



# Facile, low-cost, and sustainable preparation of hierarchical porous carbons from ion exchange resin: An improved potassium activation strategy



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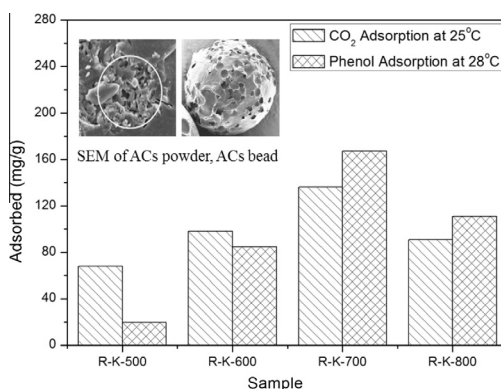
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## HIGHLIGHTS

- A series of activated carbon was derived from low-cost ion exchange resin.
- Highly dispersed potassium ions were induced which served as activating agent.
- Considerable lower amount of KOH is needed for carbon activation.

## GRAPHICAL ABSTRACT

Porous activated carbons with promising performance in CO<sub>2</sub> and phenol adsorption were prepared from low cost ion exchange resin by a sustainable way.



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## ABSTRACT

Active carbons were prepared from low cost ion exchange resin, the samples were characterized by means of low temperature (−196 °C) N<sub>2</sub> adsorption, XPS, SEM, TEM, etc., and performance in CO<sub>2</sub> and phenol adsorption were evaluated. It was found that samples with hierarchical structures and highly developed micro-mesoporous system could be obtained owing to the pre-induced highly dispersed potassium species by ion exchange, which served as an efficient activation agent, this represents an important improvement as compared with the normally reported KOH activation protocol in terms of lowering the usage of the corrosive KOH, and thus the sustainability of the obtained material. The optimized sample, R-K-700, showed the highest CO<sub>2</sub> and phenol uptake of 13.6 wt.% and 167.3 mg/g, respectively, and more importantly, samples with an ordered spherical form and similar adsorption performance to the powdered sample can be easily fabricated, making the current carbons and preparation methodology a great promise for practical applications.

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## 1. Introduction

Carbon-based materials have drawn great attention because of their excellent textural properties, favorable surface chemistries, and high stability. In the past decades, a wide spectrum of applications for carbon materials has been reported by researchers such as gas storage, wastewater purification [1], drug delivery [2], and catalysis [3]. Activated carbons (ACs) [4,5], carbon nano-tubes (CNTs) [6] and graphene [7] are the most studied carbon-based materials, among them, ACs represent an important category in the carbon family.

Precursors for ACs are diverse including petroleum coke [8], coal [9], polymers [10] and biomass [11,12]. The preparation of ACs usually consist two steps of carbonization and activation. Carbonization removes volatile components at high temperatures, while activation is necessary to produce porous structures [13]. Activation can be generally classified into physical and chemical activation, the former method involves the treatment of carbon or carbon precursors in a reactive atmosphere (normally steam and/or CO<sub>2</sub>) at elevated temperatures, however, the development of porous structure during physical activation is fairly limited [14–16], and a stronger activation process, namely chemical activation, has been employed more frequently to achieve higher surface areas and pore volumes.

Chemical activation uses an activation agent such as H<sub>3</sub>PO<sub>4</sub> [17], ZnCl<sub>2</sub> [18], K<sub>2</sub>CO<sub>3</sub> [19], KOH [20] and NaOH [21], which reacts with the carbonaceous matrix and liberates gaseous products leading to the formation of a porous structure. In this regard, KOH activation represents the most used method to afford activated carbons with enhanced porosities. For example, Pu and co-workers prepared porous carbons from waste air-laid paper by KOH activation, which resulted in samples with high surface area and narrow pores [22]. Similarly, Jalilov and co-workers directly carbonized mixtures of asphalt and KOH at elevated temperatures under inert atmosphere, by which porous carbons with a higher surface area could be obtained [23]. An analogous method has also been used to obtain biomass- and resin-based ACs with extraordinary textural properties [20,24,25].

