Functional graphene nanocomposite as an electrode for the capacitive removal of FeCl₃ from water†Zhuo Wang,^a Lin Yue,^a Zhao-Tie Liu,^b Zong-Huai Liu^c and Zhengping Hao^{*a}

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Capacitive deionization (CDI) is a promising desalination technology which has attracted enormous interest in recent years due to its economic advantages over traditional technologies. In this paper, the facilely synthesized graphene and resol (RGO–RF) nanocomposite was proposed as a CDI electrode for the removal of ferric ions. The addition of resol led to less aggregation of the graphite oxide, while after calcination the structure collapsed and the pore size distribution widened. This was confirmed by Brunauer–Emmett–Teller (BET) techniques. The electrode's performances, involving the adsorption isotherm and kinetics, were investigated through batch mode experiment. It was found that the electrosorptive capacity of the RGO–RF electrode was 3.47 mg g^{−1} with an electrical voltage of 2.0 V and initial solution concentration of 40 mg L^{−1}. This is higher than the corresponding activated carbon and graphene electrode due to the presence of resol which is beneficial in restricting the aggregation of graphene, resulting in a high specific surface area and therefore a high electrosorption capacity. Further, the electrosorption of ferric ions onto RGO–RF follows the Langmuir isotherm, implying monolayer adsorption. Meanwhile, regardless of the electrical voltage, the kinetic analysis illustrated that the pseudo-first-order model can describe the electrosorption behaviour of the RGO–RF electrode very well.

1. Introduction

Nowadays, water scarcity is one of the most serious challenges all over the world, and it will become worse with population growth, industrialization, contamination of available freshwater resources and climate change.^{1–5} So there are scientists who have dedicated themselves to alleviating the stresses on freshwater supply. Taking ferric ions as an example, which are common hazardous pollutants in wastewater and are often released by metallurgical, electroplating, circuits printing, fertilizer manufacturing and refinery industries in their effluent. It is therefore necessary to seek an effective method to remove these ferric ions from water at a low cost and with non-secondary pollution. Tremendous research has been done to identify robust new methods of purifying water at a lower cost and with less energy, while at the same time minimizing the use of chemicals and impact on the environment. Currently, there are various

approaches for water purification, such as reverse osmosis, thermal processes, electrodialysis and ion exchange.^{6–11} However these technologies mentioned above have their own disadvantages, for example both the reverse osmosis and electrodialysis procedure are highly energy consuming and the ion exchange process produces secondary chemical waste. Hence, it is vital to develop a new method which can achieve desalination with a low energy consumption and low cost.

Capacitive deionization (CDI) is defined as a potential-driven adsorption of ions onto a charged electrode surface and is a novel and environmentally friendly process. It overcomes the disadvantages of the other techniques which are capital and energy-consuming.^{12–15} It is conducted at low voltage (typically 0.8–1.5 V) with a pump and acts as a “flow-through” capacitor.^{16,17} The basic concept is that when the water containing dissolved solutes is pumped through a high surface area electrode cell, the positive ions are attracted to the negatively charged plate (cathode), while the negative ions attract oppositely. The efficiency of CDI strongly depends on the surface area and the adsorption properties of the electrodes.

Graphene as a newly found carbon material has become one of the most attractive materials due to several breakthroughs in fundamental research and some promising practical applications.^{18–21} As a low dimension material, graphene has a huge theoretical specific surface area of 2600 m² g^{−1},²² which is twice that of finely divided activated carbon (AC). At the same time,

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graphene presents an excellent electrical conductivity of 7200 S m^{-1} at room temperature.²³ These intriguing properties enable graphene to be used as an electrode material for energy storage device, as well as CDI, due to their similar working principles. Up to now, the graphene has been successfully proposed and developed as a CDI electrode for the removal of salty ions from brackish water.^{3,24} However, it is found that the specific surface area of as prepared graphene is much less than its theoretical value, which is attributed to the serious aggregation during the preparation. Hence, in the present paper, we proposed a reduced graphene and resol (RGO–RF) nanocomposite as a CDI electrode for the electrosorption of ferric ions. It is found that the addition of resol is suitable for the pore size distribution of the electrode material, which results in the good performance in the electrosorptive process. The microstructure and porosity of RGO–RF were characterized by transmission electron microscopy (TEM) and N_2 adsorption–desorption techniques. Further, batch mode experiments were carried out to explore the electrosorption performance of the RGO–RF electrode as well as its electrosorption behaviour including the isotherm and kinetics.

