Accepted Manuscript

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S0926-860X(14)00471-2
http://dx.doi.org/doi:10.1016/j.apcata.2014.07.041
APCATA 14934
Applied Catalysis A: General
21-5-2014
16-7-2014
18-7-2014

Please cite this article as: L. Xu, X. Li, J. Ma, Y. Wen, W. Liu, Nano-MnO_x on activated carbon prepared by hydrothermal process for fast and highly efficient degradation of azo dyes, *Applied Catalysis A, General* (2014), http://dx.doi.org/10.1016/j.apcata.2014.07.041

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Nano-MnO_x on activated carbon prepared by hydrothermal process for fast and highly efficient degradation of azo dyes

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3		Research highlights
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5	λ	A facile and green method for carbon supported nanostructure MnO_X was
6		proposed.
7	λ	MnO _X @actived carbon could efficiently and rapidly degrade azo dyes.
8	λ	The mixed-valent MnO_X system could cause the high degradation reactivity.
9	λ	MnO _X @actived carbon exhibit good stability after twenty consecutive cycles.
10	λ	The detectable degradation products are mainly biologically degradable.
11		
12		
13		
14		Abstract
15		Azo dyes are recalcitrant and refractory pollutants that pose a threat to
16	env	vironmental safety. Therefore, it is of significance to develop fast, cheap and highly
17	effective materials for removal of azo dyes in water. Herein, fast oxidative removal of	
18	azo dyes by highly active nano- MnO_x on activated carbon prepared via hydrothermal	
19	pro	cess was explored. Active manganese oxide was supported on coconut shell
20	act	ivated carbon (CSAC) via hydrothermal method and was characterized. The
21	hyo	drothermal treatment changed the morphology of the MnO _x @CSAC and led to the
22	in	situ synthesis of nano-MnO _x onto CSAC surfaces with the incorporation of the

23	multi-valence oxidation states (Mn^{4+} and Mn^{3+}) of manganese. The decolorization
24	reactions by $MnO_x@CSAC$ were fast and the dye removal was most pronounced at
25	pH 3 (99.1%). Through GC-MS analyses, the most detectable degradation products
26	were identified and possible degradation pathway was proposed. Additionally, the
27	$MnO_x@CSAC$ also could effectively degrade other anionic dyes. The oxidative
28	degradation of C. I. Acid Red 73 was still strong after twenty usage cycles, with a
29	maximum removal rate of 99.1% and a minimum removal rate of 89.7% from the
30	same sample. Overall, these results indicate that highly active nano-MnO _x @CSAC
31	prepared via a hydrothermal method is very attractive, implying that this material has
32	potential practical applications for treating azo dyeing effluent.
33	<i>Keywords:</i> nano-MnO _x ; activated carbon; hydrothermal process; oxidative removal;
34	azo dye

1 1. Introduction

2 Textile industries produce large volumes of wastewater polluted with dyes. It has 3 been estimated that approximately 10-15% of manufactured dyes are discharged into wastewater streams [1, 2]. Among these dyes, azo dyes represent the largest class of 4 dyes [3]. Azo dyes are not readily biodegradable under aerobic conditions; in addition, 5 6 under anaerobic conditions, they can be reduced to potentially hazardous aromatic 7 amines and other compounds. Furthermore, the degradation by-products of azo dyes can be mutagenic, carcinogenic, or teratogenic and can cause long-term health effects 8 [4-7]. Therefore, developing inexpensive and highly effective materials for the rapid 9 removal of azo dyes in water is of importance. 10

Recently, manganese oxides, which are naturally present in sediments and soils, 11 12 have attracted considerable interest and have demonstrated rapid oxidation properties suitable for the removal of organic pollutants in water without the addition of other 13 14 oxidizing agents, such an ozone or H_2O_2 . For example, Huguet et al. proposed that the 15 use of natural manganese oxide alone (79% MnO₂) as a bed filter can be very efficient for the chemical oxidation of diclofenac [8]. AquaMandix, a natural Mn material, has 16 already been found to be efficient for the removal of estrogenic hormones in 17 18 wastewater treatment plants [9]. In addition, a Mn oxide containing mine tailings has been shown to promote the complete oxidative decolorization of acid azo dyes after a 19 20 reaction period of 24 hours [10]. However, the quantity of natural manganese is 21 limited. Thus, synthetic manganese oxides have been used for the oxidative removal of organic contaminants, such as phenols and pharmaceuticals, in water. However, 22