In most studies, KOH is introduced by either impregnation or physical mixing, which in general produces bulky potassium species with limited contact with the carbons to be activated. To enhance activation, large amounts of KOH are normally used, i.e. the weight ratios of KOH to carbon are in the range of 3–7 in most cases [26–29]. This not only increased the preparation costs of the material, but also gave rise to potential environmental risks as KOH is corrosive, and the activated products need tedious washing with acid solutions, which also incurs sustainable concerns. Consequently, more effective methodologies for potassium activation are highly desirable.

Recently, novel potassium salt assisted synthesis of microporous carbon was reported by Ludwinowicz and co-workers, where potassium oxalate was directly added into a resorcinol–formaldehyde system, after polymerization, this led to evenly distributed potassium species in the resulted phenolic resins, and highly-developed porous structure could be induced after thermal treatment [30]. To the best of our knowledge, this is the first work that systematically demonstrated the importance of potassium dispersion in terms of efficient activation. In the present work, we are attempting to introduce highly-dispersed K<sup>+</sup> which served as activation agent to prepare porous carbon. To this end, commercially available ion exchange resin was specially selected as the carbon precursor owing to its natural capability in involving potassium cation by ion exchange, meanwhile, the material is relatively cheap as compared with synthetic polymers. We believe the current preparation methodology represents an important improvement

of the regular KOH activation in view of sustainability as the dosing of KOH can be decreased significantly, and the preparation cost may be further controlled by using biomass as starting materials. Samples prepared in this study showed promising performance in CO<sub>2</sub> and phenol adsorption. It is also possible to retain the spherical form of the resins, and the obtained carbon beads with well-defined spherical morphology can be prepared with adsorption capacity similar to that on the powdered samples.

## 2. Experimental

### 2.1. Sample preparation

Commercially available 001 × 7 ion exchange resin (Shanghai HuiZhu Resin Co., Ltd., China) was firstly treated by nitric acid (Qrec, 69%) solution to remove any metallic impurities, and then washed with copious de-ionized water, the obtained samples were mixed with 1.0 M potassium hydroxide (Qrec, 99%) aqueous solution and stirred for 48 h, and the KOH aqueous solution was renewed every 8 h. After ion exchange, the samples were rinsed several times with de-ionized water to neutral and then dried at 105 °C overnight.

The obtained samples were then thermally treated in nitrogen atmosphere (100 mL/min) at different temperatures (500–800 °C) for 5 h with a ramping rate of 2 °C/min, the resulted carbons were washed with 1.0 M hydrochloric acid (Qrec, 39%) solution and de-ionized water to remove any residual K<sup>+</sup>, and dried at 105 °C overnight. The samples were denoted as R-K-T, where K indicates the involving of potassium species by ion-exchange, and T represents the temperature of the thermal treatment.

For comparison purposes, a sample named as R-800 was also prepared following the same method (treated at 800 °C) as the R-K-T series without the K<sup>+</sup> exchange step. In addition, to demonstrate the merits of K<sup>+</sup> introduction by ion exchange, KOH was physically mixed with either the raw ion exchange resin or R-800 and thermally treated at 700 °C, to ensure the evenly mixing, the mixture was grinded in a mortar, and the amount of added KOH was controlled according to ICP measurement to be identical to the R-K-T series. The obtained samples were denoted as R-KOH-700 and C-KOH-700, respectively.

### 2.2. Characterizations

Low temperature (−196 °C) N<sub>2</sub> physisorption was measured on a Micromeritics Tristar II 3020 analyzer. The specific surface area was calculated according to the method suggested by Parra et al. [31]. The cumulative pore volumes ( $V_{\text{total}}$ ) were calculated from the amount of nitrogen adsorbed at  $P/P_0$  of ca. 0.99, and the average pore diameter ( $D_{\text{avg}}$ ) was calculated by  $4V_{\text{total}}/S_{\text{BET}}$ . Micropore volume ( $V_{\text{micro}}$ ) and surface area ( $S_{\text{micro}}$ ) were determined by the t-plot method. Prior to any tests, samples were degassed at 200 °C for 8 h. Organic element analysis was carried out on a FLASH2000 CHNS analyzer (Thermo Fisher). Potassium content was measured by inductive couple plasma (Optima 8000, Germany), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on a ZEISS EVO18 and a JEOL JEM-2100 instrument, respectively. X-ray photoelectron spectroscopy (XPS) of the samples was analyzed on a PHI-5000C ESCA System.

