Highly enhanced adsorption of Congo red by functionalized finger-citron-leaf-based porous carbon

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ABSTRACT

A novel high-performance porous carbon material, lanthanum(III)-doped finger-citron-leaf-based porous carbon (La/FPC), has been synthesized and used as an adsorbent for anion dye Congo red (CR). The La/FPC was characterized by nitrogen adsorption and desorption isotherms, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The adsorption performance of CR by the FPC and La/FPC composites with different contents of lanthanum(III) were evaluated in fixed-bed breakthrough experiments and batch tests at room temperature (298 K). The La/FPC had a high CR uptake capacity, which was superior to those previously reported for other adsorbents. The La/FPC sorbents can be easily regenerated using an ethanol elution technique, and after five cycles the reused La/FPC maintained about 98% of its original CR adsorption capacity. The adsorption kinetics of CR onto the lanthanum(III)-doped FPCs followed a pseudo-second-order kinetic model and fitted well with a Langmuir adsorption isotherm. La/FPC is a promising adsorbent for the removal of the anionic dyes from wastewater.

Key words | adsorption capacity, Congo red, Langmuir model, non-hazardous, physico-chemical treatment

INTRODUCTION

Porous carbons are the most popular sorbent material for the removal of pollutants from wastewater (Hu et al. 2016; Yu et al. 2016) and they are particularly effective for the removal of a large variety of dyes from wastewaters, which has made them excellent alternatives to other expensive treatment options. However, porous carbons possess several disadvantages, such as being non-selective, and they are ineffective for vat dyes (Dai et al. 2015; Yu et al. 2015). In addition, most carbon-based adsorbents are derived from relatively expensive starting materials which make them costly. These problems have inspired the search for low cost and highly selective adsorbents.

Ideally precursors for porous carbons should be readily available, inexpensive and non-hazardous in nature. In recent years, a number of inexpensive agro-wastes, rice straw (Hameed & El-Khaiary 2008a, 2008b), soybean hulls (Gong et al. 2008), waste apricots (Önal 2006), degreased coffee beans (Baek et al. 2010), lemon peels (Kumar 2007), de-oiled soya (Mittal et al. 2003), and other natural products (Mittal 2006; Saha et al. 2010) have been used to remove anionic dyes from wastewater. The advantage of using waste resources is that it saves disposal costs and helps in alleviating potential environmental problems.

Finger citron is the fruit of the evergreen shrub Citrus medica L. var. sarcodactylis Swingle, of the family Rutaceae (Gong et al. 2013). The tree is cultivated in West Indies, Australia, South America, Iraq, Turkey, and China. Finger citron can be used to produce tea, jam, beverages, etc. However, a lot of finger citron leaves (FCLs) are produced during the production process. As waste materials, the FCLs have been disposed as garbage, which can also sometimes cause another environment problem. In our previous work (Gong et al. 2013), finger-citron-residue-based porous carbon was successfully prepared from finger citron residues. Thus, FCLs should be an optimal precursor for the preparation of inexpensive porous carbon materials.

Recently a great deal of research has focused on improving the selectivity of porous carbon materials by modifying their properties to give them an affinity for specific dyes. For example, effective adsorbents have been developed for methyl orange (Gong et al. 2013), Congo red (CR) (Hu et al. 2014), rhodamine B (Dong et al. 2012), malachite
green (Tian et al. 2011), methylene blue (Marczewski 2010), and orange II (Peng et al. 2014). In most these cases, the surface chemistry and the pore structure of the material play a role in the specific application (Zhang et al. 2016).

Porous carbons with controlled porosities and defined surface properties have been widely used as supports for the adsorption and separation of anionic dyes (Hu et al. 2014). The fabrication of these adsorbents requires an initial preparation of the porous carbon material followed by impregnation with a metal ion salt which is sometimes then reduced to the metallic state (Hu et al. 2014). This impregnation procedure results in metallic nano particles in the pores. Charge attractions between the metal ions and anionic dyes material greatly improve the selectivity and the adsorption capacity of the porous carbon for the anionic dye (Yin et al. 2007; Yagub et al. 2014). However, these types of adsorbents still have major problems such as poor selectivities and low uptake capacities for some dyes and they are difficult to recycle (Mezohegyi et al. 2012). Usually, orange, pomelo, lemon and finger citron come from the Rutaceae family (Gong et al. 2013). Therefore, they have similar leaf shape, components and structure. In this work, the waste leaf of finger citron was investigated for the first time as an alternative low-cost precursor to prepare nanoporous carbon materials (FPCs). In addition, the preparation method of FPCs is a conventional KOH activation procedure that was previously proposed in the literature (Gong et al. 2013). Thus, this work could bring more general results, which could provide useful information and insight in this research field.

