycles, the R_E was still up to 76.9%, though the R_S value was slightly high (14.7%). Therefore, the weight loss of the SAC during MW regeneration should be discussed. In the current study, the R_S value over five regeneration cycles were successively 5.2, 9.9, 12.1, 12.9 and 14.7% respectively. It could be because the high temperature and certain oxygen containing reaction environments during MW regeneration led to a weight loss for the SAC. Furthermore, the textural properties were possibly changed (shown in Fig. 5a) at high temperature, resulting in a decrease in the mechanical properties, which brought about additional weight loss by abrasion. However, the regeneration loss was not unfeasible based on laboratory scale

Fig. 1 (a) The variation of COD_{cr} removal with adsorption time and the variation of $\text{BOD}_5/\text{COD}_{\text{cr}}$ with GAC adsorption under different regeneration cycles; (b) the variation of regeneration efficiency and regeneration loss with the MW regeneration cycles. Error bars represent standard deviation of three samples each from an independent run of the reactor.

testing results, suggesting that the MW regeneration process is still could be economically viable during the scale-up of MW regeneration in the near future.

3.1.2 Adsorption equilibrium isotherms. Fig. 2 shows that the regeneration process has a small effect on the nature of adsorption, with little difference in adsorption isotherm shape between 5th-RAC and OAC. With the analysis of different adsorption isotherms including Langmuir isotherm, Freundlich isotherm, and Temkin isotherm, isotherms of 5th-RAC and OAC exhibited very good fits with the Langmuir isotherm. The Langmuir adsorption isotherm describes the gas–solid-phase adsorption onto activated carbon, which was always applied to quantify and contrast the performance of different bio-sorbents.³⁶ In its derivation, the Langmuir isotherm refers to homogeneous adsorption, where each molecule possesses constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate), with no transmigration of the adsorbate in the plane of the surface.³⁷ According to the slope and intercept of the Langmuir equation (inset of Fig. 2b), the Langmuir constants of OAC (K_{L1}) and 5th-RAC (K_{L2}) are 0.013 L mg^{-1} and 0.0027 L mg^{-1} . Therefore, a dimensionless constant, commonly known as a separation factor (R_L) defined by Weber and Chakravorti,³⁸ can be represented as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where K_L (L mg^{-1}) refers to the Langmuir constant and C_0 is denoted to be the adsorbate initial concentration (mg L^{-1}). In

this study, a lower R_L value reflects that adsorption is favourable. The R_L value indicates the shape of the isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 0$) or unfavourable ($R_L > 1$).^{37,39} The calculated R_{L1} and R_{L2} values are 0.031 and 0.137. Both R_L values were between 0 and 1, indicating that the adsorption of ester-containing pollutants on the activated carbon was favourable in this study. In addition, the Langmuir adsorption capacity of OAC (q_{m1}) and 5th-RAC (q_{m2}) are 162.08 mg g^{-1} and 129.02 mg g^{-1} , respectively, where q_{m2} has a 20.4% reduction in comparison to OAC. It was found that the adsorption capacity (q_m) of GAC for ester-containing pollutants decreased after MW regeneration, which could be explained by change in the textural properties (shown in Fig. 5a).

3.1.3 Adsorption kinetics. The OAC and RAC had rapid adsorption kinetics for ester-containing pollutants and their adsorption quickly reached equilibrium after approximately 30 min under different MW cycles (Fig. 3a). In comparison to the kinetic model of pseudo-first-order and IPD, the adsorption models of GAC at various MW cycles were in accordance with pseudo-second-order (shown in Table 4). The adsorption rate constant, k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) of RAC was increased with MW cycles. A similar result was reported by Liu *et al.*,²⁶ who also found that the adsorption rate of GAC after five cycles' reuse was higher than that of virgin GAC. However, Table 4 shows that the adsorption equilibrium (q_e) decreased with MW regeneration cycles, which could be ascribed to the change of textural properties of the GAC. It can also be seen that the q_e values obtained

Fig. 2 (a) Equilibrium study on the adsorption of ester-containing pollutants onto OAC (original granular activated carbon) and 5th-RAC (5th granular regenerated activated carbon); (b) Langmuir isotherm; (c) Freundlich isotherm, and (d) Temkin isotherm for the adsorption of ester-containing pollutants onto OAC and 5th-RAC.