### 2.3. CO<sub>2</sub> and phenol adsorption

CO<sub>2</sub> isotherms were measured on a Micromeritics Tristar II 3020 analyzer, and samples were degassed at 200 °C for 8 h before any tests. Phenol adsorption was carried out by mixing and stirring

the samples with phenol aqueous solution with a starting concentration of 200 mg/L at 28 °C, adsorption capacities were calculated according to the equilibrium concentration measured by a UV-Vis spectrophotometer (HACH, DR2800, USA).

### 3. Results and discussion

#### 3.1. Characterization of the samples

The current study attempts to achieve carbonization and activation of polymers simultaneously by involving highly dispersed potassium species into the matrix of ion exchange resin. Fig. 1 presents the full range XPS spectra of the ion exchanged and washed resins (sample R-K), peaks attributable to potassium could be found and it was confirmed by fine scan that  $K^+$  is the major potassium species. Fig. 2 presents the potassium mapping of R-K, evenly distributed  $K^+$  on the non-porous resin could be observed. According to ICP analysis, the sample possessed approximately 19.6 wt.% of potassium. These results evidenced the successful introduction of highly dispersed potassium ions into the resin matrix.

R-K and untreated resin as a reference were then treated in an inert atmosphere at 800 °C, it can be seen from Fig. 2 that the starting material is generally non-porous, carbonization led to the formation of a porous structure, which can be indicated by the considerable increasing of  $SA_{BET}$  to 138 m<sup>2</sup>/g for the sample R-800 (carbonized from untreated resin). More importantly, this value increased to 647 m<sup>2</sup>/g (near 370% increase) when  $K^+$  was introduced before thermal treatment (sample R-K-800, Table 1). Consequently, the presence of  $K^+$  in the resin matrix possessed an activation effect similar to the well-reported KOH activation process [9,15,29].

Fig. 3 shows the low temperature (−196 °C)  $N_2$  isotherms of the R-K-T samples carbonized at temperatures ranging from 500 to 800 °C. All the samples exhibited similar patterns, namely sharp increasing of  $N_2$  uptake at low  $P/P_0$  region, and hysteresis loops were found at mid-high pressures. This result indicated the present ion exchange resin derived carbons possessed hierarchical porous structures with combinative features of micropores and mesopores, which has been demonstrated as an important character for adsorbents as the mesopores play a key role in enhancing the diffusion of adsorptive molecule while micropores are the major adsorption sites [32,33]. From Table 1, the BET surface areas and pore volumes of the samples increased with the increase of treatment temperature up to 700 °C (366, 659, 859 m<sup>2</sup>/g for R-K-500, R-K-600, R-K-700, respectively), indicating the enhancement of carbonization and activation at higher temperatures. When compared with R-K-700, the sample treated at 800 °C (R-K-800) exhibited a lower surface area of 647 m<sup>2</sup>/g owing to over-activation. This can be confirmed by the results of pore volume and diameter, i.e. with the increase of treatment temperature up to 700 °C, both the total pore volume and micropore volume increased with decrease of average pore diameter, indicating the preferable formation of micropores in these conditions. When the treatment temperature further increased to 800 °C, the micropore volume decreased while the total pore volume increased accompanied with an increase of average pore diameter, this is a strong evidence of micropore enlargement owing to over-activation.