To the best of our knowledge, there are no studies that have investigated the effects of doping lanthanum(III) metal ions on the adsorption of dyes by porous carbon materials. In order to obtain porous carbons with high selectivities and capacities, these types of studies are critical. So in this work, FCL based adsorbents modified with different amounts of lanthanum(III) were synthesized and characterized. Their performance as adsorbents in the removal of CR (a typical anionic dye) from aqueous solutions was tested. Adsorptive breakthrough curves (dynamic tests) and batch tests (static tests) were both conducted in order to study the adsorption and desorption performances of these new carbon materials.

**MATERIALS AND METHODS**

**Materials**

FCLs were collected from the campus of Zhejiang Normal University, Jinhua, China. Potassium hydroxide and lanthanum(III) chloride were purchased from Sigma Chemical Company (St Louis, MO, USA). High purity nitrogen (99.995%) was provided by Gas Supplier Center of Datong Co., Ltd, Jinhua, China. All other reagents were of analytical reagent grade.

**Preparation of porous carbons**

The procedure to prepare the FPCs has been described previously (Yu et al. 2015, 2016). Briefly, the FCLs were first washed with deionized water to remove dirt from their surfaces and were then dried overnight in an oven at 378 K. The dried leaves were cut and sieved into pieces of ∼200 μm and then mixed with KOH (KOH:FCLs mass ratio was 4:1). The resulting mixture was placed into a horizontal pipe reactor (50 mm o.d.). The temperature of the reactor was raised to the activation temperature (973 K) at a heating rate of 1 K/min. During the carbonization process, high purity nitrogen (99.99%) was flowed through the reactor at a flow rate of 30 mL/min. Finally, the sample was cooled to room temperature. The samples were then washed with deionized water until the pH of the filtrate was neutral. The final samples (FPCs) were obtained by heating the samples at 393 K under vacuum for 24 h.

**Modification of the porous carbons**

An incipient wetness technique was used to impregnate the FPCs with an aqueous solution of lanthanum(III) chloride. One gram of FPCs was soaked in 200 mL deionized water with 0.3, 0.5, 0.8 and 1 mmol lanthanum(III) chloride. Then the solution was kept for 24 h at room temperature (298 K). After impregnation the adsorbents were dried at 373 K for 5 h and then heated under a nitrogen atmosphere for 3 h at 973 K. The obtained samples are denoted as: La5/FPC, La5/FPC, La8/FPC and La10/FPC, where the number represents the concentration of the La(III) impregnation solution in mmol.

**Sample characterization**

Characterization of the pore structures of the samples was performed using low-temperature nitrogen adsorption–desorption isotherms measured on an automated adsorption apparatus (Micromeritics, ASAP 2020). The materials were pre-treated in situ under vacuum at 573 K. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method (the relative pressure P/P₀ range for the BET calculations was 0.005–0.2). For transmission electron microscopy (TEM) measurements, powdered samples were deposited on a grid with a perforated...
carbon film and transferred to a JEOL2100F electron microscope operating at 80 kV. Scanning electron microscopy (SEM) images were obtained using a scanning electron microscope made by Philips (The Netherlands), with a working distance of 14 mm, an accelerating voltage of 15 kV and digital image recording. The influence of La(III)-related defects on the electronic structure of the La/FPC surfaces was studied using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi).