2. Experimental details

2.1. Preparation of RGO and RGO–RF

The method for the synthesis of graphite oxide (GO) was published elsewhere.^{3,25} RGO–RF was prepared by modifying the method reported by William *et al.*²⁶ To enable the preparation of RGO–RF, 2 mg mL^{-1} of GO suspension was thoroughly dispersed in deionized water by ultra-sonication for at least 2 h. Then, resorcinol (R), formaldehyde (F) and sodium carbonate catalyst (C) were added to the mixture slowly altogether. The ratio of R to C was 200. Following this, the solution was transferred to a 100 mL Teflon®-lined autoclave and maintained at 85°C for 3 days. After that, the resulting mixture was washed with acetone several times to remove the water from the pores of the mixture. The mixture was then reduced by calcination at 900°C under N_2 atmosphere, resulting in the reduced graphite oxide–resol like material, named RGO–RF.

2.2. Fabrication of the CDI electrodes

The target carbon materials (RGO–RF, RGO and AC) and polytetrafluoroethylene (PTFE) as the binder were employed to fabricate the electrodes and their percentages were 80% and 20%, respectively. Each electrode was about $70 \text{ mm wide} \times 140 \text{ mm long} \times 0.3 \text{ mm thick}$ and had a flow-through hole with a diameter of 4 mm. Ethanol ($10\text{--}20 \text{ mL}$) was added dropwise to the mixture to increase the moisture and then the mixture was pressed onto nickel foam and dried at 50°C for 8 h. Finally, the electrodes were assembled into a self-made CDI unit cell.

2.3. Characterization

The morphology, fine structure and porosity of the sample were characterized by transmission electron microscopy (TEM, JEOL 3010), X-ray diffraction (XRD, D/MAX-RB) and N_2 adsorption–desorption techniques, respectively. The XRD patterns of all of the samples were measured on a Rigaku powder diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at a scanning rate of 4° per

min in $2\theta = 10\text{--}80^\circ$. Adsorption and desorption isotherms of nitrogen were measured with a NOVA 1200 gas sorption analyser at liquid nitrogen temperature (-196°C). Before the measurements were taken, the samples were degassed under vacuum condition at 300°C for 3 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area using adsorption data acquired at a relative pressure (P/P_0) range of $0.5\text{--}0.25$. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution curves were calculated from the analysis of the desorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) algorithm. The micropore volume and micropore surface area were estimated by a t -plot method.

The cyclic voltammetry (CV) measurements of RGO–RF, RGO and AC were performed on an electrochemical workstation (CHI 600 D, Shanghai CH Instrument Company, China) with a typical three-compartment cell at ambient temperature. The as-synthesized materials, a Pt wire and an Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode, respectively. The electrolyte was 1 M NaCl aqueous solution (vs. Ag/AgCl electrode). The capacitance was calculated from the Current–Voltage curves according to the following equation:

$$C = \frac{\int IdV}{vmV} \quad (1)$$

where C is the specific capacitance (F g^{-1}), I is the response current (A), V is the potential (V), v is the potential scan rate (V s^{-1}), and m is the mass of the electroactive materials in the electrodes (g).

2.4. Electrosorption experiment

The removal of FeCl_3 was measured using a continuously recycling system including a CDI unit cell, a peristaltic pump, a power supply and a conductivity monitor. In a typical experiment, the FeCl_3 with initial conductivity of around $105 \mu\text{S cm}^{-1}$ (about 40 mg L^{-1}) and volume of 200 mL was employed as feed solution. The flow rate was 20 mL min^{-1} and a direct voltage of 2.0 V . The variation of the solution conductivity was monitored instantly by a multi-function conductivity meter (DDS-11A LiDa instrument). The correlation of conductivity ($\mu\text{S cm}^{-1}$) and concentration (mg L^{-1}) was calibrated prior to the experiment.

In our experiment, the electrosorptive capacity was defined as below,

$$\text{Electrosorptive capacity (mg g}^{-1}\text{)} = \frac{(C_0 - C_t)V}{M} \quad (2)$$

where C_0 and C_t (mg L^{-1}) represent the initial and final concentration, respectively, and V is the volume of the solution (L), and M is the total mass of both electrodes (g). Fig. S1† gives the relationship between the conductivity ($\mu\text{S cm}^{-1}$) and the solution concentration (mg L^{-1}).

3. Results and discussion

3.1. Morphology of RGO–RF and GO

Fig. 1(a) and (b) show the TEM images of GO and RGO–RF, respectively. It is observed from Fig. 1(a) that GO has a crumpled

Fig. 1 TEM images of GO (a) and RGO–RF (b), SEM images of GO (c) and RGO–RF (d).

and layered structure with several stacking layers, indicating that the GO sheets were synthesized successfully. From Fig. 1(b), it is clearly found that the resol entangled with RGO, in this case, the GO sheets were well separated due to the presence of resol, leading to a high specific surface area. Besides it is confirmed by SEM in Fig. 1(c), from Fig. 1(d) the characteristic structure of RGO was destroyed, this illustrated that the additional resol mixed with GO well, and there are pore structures present in it.