Controlled experiments were carried out by mixing KOH with the bare resin (R) and R-800, the amounts of used KOH in both cases were calculated to keep the weight percent of  $K^+$  in the mixtures identical to that of the R-K-T series. The mixtures were then treated at 700 °C, and the porous structures were measured. As

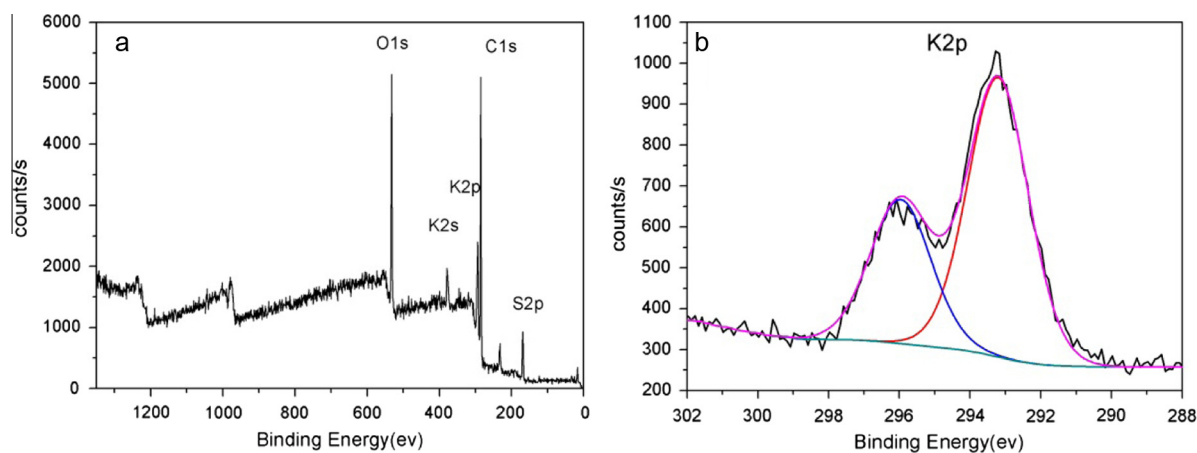


Fig. 1. Full range XPS spectra (a) and K2p fine scan (b) of R-K.

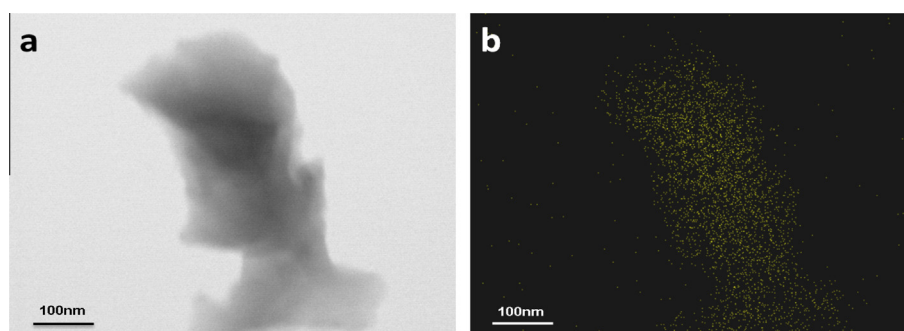
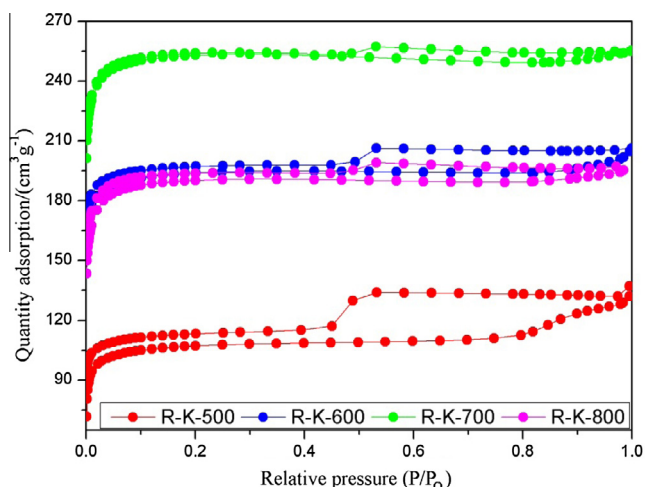


Fig. 2. TEM image (a) and potassium mapping (b) of R-K.