Fig. 3 (a) Effect of contact time on the adsorption of ester-containing pollutants by the original granular activated carbon (GAC); (b) pseudo-first-order; (c) pseudo-second-order, and (d) Elovich kinetic models for the adsorption of ester-containing pollutants by the GAC at various MW cycles.

Table 4 Comparison of the pseudo-first-order, pseudo-second-order and Elovich kinetic models for the adsorption of ester-containing pollutants by the GAC at various MW cycles

MW cycles	$q_{e,exp}$ (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order			Elovich		
		k_1 (min ⁻¹)	$q_{e,calc}$ (mg g ⁻¹)	R_1^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e,calc}$ (mg g ⁻¹)	R_2^2	a (g mg ⁻¹ min ⁻¹)	b (g mg ⁻¹)	R_3^2
OAC	156.95	0.0450	59.62	0.8233	0.00212	165.84	0.9996	5.02×10^4	1.00045	0.6830
1st-RAC	155.13	0.0451	58.03	0.8154	0.00218	163.40	0.9995	5.52×10^4	1.00047	0.6703
2nd-RAC	147.95	0.0502	59.46	0.8704	0.00232	157.23	0.9996	3.76×10^4	1.00042	0.6947
3rd-RAC	142.72	0.0802	101.9	0.9524	0.00243	150.15	0.9995	6.60×10^4	1.00046	0.6675
4th-RAC	141.55	0.0544	60.73	0.8972	0.00247	149.48	0.9996	4.99×10^4	1.00040	0.6828
5th-RAC	124.38	0.0465	54.49	0.8602	0.00251	132.28	0.9996	3.21×10^4	1.00036	0.7241

from the pseudo second-order kinetic model ($q_{e,calc}$) of GAC for each of the MW cycles were similar to the obtained values from the experiment ($q_{e,exp}$). Therefore, it can be ascertained that the pseudo second-order kinetic model is suitable to describe the adsorption of ester-containing pollutants by GAC at various MW cycles. That the pseudo-second-order model fits these data indicates that the rate of adsorption is dependent on the availability of the adsorption sites rather than the concentrations of adsorbate in the bulk solution.

3.1.4 Adsorption mechanism. The pseudo-first-order and pseudo-second order kinetic models do not explain the diffusion mechanism between solutes and particles. The intra-particle diffusion (IPD) mechanism describes whether the

adsorption process followed the IPD or not. The curve-fitting plots of the IPD model are demonstrated in Fig. 4, and the IPD parameters can be seen from Table 5. This plot can be divided into three portions: a sharp rise portion, a less steep portion and a plateau portion. The first linear step is due to diffusion through the mesopores of ester-containing pollutants, where the high value of the correlation coefficient ($R_{d1}^2 > 0.9996$) at various MW cycles indicates that IPD occurred. Moreover, the plot passed near the origin (as shown in Table 5), suggesting that IPD was the dominating rate-limiting mechanism. The adsorption rate constant, k_{d1} (g mg⁻¹ min⁻¹) of RAC decreases with the MW cycle increment, which is the result of the destruction rate of mesopores to macropores being higher

Fig. 4 Plot of an intraparticle diffusion (IPD) model for the adsorption of ester-containing pollutants onto the GAC at various MW cycles.

than the generation speed of mesopores from micropores (the mesopores of OAC and 5th-RAC are shown in Fig. 5d). The second linear step represents micropore diffusion. The regression is nearly linear for each MW cycle, but the high value of the intercept ($C_{d2} = 140.5 \pm 12.2$) indicates that, IPD was not the sole limiting mechanism. This is because the boundary layer thickness increased over adsorption time, and the external mass transfer resistance for ester-containing pollutants became stronger. The third region is the final equilibrium stage, still with a high correlation coefficient ($R_{d3}^2 = 0.9945 \pm 0.004$), indicating that IPD slowed as a result of the relative high concentrations of ester-containing pollutants in the wastewater. Moreover, the slope (k_{di}) of the three linear portions, decreased with increasing contact time under various MW cycles, indicating that the adsorption driving force was weaker and consequently that there was a reduced diffusion rate.⁴⁰ As the ester-containing pollutant molecules diffuse into the inner structure of GAC, the pores become smaller. Therefore, the free path of molecules in the pore decreases and the molecules may also be blocked, which affects the adsorption rate.