Fig. 2(a) and (b) present the N_2 adsorption–desorption isotherm and the pore size distribution of the electrode materials. It is observed from Fig. 2(a) that the RGO–RF adopts a typical type-IV isotherm with a sharp capillary condensation step at $P/P_0 = 0.4$, indicating the presence of uniform mesopores.²⁷ While RGO and AC adopt typical type-III and type-I isotherms, respectively. Detailed parameters involving the specific surface area and pore volume are summarized in Table 1. As it can be seen the AC has the largest specific surface area of $836 \text{ m}^2 \text{ g}^{-1}$, which is much higher than that of RGO–RF with $475.6 \text{ m}^2 \text{ g}^{-1}$. However, inside the AC, the micropores occupied a very large fraction which is not beneficial to electrosorption because of the overlapping effect. Further, as can be observed from Fig. 2(b), there is a very sharp dominant peak focused at 4 nm in the RGO–RF branch, which together with N_2 adsorption–desorption isotherm, illustrates that the specific surface area of the RGO–RF is mainly from the contribution from the mesopores (2–50 nm), according to the IUPAC classification. Table 1 gives the details of the parameters of the samples.

3.2. Electrochemical property

The CV measurements of the RGO–RF and RGO electrodes were carried out in 1 M NaCl aqueous solution at certain sweep rates including 10, 20, 30, 40 and 100 mV s^{-1} . Fig. 3(a) and (b) show the CV curves of RGO–RF and RGO at different sweep rates, Fig. 3(c) and (d) present the corresponding specific capacity. From Fig. 3(a), it is obviously seen that the CV curve of RGO–RF is symmetric without any peaks appearing in the

Fig. 2 N_2 adsorption–desorption isotherm (a) and pore size distribution (b) of samples at 77 K.

curve, implying no redox reaction took place during the test and the electrosorption process is reversible. In the case of the RGO electrode, it exhibits an inferior capacitance behaviour with a lower current response than that of the RGO–RF electrode. Obviously, the CV curves of RGO show a disordered rectangular shape, which may be explained as follows: (i) Faradaic reactions took place during the sweeping processes;²⁸ (ii) the diffusion limitation of ions in the electrode;²⁹ (iii) the incomplete reduction from GO to RGO. Specifically, taking the sweep rate at 10 mV s^{-1} for example, the specific capacitance of RGO and RGO–RF are 110.63 F g^{-1} and 145.75 F g^{-1} , respectively. The specific capacitance of RGO–RF is nearly 30% larger than RGO, this indicates that the introduction of resol is beneficial to enhance the specific capacitance. This is probably due to the fact that the resol can effectively decrease the aggregation of the RGO layers (the strong van der Waals interactions among these reduced graphene sheets could result in aggregation³⁰), resulting in a high specific surface area.

3.3. Effect of electrical voltage

It is well known that the CDI process is ultimately related to the electrical voltage. As expected, a higher electrical voltage results in

Table 1 Pore parameters in relation to various electrodes

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{micropore}}$ ($\text{m}^3 \text{g}^{-1}$)	$S_{\text{micropore}}$ ($\text{m}^2 \text{g}^{-1}$)
RGO–RF	475.6	0.5573	0.1562	338.3
RGO	56.06	0.101	—	—
AC	836.0	0.418	0.345	754.4

a higher electrosorptive capacity because of the strong Coulombic interaction. Fig. 4(a) shows the electrosorptive performance of the RGO–RF at different electrical voltages in FeCl_3 solution and the inset illustrates the corresponding electrosorptive capacity. The initial concentration was 40 mg L^{-1} and the flow rate was 20 mL min^{-1} . As the voltage increased from 0 V to 2.0 V, the electrosorptive capacity is gradually enhanced from 2.12 to 3.47 mg g^{-1} . Interestingly, the electrosorptive capacity of the RGO–RF without applying voltage is as high as 2.12 mg g^{-1} , which is probably ascribed to its high specific surface area and abundant functional groups.³¹ Fig. 4(b) depicts the electrosorptive performance of the RGO–RF, RGO and AC electrodes in FeCl_3 solution with an initial concentration of 40 mg L^{-1} and electrical voltage of 2.0 V. Obviously, as the time goes by, the solution conductivity decreases. Among the three electrodes, the RGO–RF has the largest electrosorptive capacity of 3.47 mg g^{-1} . For the RGO and AC electrode, the electrosorptive capacities are 2.46 and 1.41 mg g^{-1} , respectively. This is again confirming that RGO–RF is a suitable candidate as the electrode material for CDI.