**Table 1**Textural properties and CO<sub>2</sub> adsorption of various carbon materials.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>A<sub>micro</sub></sub> (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	V <sub>micro</sub> (cm <sup>3</sup> /g)	D <sub>avg</sub> (nm)	CO <sub>2</sub> uptake (wt.%)	
						Measured (25 °C, 1 bar)	Saturation <sup>a</sup>
R-800	138	119	0.07	0.06	2.1	3.1	4.8
R-K-500	366	199	0.21	0.08	2.3	6.8	8.9
R-K-600	659	445	0.32	0.20	1.9	9.8	14.1
R-K-700	859	545	0.40	0.24	1.8	13.6	22.4
R-K-800	647	335	0.45	0.15	2.8	9.1	19.4
R-KOH-700	570	207	0.30	0.08	2.1	10.0	–
C-KOH-700	247	87	0.12	0.03	2.0	8.8	–

<sup>a</sup> Fitted value from Langmuir equation.**Fig. 3.** Low temperature (−196 °C) N<sub>2</sub> isotherms of the R-K-T series.

listed in Table 1, both samples exhibited considerably lower textural properties than KOH activated ACs reported in the literatures [34,35] probably due to the low KOH amounts used (weight ratio of KOH to carbon precursor of 0.2 and 3–7 in the present study and literatures, respectively). More importantly, the obtained surface areas and pore volumes of the two KOH activated samples are also lower than those on R-K-700 as well, this clearly demonstrated the advantage and improvement of the current methodology for inducing potassium activation agent by ion exchange as compared with the widely reported physical mixing and/or

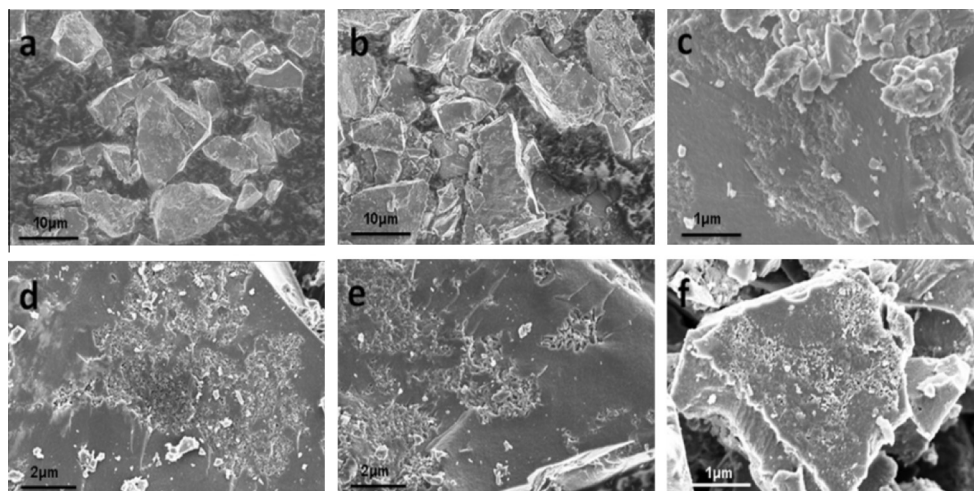
impregnation method [36], namely ion exchange can promisingly lowering the amount of used KOH for activation of carbons and combine carbonization and activation into one step, these are able to offer both economic and sustainable benefits for the practical utilization of the materials.

The morphology of the samples were investigated by SEM, and the obtained images are showed in Figs. 4 and 5. To examine the internal surface, the as-prepared carbon beads (vide infra) were firstly ground into powders, it can be seen that the samples are composed by granules of irregular shapes (Fig. 4a and b), a closer check indicated that for sample R-K-500, the surface is generally smooth (Fig. 4c), a few rough regions (white circle) with small openings (ca. 10 nm) can be observed (Fig. 5a) probably arose from thermal contraction and surface peeling of the resin beads because carbonization and activation are not effective at temperature as low as 500 °C (Table 1 and [13]). At treatment temperatures of 600–800 °C, larger amounts of well-defined pores can be seen (Fig. 4d–f), and from Fig. 5b–d, it seems comprehensive macroporous structures were formed deeply into the particles especially for the sample R-K-700 and R-K-800 (white circles), indicating the proper carbonization and activation of these samples.