3.2 The change of textural properties of OAC and RAC

The adsorption rate constant, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) of RAC increased with an increase in the number of MW cycles. This is

in contrast with adsorption models of GAC for the ester-containing pollutants. The change in RAC could be caused by a textural change in the regenerated GAC.

The adsorption capacity of GAC is reflected by the values calculated through application of the BET theorem. The N_2 -adsorption/desorption isotherms of OAC and 5th-RAC, as well as the DFT and HK pore size distributions were investigated to find out the influence of MW regeneration on GAC structure (shown in Fig. 5).

Fig. 5a shows the N_2 -adsorption/desorption isotherms of OAC and 5th-RAC. The adsorption/desorption isotherms of the two samples shows the first N_2 uptake in the low-pressure region where $p/p_0 < 0.02$, indicating the presence of micropores (diameter < 2 nm); there N_2 uptake continues to increase after the low-pressure region, indicating the presence of a large amount of mesopores ($2 \text{ nm} < \text{diameter} < 50 \text{ nm}$). The 5th-RAC presents a significant decrease in N_2 adsorption/desorption capacity in comparison to OAC. Similar results were also derived in previous literature.^{26,41} A sharp decrease in the amount of adsorbed nitrogen was also reported after successive cycles of MW regeneration. Based on the nitrogen quantity adsorbed at different relative pressures, the main textural parameters of GAC were calculated (Fig. 5a). The BET surface area (S_{BET}) of 5th-RAC was $892 \text{ m}^2 \text{g}^{-1}$, which was 79.6% of the OAC (S_{BET} of $1121 \text{ m}^2 \text{g}^{-1}$). The total volume of 5th-RAC was lower than that of OAC. However, the total volume (V_{total}) of 5th-RAC was still as high as $0.511 \text{ cm}^3 \text{g}^{-1}$, corresponding to a 24.4% destruction of the OAC ($V_{\text{total}} = 0.676 \text{ cm}^3 \text{g}^{-1}$).

The DFT curve of OAC and 5th-RAC reached a maximum at pore diameters of about 0.78 nm and 0.98 nm, which shows that the maximum peak shifts after five MW regeneration cycles. This phenomenon was consistent despite the variation of S_{BET} and V_{total} . Further, the curve of the two samples also had two minor peaks represented by pores sizes of about 1.02 to 1.78 nm, indicating the presence of supermicropores (diameter between 0.7 and 2 nm). The HK and BJH pore size distribution curves of OAC and 5th-RAC are presented in Fig. 5c and d. The HK curve of two samples had a maximum derivative micropore volume (dV_{micro}) value of $0.099 \text{ cm}^3 \text{g}^{-1}$ and $0.075 \text{ cm}^3 \text{g}^{-1}$ at 0.56 nm and 0.61 nm, respectively, as corresponding to the V_{micro} of 0.471 and $0.363 \text{ cm}^3 \text{g}^{-1}$. It was revealed that the 5th-RAC still had potential for the adsorption of micromolecular organics from aqueous phase (diameter between 0.4 and 0.9 nm). This conclusion is consistent with the GAC adsorption

Table 5 Parameters of an intraparticle diffusion (IPD) model for the adsorption of ester-containing pollutants onto the GAC at various MW cycles