Adsorption studies

A series of CR solutions with concentrations ranging from 50 to 1,200 mg/L were prepared by dissolving the appropriate amount of dye in deionized water. In each batch experiment, 20 mg of adsorbent was suspended in 50 mL of the dye solution. First, the time dependence of the CR adsorption for each type of adsorbent was investigated to determine the time required for adsorption equilibrium. During the adsorption experiments, the mixtures were continuously shaken in a shaking bath at a constant temperature (298 K). At the end of the adsorption, the samples were filtered and the residual concentrations of CR in the filtrate were determined using a UV-visible spectrophotometer (Thermo Fisher Evolution 300 PC) at the maximum wavelength (497 nm). The adsorbed amount of CR at equilibrium, \( q_e \) (mg/g), was calculated from:

\[
q_e = \frac{(C_0 - C_e) \cdot V}{W}
\]

where \( C_0 \) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of CR solution, respectively, \( V \) (L) is the volume of solution, and \( W \) (g) is the weight of the adsorbents used. All experiments were done in duplicate and the average values are reported. The average deviation of the duplicate results was found to be within ±1%.

The linear forms of a Langmuir isotherm model (Goscińska et al. 2015), Freundlich model (Goscińska et al. 2014) and Dubinin–Radushkevich (D-R) model (Dai et al. 2015) were used to study the adsorption performance of the adsorbents. Equations (2)–(4) are presented in Table S.I.1, Supplementary Information (available with the online version of this paper).

Breakthrough experiments

The adsorption performance of the La/FPC was tested using breakthrough curves. The experiments to collect the breakthrough curves were performed in a vertical quartz column (length 300 mm, inner diameter 10 mm) with a glass grid for supporting the adsorbent. The adsorption materials (~5 g) were loaded into the adsorption column inside a glove box to avoid contact with air. The CR solution was delivered with a mini creep pump (BT01-YZ1515, Zhejiang Nade Company, China). Prior to each adsorption measurement, the adsorbent was activated by heating to 473 K for 2 h in a stream of nitrogen. After cooling to room temperature (298 K) in a stream of nitrogen, the sorbent was consolidated by lightly tapping the column.

The adsorption experiments were carried out at 298 K and atmospheric pressure. First, the fixed bed was flushed downward with deionized water at a flow rate of 0.2 cm³/min for 30 min, and then the feed was switched to the CR solution with the same flow rate. Samples were taken at regular intervals to examine the formaldehyde content in the solutions until saturation was reached. Breakthrough curves were obtained by plotting the transient CR concentration versus the cumulative solution volume. The concentrations were normalized with the total CR content in the feed, and the cumulative solution volumes were normalized with the volume of the adsorbent bed. Table S.I.2 (available online) shows the calculation equations of CR breakthrough and saturation capacity.

A pseudo-first-order model (Hu et al. 2016), a pseudo-second-order model (Yu et al. 2015), and an intra-particle diffusion model (Dai et al. 2015) were used to analyze the kinetic data. These models are given in Table S.I.2. In order to quantitatively compare the applicability of different kinetic models, a normalized standard deviation can also be found in Table S.I.2.

RESULTS AND DISCUSSION

Material characterization

The nitrogen adsorption isotherms and pore size distribution for FPC, La3/FPC, La5/FPC, La8/FPC and La10/FPCat77 K are shown in Figures 1 and 2, respectively. All the samples have type I adsorption isotherms according to the IUPAC classification system (Gong et al. 2013; Hu et al. 2016). The properties of the adsorbents are given in Table S.I.3 (available with the online version of this paper). The BET surface area and the total pore volume of FPC were 1,949 m²/g and 1.10 cm³/g, respectively. Adding La decreased both the BET surface area and the total pore volume, and higher La loadings resulted in larger decreases (i.e. the surface area and total pore volume for La10/FPC were the smallest, 828 m²/g and 0.90 cm³/g respectively). The pore size
distributions were calculated by density functional theory and the pore sizes of the FPC and La/FPC samples were all between 1.4 and 2.8 nm. A t-plot analysis of pore distribution shows that the microporous surface areas of the samples decreased and the percent of mesopores increased with increasing amounts of La. This suggests that the La modifications preferentially took place at the openings of the micropores and small mesopores and is probably due to the high potential fields in the small pores and the easy attachment that can occur at the pore openings (Gong et al. 2015). As a result, the La nano particles expanded the micropores in the FPC samples and transformed them into small mesopores in the La/FPC structures. The relatively high surface areas of FPC and the La/FPC materials should provide huge capacities for the adsorption of dye molecules inside the pore structure.

SEM was used to investigate surface image and the results for La8/FPC sample are shown in Figure 3. The image shows that the sample contains cavities and rough surfaces which are due to the carbon material preparation process (Gong et al. 2015; Yu et al. 2016). The result also proved that the La/FPC will be enhanced by the presence of increased porosity, which can hold more dye molecules from solution during adsorption. No impurities were detected in the nanostructures.