### 3.2. Sample evaluation

#### 3.2.1. CO<sub>2</sub> adsorption

CO<sub>2</sub> adsorption isotherms of the samples were analyzed at 25 °C as showed in Fig. 6, all the curves could be fitted by Langmuir equation, the obtained saturation capacities are listed in Table 1, it can be seen that R-K-700 showed the highest saturation capacity which is significantly greater than R-800. This result is in line with the adsorption capacities measured at 1 bar (Table 1), namely a

**Fig. 4.** SEM images of R-K-500 (a–c), R-K-600 (d), R-K-700 (e), R-K-800 (f).



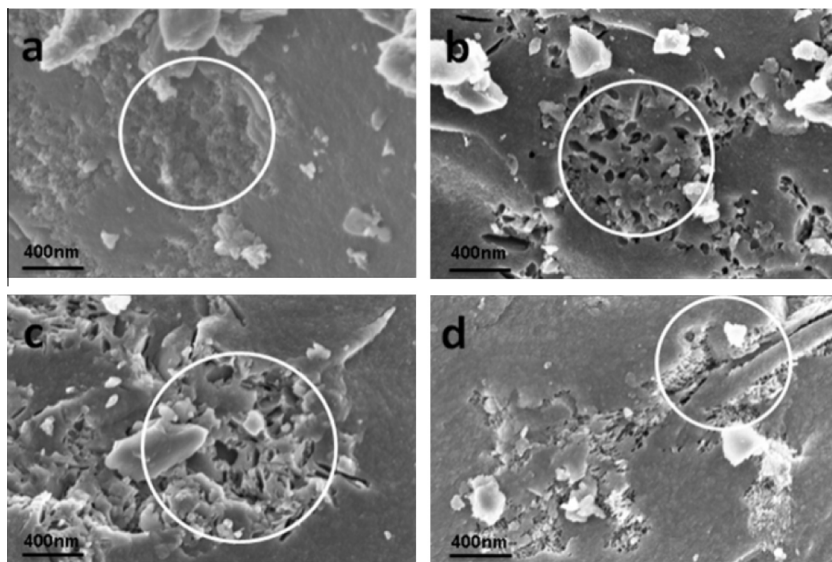


Fig. 5. High magnification SEM images of R-K-500 (a), R-K-600 (b), R-K-700 (c) and R-K-800 (d).

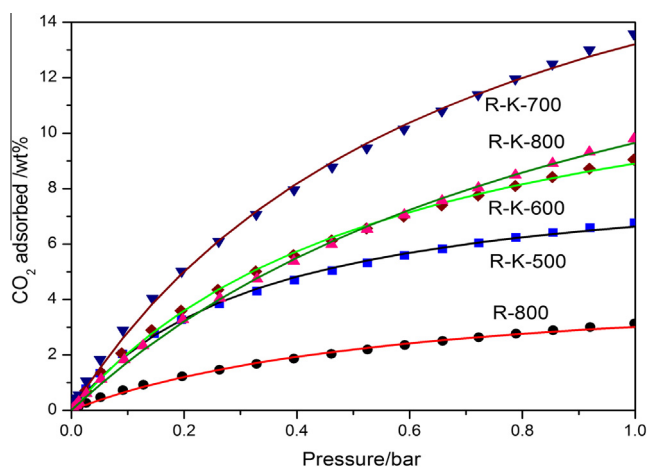


Fig. 6. CO<sub>2</sub> adsorption isotherms on R-800 and R-K-T samples (25 °C). (Dots: Experimentally measured value, curves: Langmuir fitting).