MW cycles	k_{d1} ($\text{g mg}^{-1} \text{min}^{-0.5}$)	C_1	R_{d1}^2	k_{d2} ($\text{g mg}^{-1} \text{min}^{-0.5}$)	C_2	R_{d2}^2	k_{d3} ($\text{g mg}^{-1} \text{min}^{-0.5}$)	C_3	R_{d3}^2
OAC	33.71	0.4193	0.99965	0.7049	153.2	0.98305	0.6131	155.4	0.99145
1st-RAC	33.21	0.2795	0.99984	0.5976	151.8	0.95792	0.5757	153.4	0.99515
2nd-RAC	31.90	0.1398	0.99996	0.9862	143.2	0.82952	0.3976	149.1	0.99706
3rd-RAC	30.82	0.0000	0.99999	0.9351	137.8	0.96482	0.0186	146.3	0.99981
4th-RAC	30.50	-0.1398	0.99995	0.8688	137.0	0.96272	0.2353	143.4	0.99289
5th-RAC	26.78	-0.2795	0.99976	0.7766	119.8	0.91660	0.4195	124.4	0.99075

Fig. 5 (a) N₂-adsorption/desorption isotherms and main textural parameters (inset); (b) DFT pore size distribution; (c) HK pore size distribution and (d) BJH pore size distribution of original granular activated carbon (OAC) and 5th regenerated granular activated carbon (5th-RAC).

mechanism for ester-containing pollutants, where the intercept (C_2) in the second linear step of IPD decreased slightly (shown in Table 5). Moreover, the BJH curve of OAC and 5th-RAC reached a maximum at 3.79 nm and 3.81 nm respectively, corresponding to mesopore volumes (V_{meso}) of 0.471 cm³ g⁻¹ and 0.363 cm³ g⁻¹, indicating that the mesopores can provide channels for some macromolecular adsorbates. It can also be concluded that the decreasing V_{meso} caused the decrement of the diffusion rate constant, k_{d1} (g mg⁻¹ min⁻¹), where the k_{d1} of OAC and 5th-RAC were 33.71 g mg⁻¹ min^{-0.5} and 26.78 g mg⁻¹ min^{-0.5} (shown in Table 5).

Therefore, though the adsorption rate constant of the pseudo-second-order model of RAC, k_2 (g mg⁻¹ min⁻¹), increased through MW cycles, the adsorption capacity (q_m) decreased due to the decreasing S_{BET} and the k_{d1} (g mg⁻¹ min⁻¹).

3.3 The mechanism of MW regeneration

In order to investigate the mechanism of the MW regeneration process, the surface functional groups and TG-DTG of the GAC samples were investigated.

3.3.1 Surface functional groups. FTIR spectra recorded for the GAC samples and the variation of groups over MW cycles can be seen in Fig. 6. The functional groups identified from the FTIR spectra are given in Table 6. Moreover, the structural formula of the surface function groups of GAC is shown in Fig. S1.†

For OAC, the band centred at 3429 cm⁻¹ indicates the presence of -OH functional groups; two weak bands at 2922 cm⁻¹ and 2854 cm⁻¹ can be assigned to asymmetric C-H and symmetric C-H bands, respectively; the band at 2360 cm⁻¹ was attributed to C=O asymmetric stretching vibration in CO₂; the intense band occurring at 1117 cm⁻¹ demonstrated the C-O asymmetric stretching. SAC and RAC had similar functional groups to OAC, except for the absorption band at 1635 cm⁻¹ and 1587 cm⁻¹. The absorption peak at 1635 cm⁻¹ of OAC was transferred to 1587 cm⁻¹ in SAC after the adsorption stage, which might be ascribed to variation in their surface groups. Compared with OAC, the RAC peak at 1587 cm⁻¹ represented the in-plane skeletal vibrations in aromatic rings. This could be explained by that the phenolic hydroxyl groups (PhOH) on the surface of OAC increasing with the number of MW cycles (Fig. 6b).

Fig. 6 (a) FTIR spectrum for activated carbon of original granular activated carbon (OAC), saturated granular activated carbon (SAC), and regenerated granular activated carbon for the first regeneration cycle (RAC); (b) variation in the amounts of different surface function group with the regeneration cycles. Error bars in (b) represent the standard deviation of three samples each from an independent run of the reactor.