1	both natural and synthetic manganese oxides suffer from low efficacies. For example,
2	Forrez et al. tested the oxidative removal of diclofenac using synthetic MnO_2 and
3	$BioMnO_x$ and found that both oxides required approximately 20 hours to completely
4	remove organic contaminants [11]. Thus, to enhance efficacy, more MnO ₂ was added
5	to the reaction solutions. Lin et al. reported the nearly oxidative removal of bisphenol
6	A in 6 minutes in a pH 4.5 solution that initially contained 800 μM MnO_2 and 4.4 μM
7	bisphenol A [12]. It is known that the oxidative activity of metal oxides depends on
8	the size distributions and morphologies of the particles. Hence, reducing the diameter
9	of the material to the nanometer scale may result in enhanced its efficacy [13]. Thus,
10	synthetic nanostructured manganese oxides have been reported to oxidize organic
11	contaminants [14, 15]. Nevertheless, nano-materials are difficult to separate from
12	water, which becomes the major limitation for the application of nano-materials in
13	this field [16, 17]. Therefore, it is very desirable to develop a strategy to prepare nano
14	MnO_x on a suitable support to obtain good separability and remarkable oxidation
15	properties for wastewater treatment.

Granular activated carbon has been widely used as a reaction support or promoter in wastewater purification due to its high surface area to volume ratio and good adsorption capacity for a large number of organic contaminants, which prompted us to investigate whether suitable active MnO_x on activated carbon are accessible. Supported manganese oxides are generally prepared using the wet impregnation method with a metal salt followed by calcinations under an air or nitrogen atmosphere [18-20]. However, preparing active $MnO_x@$ activated carbon by calcination under an

air atmosphere is difficult due to carbon ashing. Furthermore, to the best of our
knowledge, little work has been published in the literature concerning the preparation
of this material under a nitrogen atmosphere. The majority of previous studies focused
on carbon-supported manganese oxides as catalysts to assist oxidants, such as ozone,
in degrading organic contaminants in water [20, 21]. To date, the direct synthesis of
active MnO_x with a defined crystal structure on activated carbon remains a formidable
challenge.

Hydrothermal treatment has been intensively studied over the past few years as a 8 9 sustainable synthesis method with numerous applications. This synthesis method is conducted in and requires water, and it is also conducted under self-generated 10 pressures in closed systems and with mild temperatures (i.e., 120-250 °C). From an 11 12 energetical perspective, hydrothermal treatment is an exothermic process in contrast to the standard high-temperature treatment. Therefore, hydrothermal treatment is 13 14 considered to be a green route for the synthesis of advanced materials [22-24]. Thus, in this study, the in situ combination of coconut shell activated carbon (CSAC) with 15 nanoscale MnO_x produced by hydrothermal treatment and its application in the 16 degradation of azo dyes were investigated. It was determined that MnO_x@CSAC 17 18 exhibited the best degradation activity for C. I. Acid Red 73 (AR 73) as well as good 19 stability, which can be suitable for environmental applications. Compared with 20 manganese-supported activated carbon materials obtained through conventional 21 preparation methods, the in situ synthesis of nanostructured MnO_x on CSAC $(MnO_x@CSAC)$ through the hydrothermal route is a facile and green approach. 22

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2. Experimental 1

2 2.1. Preparation of $MnO_x(a)CSAC$

3 The raw CSAC (iodine value: 900 mg/g; particle size: 1-2 mm) was ground using an agate mortar, and the resulting material was then sieved through a uniform sieve 4 with a mesh of 100. In our study, a lot of preliminary experiments were done to 5 optimize the synthesis condition of $MnO_x(a)CSAC$. In an optima experimental 6 procedure for the synthesis of $MnO_x@CSAC$, 0.3 g of CSAC was added 7 8 progressively to 10 mL of a 0.0040 M MnSO₄ solution with vigorous stirring at room temperature to obtain a well-mixed solution, which was left to stand for 12 h in a 100 9 mL Teflon-lined stainless steel autoclave. Then, 0.0048 M (NH₄)₂S₂O₈ was placed 10 into 10 mL of distilled water to form a homogeneous solution, which was also 11 transferred into the autoclave and maintained at 120 °C for 12 h. The resulting product 12 13 was centrifuged, decanted, washed with deionized water and dried at 80 °C in air.