very low CO<sub>2</sub> uptake of 3.1 wt.% was measured on sample R-800 due to its poor textural properties, and thanks to the activation effect of the exchanged K<sup>+</sup>, enhanced CO<sub>2</sub> uptakes were observed in the R-K-T series. Akin to the trend of BET surface area, the CO<sub>2</sub> adsorption capacities increased with the increase of treatment temperature and peaked at 700 °C, where a CO<sub>2</sub> uptake of 13.6 wt.% was obtained on the sample R-K-700. This value is generally higher than most of the non- or physically activated carbons, but substantially lower than those prepared from KOH activation of synthetic nitrogen-incorporated polymers [37–39]. None the less, we still believe that the samples reported here and the developed activation method hold the promise for further improvement if one considers the significantly lower KOH (which is a corrosive reagent) amount needed and especially, the wide availability and cost effectiveness of ion-exchange resins as compared with those reported synthetic polymers.

CO<sub>2</sub> adsorption was also measured on the reference samples (R-KOH-700 and C-KOH-700) as listed in Table 1, as can be expected from the surface area data, their performance is lower than sample R-K-700. Based on these results, it is reasonable to assume that the highly dispersed K<sup>+</sup> species introduced by ion

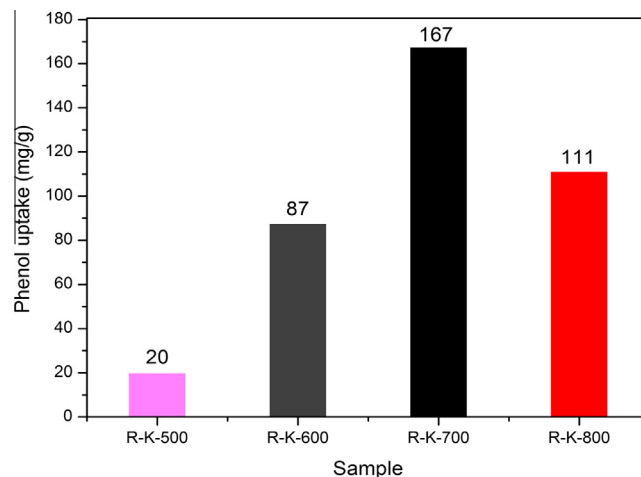


Fig. 7. Phenol adsorption capacities on the R-K-T samples (28 °C).

exchange dictated a more homogeneous activation process during the thermal treatment, therefore the resulted samples can be better activated although the amount of activation agent is low. On the contrary, contact between KOH and resin/carbon surface in the physical mixing samples is by and large limited, leading to relatively weak activation and adsorption capabilities.

### 3.2.2. Phenol adsorption

Phenol is a common pollutant found in industrial waste water, which is harmful to human health as well as the environment. Removal capabilities of phenol (as a large molecule comparing with CO<sub>2</sub>) of the current carbons were also investigated as showed in Fig. 7. The optimized sample, R-K-700, showed the maximum phenol uptake of 167 mg/g, which is among the highest adsorption capacities reported for similar materials under similar conditions. For example, Ali and co-workers prepared ACs from tea industry wastes and the obtained samples exhibiting phenol adsorption capacity less than 96 mg/g [40], and recently, Hameed achieved a higher value of 140 mg/g on a sawdust-derived AC [41]. These results indicated that except small molecule such as CO<sub>2</sub>, the R-K-700 sample occurs to be a good candidate as adsorbent for the

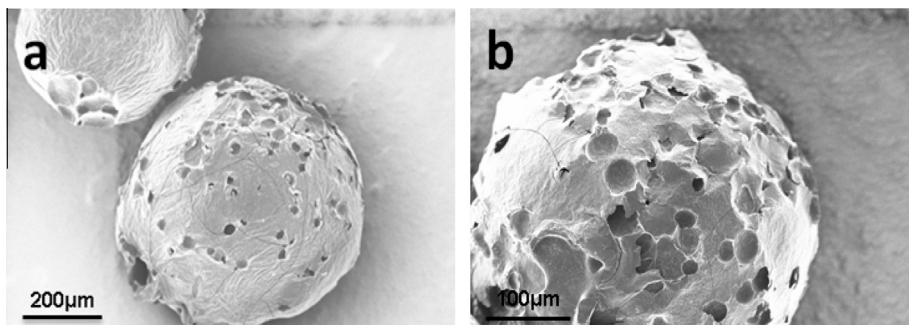


Fig. 8. SEM images of R-K-700-S (a) and R-K-ox-700-S (b).