Table 6 The main FTIR bands for OAC, SAC and RAC

Wavenumber (cm^{-1})	Peak assignment	Description
3429	–OH stretching	Phenols and alcohols
2922	Aliphatic CH_3 stretching	Alkanes
2854	Aliphatic CH_2 stretching	Alkanes
2360	$\text{C}=\text{O}$ asymmetric stretching	CO_2
1635	$\text{C}=\text{O}$ stretching	(Acid, aldehyde and ketone)
1587	In-plane skeletal vibrations of $\text{C}=\text{C}$ in aromatic rings	—
1117	$\text{C}-\text{O}$ stretching	Ester

The peaks at 1117 cm^{-1} in SAC was apparently sharper than that in OAC. The differences between the FTIR results of SAC and OAC demonstrate that ester containing organic matter was absorbed onto the OAC. The 1117 cm^{-1} peak of RAC was slightly sharper than that of OAC, which could have been caused by an increase in carboxyl groups on the surface of OAC, though adsorbed ester-containing contaminants were removed during MW regeneration (Fig. 6a). In addition, carboxyl groups and phenolic hydroxyl groups (PhOH) on the surface of OAC increased with the increase in regeneration cycles (Fig. 6b). The variation of lactone groups was stable throughout all regeneration cycles. The amount of basic surface groups rapidly decreased and then gradually increased during the five MW regeneration cycles. pH in wastewater decreases with a decrease in the amount of basic surface groups, and lower pH has a positive influence on adsorption due to the enhancement of the hydrophilic properties of GAC.^{42–44} Franz *et al.*⁴⁵ reported that the adsorption of phenol by activated carbon at pH of 3 was significantly higher than that at a pH of 11.0. Furthermore, the regeneration efficiency had a negative correlation with the amount of basic surface groups for the last three MW regeneration cycles, which decreased with the increase in basic surface groups. A similar phenomenon was also derived by Liu *et al.*²⁹ who reported that regeneration efficiency decreased for the regenerated GAC while the surface basicity increased instead.

3.3.2 TG-DTG. The TG and derivative thermogravimetric (DTG) curves of OAC and SAC are shown in Fig. 7.

The weight loss of OAC and SAC below 100°C was attributed to the loss of adsorbed water. The weight loss of OAC and SAC from 300 to 900°C were similar. Compared with OAC, the weight loss of SAC between 120 and 260°C may have been caused by the decomposition of small ester organic molecules,

Fig. 7 The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of original granular activated carbon (OAC) and saturated granular activated carbon (SAC).

such as DMC, CEM, DC, and EC, which were adsorbed in the adsorption stage. The result shows that the ester organic pollutants in SAC were easily regenerated at lower temperatures. This may have been because the binding forces between the adsorption sites of the GAC and the ester contaminants were weak and easily destroyed by the absorption of MW energy during MW regeneration.

4 Conclusion

This study provides an understanding of the mechanism of a GAC adsorption/MW irradiation process for the treatment of ester-containing wastewater from a LIB factory. The results show that the adsorption isotherms and kinetics are in accordance with the Langmuir isotherm and pseudo second-order kinetic model. The adsorption rate constant, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) of RAC increased with MW regeneration cycles, the adsorption capacity (q_m) decreased where the q_m of 5th-GAC had a 20.4% reduction in comparison to the determined OAC, which could be explained by a change in GAC textural properties. FTIR analysis showed that the GAC adsorption/MW process for the ester-containing pollutants mainly occurred at the peak of 1117 cm^{-1} . Based on TG-DTG analysis, the weight loss of SAC took place between 120 and 260°C , which indicates that the ester contaminants that polluted GAC can be easily regenerated by MW.

Abbreviations

GAC	Granular activated carbon
OAC	Original GAC
SAC	Saturated GAC
RAC	Regenerated GAC
R_E	Regeneration efficiency
R_S	Regeneration loss
MW	Microwave
LIB	Lithium-ion battery
DMC	Dimethyl carbonate
CEM	Carbonic acid ethyl methylester
DC	Diethyl carbonate
EC	Ethylene carbonate
NMP	N-Methylpyrrolidone
LiPF_6	Lithium hexafluoro phosphate
IPD	Intraparticle diffusion

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