3.4. Effect of cations

In order to investigate the electrosorption performance of the RGO–RF electrode on different cations, batch experiments were conducted in NaCl , MgCl_2 , and FeCl_3 solutions with the same experimental conditions. Theoretically, for the electrosorption process, ions with high valence and a small hydrated radius can be more effectively removed because of the stronger electrostatic force.³² Thereby, it is estimated that the preferential ion electrosorption for alkali and alkaline-earth metals are as follows: $\text{Fe}^{3+} > \text{Mg}^{2+} > \text{Na}^+$.

Fig. 5 depicts the transient conductivity over 100 minutes in NaCl , MgCl_2 and FeCl_3 solutions. The electrical voltage was 2.0 V and the flow rate was 20 mL min^{-1} . The electrosorptive capacity of FeCl_3 , MgCl_2 and NaCl were 3.41, 2.84 and 2.36 mg g^{-1} , respectively, following the order mentioned above. This confirms that when the hydrated cations are electrically adsorbed on a negatively charged carbon electrode, highly charged multivalent ions with a smaller hydrated radius would be strongly attracted.

Fig. 3 CV curves of RGO–RF (a) and RGO (b) at different sweep rate in 1 M NaCl aqueous solution and corresponding specific capacitance of (c) RGO–RF and (d) RGO.

Fig. 4 (a) Electrosorption of FeCl_3 onto the RGO-RF electrode at different electrical voltages, (b) comparative results of RGO-RF, RGO and AC electrodes in terms of electrodesorptive performance in 1 M FeCl_3 aqueous solution.

Fig. 5 Electrosorptive performance of the RGO-RF electrode in NaCl , MgCl_2 and FeCl_3 solutions, respectively.

3.5. Effect of anions

To explore the impact of anions on the electrosorption performance of the RGO-RF electrode, batch mode experiments were performed in FeCl_3 , $\text{Fe}(\text{NO}_3)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ solutions with the same experimental conditions. It is known that electrosorption in liquid is strongly related to the size and potential of the ions and the solubility of the solute. Ions with a high charge will have a good affinity because of the strong electrostatic force. On the other hand, when the charge is the same, the ions with a smaller hydrated radius will be preferable to adsorb onto electrode. Fig. 6 illustrates the electrosorption of different anions onto the RGO-RF electrode at a flow rate of 20 mL min^{-1} and applied voltage of 2.0 V. The electrodesorptive capacity of $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}(\text{NO}_3)_3$ and FeCl_3 are 3.69, 3.58 and 3.41 mg g^{-1} , respectively. The order of the anions removal efficiency was $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$. This indicates that the removal of solutes has a great relation to ionic charge and molecular size. The removal manner was that the larger multivalent ions are more favorable to be removed than smaller ones. Also the degree of hydration depends on the properties of the ions, where the smaller ions with higher charges show a greater degree of ion hydration (e.g. SO_4^{2-})^{33,34}

3.6. Electrosorption isotherm

To further investigate the electrosorption isotherm of the RGO-RF electrode, batch electrosorption experiments were carried out at different initial concentrations, which were 40, 60, 135, 235, 335, 550 and 750 mg L^{-1} with an electrical voltage of 2.0 V and a flow rate of 20 mL min^{-1} . Langmuir isotherm (3) and Freundlich isotherm (4) were utilized to simulate the experimental data for FeCl_3 adsorbed on the RGO-RF electrode, which is as listed below:

$$Q = \frac{Q_m K_L C}{1 + K_L C} \quad (3)$$

$$Q = K_F C^{1/n} \quad (4)$$

Fig. 6 Electrosorptive performance of RGO-RF in FeCl_3 , $\text{Fe}(\text{NO}_3)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ solution.

where C is the equilibrium concentration (mg L^{-1}), Q is the amount of adsorbed FeCl_3 (mg g^{-1}), Q_m is the maximum adsorption capacity corresponding to complete monolayer coverage (mg g^{-1}). K_L is the Langmuir constant related to the binding energy (L mg^{-1}), K_F and n are the Freundlich constants related to the capacity of the adsorbent to adsorb and the tendency of the adsorbate to be adsorbed, respectively. Table 2 shows the determined parameters and regression coefficients R^2 , K_L and K_F of Langmuir and Freundlich isotherms for RGO-based CDI, respectively.