14

2.2. Characterization of MnO_x@CSAC

Surface morphology was studied with an electron microscope. The scanning 15 electron microscopy (SEM) micrographs were recorded using a field emission 16 scanning electron microscope (FEI, SIRON) at a voltage of 25.0 kV. The nitrogen 17 adsorption and desorption isotherms at 77 K were measured using a NOVA2000e 18 19 surface area & pore size analyzer (Quantachrome, USA). The specific surface area was calculated by Brunauer-Emmet-Teller (BET) equation. The sample surfaces were 20 21 gold coated before analysis. The transmission electron microscopy (TEM)

1 micrographs were obtained with a JEM-1230 (JEOL, Japan) transmission electron 2 microscope at an accelerating voltage of 200 kV. Synchrotron-based scanning 3 transmission X-ray microscopy (STXM) was performed at beamline BL08U1 of the Shanghai Synchrotron Radiation Facility (SSRF). The materials were ultrasonically 4 dispersed in ethanol and dropped directly onto a TEM grid. After evaporation of 5 6 excess ethanol, the grids were fixed to the sample holder of the STXM device. 7 Single-energy images at energies of L edge and pre-edge of Mn were scanned and 8 recorded as raw data. Then, image differences were calculated and analyzed for mapping chemical species over the scanned areas using the dual-energy ratio contrast 9 analysis method. The 2D spatial distribution of Mn element can be mapped 10 quantitatively from its absorption difference at two photon energies, 636.35 eV and 11 12 642 eV, which are just on pre-peak and peak of Mn absorption edge, respectively. Furthermore, the crystalline structure and the valence of manganese were obtained 13 14 from X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), 15 respectively. Detailed procedures are presented in the SI Text S1-2.

16 2.3. General Procedure for degradation of dyes by the $MnO_x@CSAC$ system

All of the dye degradation experiments were performed by placing 0.1 g of MnO_x@CSAC in contact with 100 mL of the dye solution (50 mg/L) in 250 mL flasks during 2 minutes of constant stirring at 25 °C. The pH of the dye solution was varied by adding 2.0 M H₂SO₄ or 0.1 M NaOH. For the MnO_x@CSAC reuse studies, the materials were collected by centrifugation and were dried at 80 °C following the degradation reaction. The chemical structures of dyes are shown in Figure S1 in the

Supporting Information. The dye concentrations were analyzed using a Shimadzu

2 UV-2401PC UV-Vis spectrometer (Tokyo, Japan) at the absorbance maximum of the dyes. The decolorization rate η (%) of dyes can be calculated as: $\eta = \frac{C_0 - C_t}{C_0} \times 100\%$ 3 where C_0 is the initial concentration of dye solution (mg/L), C_t is the concentration of 4 dye solution at the desired time, t (mg/L). GC-MS analysis of the degradation products 5 was performed using an Agilent 7890-5975C (American Agilent Technologies Co. Ltd.) 6 instrument equipped with a HP-5 capillary column (30 m \times 0.25 mm \times 0.25 μ m). The 7 carrier gas was helium, and the temperature of the injection port was 250 °C. The 8 9 temperature program of the column was set to an initial oven temperature of 50 °C and was increased at a rate of 10 °C/min to 250 °C, and the oven was held at 250 °C 10 for 10 min. The sample for GC-MS analysis was prepared as follows [25]: after 11 12 reaction with MnO_x@CSAC, the AR 73 solution was withdrawn, and the water was 13 removed using a vacuum rotatory evaporator, which left a pale yellow residue. The residue was dissolved using a sufficient volume of 3 M HCl, and the resulting solution 14 was saturated with NaCl, extracted with diethyl ether, and then dried with anhydrous 15 sodium sulfate; the ether was evaporated under vacuum. The residue was dissolved in 16 17 1 mL of methanol, and 0.5 mL of 0.2 M trimethylsulfonium hydroxide (Me_3S^+OH) in methanol was added to the methanol solution before GC-MS analysis. 18

19 **3. Results and discussion**

1

20 3.1. Hydrothermal synthesis of $MnO_x@CSAC$: morphology and structure analysis