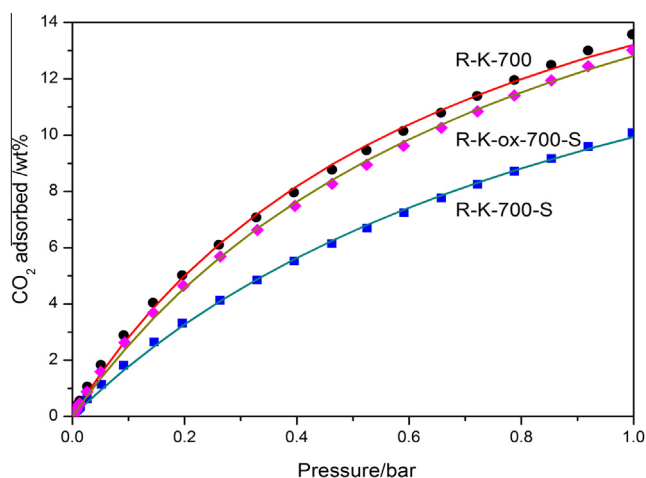


Fig. 9. CO<sub>2</sub> adsorption isotherms of carbon beads (25 °C). (Dots: Experimentally measured value, curves: Langmuir fitting).

removal of larger molecule as well probably due to its hierarchical porous structure.

### 3.3. Spherical samples

For any adsorbents or catalysts to be used in practical processes, the materials must possess certain physical forms, i.e. monolith, beads, etc. One of the merits by using polymers as carbon precursor is that shapes of carbons can be inherited from the polymers [42,43]. In this regard, the spherical form of the ion exchange resin was taken as an additional advantage, and carbon beads can be obtained by properly control the thermal treatment conditions (e.g. ramping history, etc.). Fig. 8 shows the SEM pictures of the obtained carbon beads, and well-defined spherical forms (ca. 500 μm in diameter) were observable, which is similar to the resin precursor. In Fig. 8b, openings and cracks can be seen on the outer surface, which provided necessary channels for the diffusion of adsorbates. Fig. 9 shows the CO<sub>2</sub> isotherms of the spherical samples, as compared with the powdered R-K-700 sample, slightly lower CO<sub>2</sub> uptake was observed on the carbon bead sample that was similarly treated at 700 °C probably due to diffusion limitations (R-K-700-S). This can be circumvented by adopting a mild oxidation step (200 °C in air) before the 700 °C temperature treatment, which led to very similar performance to that of the powdered sample (R-K-ox-700-S). By adjusting precursors and preparation conditions, we are currently working on enhancing the mechanical strength of these carbon beads to achieve a proper level for industrial adsorber.

## 4. Conclusion

Starting with commercially available low cost ion exchange resin, highly dispersed potassium species was induced by ion exchange. According to the characterization results from low temperature (−196 °C) N<sub>2</sub> adsorption, XPS, SEM, TEM, etc., it was found that the resulted material occurs to be a promising precursor for the preparation of active carbons with well-developed hierarchical porous structures, which can be attributed to the efficient activating effect of the potassium species. The BET surface area increased with the increase of thermal treatment temperature up to 700 °C, and the highest value of 859 m<sup>2</sup>/g was achieved on the sample R-K-700. Consequently, the sample showed excellent adsorption performance for CO<sub>2</sub> and phenol with uptakes of 13.6 wt.% (25 °C, 1 bar) and 167 mg/g (28 °C), these values may slightly lower than those KOH activated carbons reported in the open literatures, however, since considerably lower amount of KOH was needed in the current study as compared with the widely reported physical mixing method, and carbon materials of ordered spherical forms can be obtained, we believe the preparation protocol reported here represented an effective and more sustainable improvement for the KOH activation method.

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