In order to further investigate the pore structure and image, TEM was also used to study the samples and the results are shown in Figure 4. The TEM result shows that some of the carbon material surface appears to be covered with a metal coating.

Energy dispersive spectroscopy (EDS) was used to verify the elemental compositions of the La8/FPC sample samples and the results are shown in Figure 5.
Only three elements, C, O and La, were found. In order to obtain information about the surface of the La-doped carbon, i.e. the location and distribution of the La phases on the FPC, XPS analysis was carried out and the results are shown in Figures 6 and 7. The XPS spectrum of La8/FPC (Figure 6) has four distinct peaks, which are due to La, oxygen and carbon, respectively. The La3p3/2 peaks centered at 855 and 856 eV can be ascribed to La2O3 and La(OH)3 respectively (Goscianska et al. 2014, 2015). The La satellite peaks indicate that the La atoms are present in an oxygen environment. The peak at 861.6 eV is a satellite peak of La(OH)3 (Goscianska et al. 2014). The XPS spectrum corresponding to La 3p1/2 further confirmed the existence of element La. The La3p3/2 XPS peak binding energies of La2O3 and La(OH)3 are shifted by about 0.5 eV.

**Adsorption isotherms and breakthrough curves**

The adsorption isotherms of CR at 298 K on FPC before and after being modified with La at a solid/liquid ratio of 0.5 g/L are presented in Figure 8. The experimental equilibria adsorption data was then fitted using Langmuir, Freundlich and D-R isotherm models (Equations (2)–(4), Supplementary Information). The calculated constants for these isotherm equations along with the $R^2$ values (correlation coefficient) are presented in Table S.I.4 (available online). For all the samples, the Langmuir isotherm gave the best fit ($R^2 > 0.998$). This suggests that the dye adsorption is limited to monolayer coverage and that the surfaces are relatively homogeneous (Goscianska et al. 2014).

![Figure 5](https://iwaponline.com/wst/article-pdf/77/1/220/211799/wst077010220.pdf?220x220.pdf) | EDS spectrum of the La8/FPC sample.

![Figure 6](https://iwaponline.com/wst/article-pdf/77/1/220/211799/wst077010220.pdf?220x220.pdf) | La-XPS spectrum of the La8/FPC sample.

![Figure 7](https://iwaponline.com/wst/article-pdf/77/1/220/211799/wst077010220.pdf?220x220.pdf) | La3p3/2 XPS spectra of the La8/FPC sample.

![Figure 8](https://iwaponline.com/wst/article-pdf/77/1/220/211799/wst077010220.pdf?220x220.pdf) | Adsorption isotherms of CR on FPC, La3/FPC, La5/FPC, La8/FPC and La10/FPC samples. (t = 4 h, pH = 7, dose = 0.4 g/L, T = 298 K).
The maximum monolayer adsorption capacity \( (q_L) \) for CR was the highest for La8/FPC with the capacities decreasing in the order La8/FPC > La5/FPC > La10/FPC > La3/FPC > FPC. The La/FPC sorbents adsorb more CR than FPC because of reactions between lanthanum and the CR molecules. However, the capacities are not proportional to the amount of loaded La. This non-linear response could be a result of variations in the structures and compositions of the La/FPC surfaces, or it may be due to the inaccessibility of active La sites for some domains (Goscianska et al. 2014).

The CR breakthrough curves of FPC, La3/FPC, La5/FPC, La8/FPC and La10/FPC are shown in Figure 9. The shape of the curve provides qualitative information about the strength of the adsorption. For example, steeper slopes suggest stronger interactions with the adsorbent (Hu et al. 2016). Thus, these curves show that the La/FPC sorbents interact more strongly with CR than FPC does, indicating that lanthanum sites are beneficial to CR adsorption. The CR uptake capacity increased in the order La8/FPC > La10/FPC > La5/FPC > La3/FPC > FPC. These results can be explained by the fact that adding more lanthanum creates more active lanthanum sites but too much lanthanum can block pores, resulting in diffusion resistance during mass transfer which hinders the uptake of CR. Therefore, La8/FPC had the highest CR capacity.