The morphology of the raw CSAC and $MnO_x@CSAC$ was examined by SEM

1 (Figures 1a, 1b). Based on images Figure 1a and Figure 1b, the two materials exhibit 2 different particle sizes and pore structures. For the raw CSAC (Figures 1a), well-dispersed particles were observed and the particle sizes were small in the range 3 4 of 5-15 micrometers. However, the MnO_x@CSAC particles were in an agglomerated state with a relatively broader size distribution (about 100 micrometers) and 5 noticeable scattering of pores compared to the raw CSAC, which might be a 6 consequence of the hydrothermal treatment. Thus, to explain this phenomenon, the 7 8 raw CSAC was treated using the hydrothermal method (HT-CSAC) without the addition of MnSO₄·H₂O and the corresponding SEM image is presented in Figure 1c. 9 As shown in Figure 1c, HT-CSAC also exhibits agglomeration behavior, which is 10 consistent with the result of $MnO_x@CSAC$. This phenomenon may be attributed to 11 the following two reasons: (1) the effect of high-temperature. During the 12 13 hydrothermal process, the surface of activated carbon was modified by OH groups, 14 which resulted in a hydrogen bonding interaction between activated carbon. Then, the 15 activated carbon was promoted to further assemble the low-energy close-packed mesostructure with further cross-linking of the OH groups because the cross-linking 16 17 process occurs actively at the high temperature. Simultaneously, the high-temperature 18 hydrothermal treatment drives the small activated carbon to accumulate and rearrange 19 [26]. Consequently, a large activated carbon with a mesostructure is formed. (2) The 20 effect of stirring. The hydrothermal process was performed without stirring; thus, the raw CSAC could be promoted to further assemble into a close-packed mesoporous 21 22 structure. Additionally, the specific surface area of CSAC, HT-CSAC and MnO_x@CSAC were determined in this study. The N₂ adsorption/desorption isotherms 23 of the raw CSAC, HT-CSAC and MnO_x@CSAC are presented in Figure S2. The raw 24 25 CSAC, HT-CSAC and MnO_x@CSAC exhibited type IV adsorption/desorption

isotherms with hysteresis loops, which indicates that the three materials had a mesoporous structure. CSAC presented the highest BET surface area (723.168 m²/g), whereas MnO_x@CSAC presented the lowest surface area (504.530 m²/g). The specific surface area of HT-CSAC (703.001 m²/g) was slightly smaller than that of raw CSAC because of substantial aggregation. The BET surface area of MnO_x@CSAC decreased because of the in situ synthesis of MnO_x nano-particles into the CSAC.

8 The morphology and structure of different product are further elucidated by TEM. 9 As shown in Figure 1d, the needlelike MnO₂ nanowires with diameter 10-50 nm and 10 length up to several micrometer can be clearly seen, which are in good agreement 11 with the SEM observation (the inset of Figure 1d). Compared with the raw CSAC 12 (Figure 1e), TEM image of MnO_x@CSAC (Figure 1f) demonstrates that ribbon-like 13 nanowires of MnO_x nanocrystals anchored randomly into the amorphous CSAC, as 14 well as the higher-magnification TEM image depicted in the inset of Figure 1f.

15 The as-synthesized products are also characterized by X-ray diffraction (XRD) to identify their crystallographic structures (Figure 2). According to a previous report 16 17 [27], the pattern of the as-prepared MnO_2 can be assigned to the MnO_2 phase (JCPDS) No. 72-1982). In this work, the two obvious diffraction peaks were observed at 18 approximately $2\theta = 22^{\circ}$ and 43° , which are common to activated carbon, correspond to 19 (002) and (110) reflections due to the stacking structure of aromatic layers. The XRD 20 patterns of MnO_x@CSAC show that the FWHM of the 22° signal broadened because 21 of the small dimensions of crystallites perpendicular to the aromatic layers. In 22 23 addition, weakly crystallized structure signals corresponding to MnO₂ were observed

because the MnO_x@CSAC contained a considerable amount of amorphous
 carbonaceous organic compounds.

In addition, the valence of manganese in MnO_x@CSAC after hydrothermal treatment was determined by XPS analysis (Figure S3). The Mn 2p3/2 and Mn 2p1/2 binding energies are 641.9 and 653.7 eV, respectively, with a spin-energy separation of 11.8 eV. This doublet can be assigned to a mixed-valent manganese system, most likely Mn⁴⁺ and Mn³⁺ [28].

8 From the above results, the hydrothermal treatment changed the morphology of
9 the MnO_x@CSAC. Meanwhile, the in situ synthesis of nano-MnO_x onto CSAC
10 surfaces led to the incorporation of the multi-valence oxidation states of manganese.