Fig. 7 depicts both the experimental data and corresponding electrosorption isotherms of the RGO-RF electrodes. More detailed parameters are listed in Table 2. It is clearly seen from Table 2 that the electrosorption behaviour of RGO-RF obeys both the Langmuir and the Freundlich isotherm according to R^2 . This is consistent with the previous report.³² This suggested that the monolayer adsorption was the primary adsorption mechanism during the electrosorption process. Furthermore, the parameter Q_m defined as the maximum adsorption capacity is 69.52 mg g^{-1} , which is much higher than the reported data,³² implying that the RGO-RF has great potential in the electrosorption of FeCl_3 .

In order to predict the adsorption efficiency of the process, the dimensionless quantity (r) was calculated by using the following equation:

$$r = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 and K_L are the initial concentration of FeCl_3 and the Langmuir isotherm constant, respectively. According to the literature,³⁵ if the value of $r < 1$, it represents favourable adsorption while when it is greater than 1.0 it represents unfavourable adsorption. The value of r was found to be 0.94 at an initial concentration of 40 mg L^{-1} , which indicates that the present system is favourable for adsorption.

3.7. Electrosorption kinetics

The rate of FeCl_3 adsorbed onto RGO-RF electrode was examined by considering the pseudo-first-order adsorption kinetics at different bias potential of 0, 0.5, 1.0, 2.0 V and with an initial concentration of 40 mg L^{-1} . Specifically, the kinetics were determined by the Lagergren equation, which is often so-called the pseudo-first-order adsorption kinetics (eqn (6))

$$\frac{dq_t}{dt} = k(q_e - q) \quad (6)$$

where k is the adsorption rate constant (min^{-1}), q_e and q are the amount of FeCl_3 adsorbed at equilibrium (mg g^{-1}) and time t

Table 2 Determined parameters of Langmuir and Freundlich isotherms

Isotherm	Model equation	Parameter	Value
Langmuir	$Q = \frac{Q_m K_L C}{1 + K_L C}$	Q_m (mg g^{-1})	69.52139
		K_L	0.00155
		R^2	0.99039
		K_F	0.36741
Freundlich	$Q = K_F C^{1/n}$	n	1.40469
		R^2	0.99262

Fig. 7 Electrosorption isotherm of FeCl_3 onto RF-RGO electrode at 2.0 V.

(min), respectively. Integrating eqn (6) with respect to the integration conditions of $q = 0$ to $q = q_t$ at $t = 0$ to $t = t$, the kinetics expression becomes

$$\log(q_e - q) = \log q_e - \frac{kt}{2.303} \quad (7)$$

The adsorption kinetics was fitted with the Lagergren law by nonlinear regression using the method of least squares. The results are given in Fig. 8 and Table 3, and it is obviously found that the adsorption capacity and the rate were increased greatly as the bias potential increased. Besides, the maximum correlation coefficient (R^2) was 0.99 at 2.0 V and the values of q_e calculated from the equation agree with the experimental data very well. The adsorption rate at 2.0 V was increased by 43.77% as compared with the corresponding rate at 0 V. Therefore, it is definitely confirmed that increasing the voltage could effectively enhance the adsorption rate and adsorption capacity.

Fig. 8 Electrosorption kinetics of the RGO-RF electrode at different bias potentials.

Table 3 Parameters of pseudo-first-order kinetics in terms of different voltage

Bias potential (V)	q_e (mg g ⁻¹)	$K(\times 10^{-2})$	R^2
0	2.5296	2.008	0.96101
0.5	2.6403	2.248	0.97764
1	2.9412	2.534	0.98196
2	3.7095	2.887	0.99035

4. Conclusions

In summary, the reduced graphite oxide–resol like material (RGO–RF) was synthesized and used as the electrodes for the capacitive deionization (CDI) of FeCl₃. It is found that the electrosorption capacity of the RGO–RF electrode was 3.47 mg g⁻¹ with electrical voltage of 2.0 V and initial solution concentration of 40 mg L⁻¹ which is a higher capacity than attained with either the corresponding reduced graphite oxide or activated carbon electrode. Also it was seen that highly charged multivalent ions with smaller a hydrated radius would be strongly attracted whatever the anions or cations. Furthermore, the electrosorption behavior of FeCl₃ onto the RGO–RF electrode follows the Langmuir isotherm, indicating the monolayer adsorption. Besides, through investigation of the adsorption–electrosorption kinetics, it is confirmed that the electrosorption could effectively enhance the adsorption rate and adsorption capacity according to the adsorption–electrosorption rate constant as a result of pseudo-first-order adsorption.

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