The adsorption capacities of the adsorbents in this work and those for some previously reported sorbents are summarized in Table S.1.5 (available online). The CR uptake capacities of all the La/FPC sorbents are comparable or superior to those previously reported for activated carbons, zeolites and metal organic frameworks (Chou et al. 2001; Nagarethinam & Mariappan 2002; Kadirvelu et al. 2003; Bhatnagar et al. 2005; Purkait et al. 2007; Afkhami & Mousavi 2010; Hu et al. 2014, 2016; Yu et al. 2016).

**Adsorption kinetics**

The effect of contact time on the FPC and the La/FPC adsorption capacities for CR are shown in Figure 10. The adsorption capacities for CR increased with increasing contact time until adsorption equilibrium was reached, which occurred within 1.5 h for all the samples. The capacity is constant when all the parameters are fixed (298 K, 3 h contact time, 1,200 mg/L initial concentration, pH 7 and 0.4 g/L adsorbent dose), and with the evolution of time, the uptake or adsorbed amount may change. The fast adsorption at the initial stage is probably due to the availability of uncovered surface sites on the adsorbent.

Equations (7)–(9) (Supplementary Information, available online) were used to calculate the pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic constants respectively and those results along with \( R^2 \) values at different temperatures are presented in Table S.1.6 (available online). There is a large difference between the experimental and calculated adsorption capacities for the pseudo-first-order model. However, high \( R^2 \) values (> 0.99) were obtained for the linear plot of \( t/q_t \) versus \( t \), suggesting that the adsorption follows a pseudo-second-order adsorption kinetics. If the adsorption process follows an intra-particle diffusion mechanism, then the plot of \( q_t \) versus \( t^{1/2} \) will be linear, and if the plot passes through the origin, the rate limiting process is due only to the intra-particle diffusion (Yu et al. 2016). Otherwise, other mechanisms along with intra-particle diffusion are involved (Hu et al. 2016; Yu et al. 2016).
As shown in Figure 11, the plots are not linear over the whole time range and, instead, can be separated into multi-linear curves, which indicates that the adsorption process has multiple stages. The first line can be attributed to macro-pore diffusion (phase I) and the second linear portion can be attributed to micro-pore diffusion (phase II). These results indicate that the adsorption of CR onto FPC and La/FPC involve more than one process, and that intra-particle transport is not the rate limiting step. This finding is similar to those reported for other carbon materials (Gong et al. 2013; Dai et al. 2015; Yu et al. 2015, 2016).

Regeneration tests for La/FPC adsorbent

The recyclability of La/FPC is an important property if the material is to be used for pollution control and environmental protection. An ethanol elution procedure (Dai et al. 2015; Yu et al. 2015, 2016) was used to desorb the CR from the used La8/FPC sample and the desorption curves are shown in Figure 12. The concentration of CR decreased with time, and the CR was totally removed from the adsorbents after 2 h. The adsorption performance of the regenerated La/FPC was then tested. The CR breakthrough curves for five reuses of regenerated La8/FPC are shown in Figure 13. After five cycles, the CR uptake capacity for the regenerated La8/FPC was 2,722 mg/g, which is almost 98% of the initial values. Results show that about 98% of the CR adsorption capacity can be recovered after five cycles of reaction indicating its good recyclability and stability. These results indicate that the La/FPC adsorbent is recyclable and stable.

CONCLUSIONS

Porous carbons (FPCs) made from FCLs were modified with lanthanum(III) by an impregnation method. The as-prepared adsorbents were characterized by EDS, XPS, nitrogen adsorption–desorption, SEM and TEM. Compared with FPC, the La/FPCs had lower surface areas and larger pore volumes. The CR adsorption capacities of the La/FPC composite sorbents are comparable to or superior to those previously reported for other carbon-based adsorbents. The adsorption capacity of the La/FPCs increased with increasing initial CR concentration and with increasing lanthanum(III) content, which indicates that both physiosorption and chemisorption take place during the adsorption process. The equilibrium data are best described
by Langmuir isotherms, and the adsorption kinetics follow a pseudo-second-order kinetic model. The La/FPC sorbents can be easily regenerated by ethanol elution and maintain a CR uptake capacity of about 98% after five cycles of regeneration. This study highlights the potential of La/FPC as a highly efficient adsorbent for the removal of anionic dyes from wastewater.

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REFERENCES


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