11 *3.2. Oxidative degradation of AR 73*

The removal of AR 73 by different MnOx@CSAC prepared using different 12 13 approach was studied in this work. As shown in Figure 3, the removal rates of AR 73 by $MnO_x@CSAC$ (obtained via the hydrothermal method), N₂-MnO_x@CSAC 14 (obtained by calcination under a nitrogen atmosphere) and Air-MnO_x@CSAC 15 (obtained by calcination under an air atmosphere) were 99.1%, 31.6% and 24.0% after 16 10 minutes treatment, respectively. The CSAC, N₂-CSAC and Air-CSAC exhibited 17 almost the same decolorization activity, approximately 43-45%. Based on the above 18 19 data, the color removal ability of MnO_x@CSAC was much stronger than the CSAC. Conversely, comparing with the corresponding CSAC, dye removal efficiencies by 20 both N_2 -MnO_x@CSAC and Air-MnO_x@CSAC obtained through calcination method 21 22 did not enhance. These results demonstrated that $MnO_x@CSAC$ prepared via

1 hydrothermal method is a highly active material for the removal of AR 73.

2	Decolorization reactions by $MnO_x@CSAC$ were investigated within the pH
3	range of 3-7 at 25 °C. This pH range was chosen because the pH values of the raw
4	CSAC and MnO _x @CSAC were close to 7 and also acid dyes are often applied in
5	organic acid solutions resulting in acidity of textile effluents. The effect of the initial
6	solution pH on the decolorization of the dye at concentrations of 50 mg/L AR 73 and
7	1.0 g/L MnO _x @CSAC is shown in Figure 4a. The results indicated that the removal
8	rate of AR73 in solution increased as the pH decreased from 7.0 to 3.0, and the dye
9	removal was most pronounced at pH 3 (99.1%). The reason for this large variation
10	most likely stems from the surface charge of MnO_x , which strongly depends upon the
11	solution pH. The point of zero-charge (pH_{pzc}) for MnO _x is pH 4-5. Decreasing the pH
12	(below pH_{pzc}) will increase the proportion of positively charged sites on the
13	$MnO_x@CSAC$ surface, thereby increasing the potential for AR 73 (anionic dye)
14	molecules electrostatic attraction to the active MnO_x surface and further oxidation by
15	MnO _x @CSAC. When increasing the solution pH above pH_{pzc} , MnO _x @CSAC surface
16	is negatively charged while AR 73 exists as an anion. Consequently, interactions at
17	the dye-active surface are not expected. In addition, the measured UV-Vis spectra of
18	the color change (pH 3) at each reaction time are shown in Figure 4b. Notably, the
19	characteristic adsorption band of the dye in the visible region ($\lambda_{509nm})$ almost
20	disappeared after 4 minutes of contact with MnOx@CSAC, indicating a rapid
21	decolorization of azo dye. In the meantime, as a reference, the removal of dye by the
22	MnO_x without CSAC was studied. The result showed that MnO_x prepared via

hydrothermal method is also a highly active material for the removal of AR 73 (Figure S4), but the nano-MnO_x is very difficult to separate from water, which becomes the major limitation for the application of nano-materials in field of wastewater treatment.

To test whether the dye decolorization rate increasing with decreasing pH was 5 6 as a result of oxidative reaction, the raw CSAC, which was used as a reference 7 material, was investigated to adsorb AR 73. Figure 4c shows the removal rate of AR 8 73 by raw CSAC. As the pH was decreased, the removal rate of AR 73 increased. However, the raw CSAC had a low affinity for AR 73 (48.1%), even after 10 minutes 9 of contact with the dye solution at pH 3. When using MnO_x@CSAC for the 10 decolorization reaction, the removal rate was 99.1% after 10 minutes at pH 3 without 11 12 the use of any additional oxygen sources in the solution. Therefore, the data from the pH experiments with the raw CSAC indicate that $MnO_x@CSAC$ can degrade dye. 13

14 Furthermore, the initial concentration of dyes is an important parameter in 15 practical applications. The influence of the initial dye concentration, ranging from 50 to 200 mg/L, on the degradation efficiencies of AR 73 was investigated at pH 3 16 (Figure S5). The AR 73 solutions with initial concentrations of 50, 100, 150 and 200 17 18 mg/L resulted in degradation efficiencies of 99.1, 97.5, 87.3 and 84.3%, respectively, after 10 minutes of contact. Although the color removal efficiency gradually 19 20 decreased as the initial concentration increased, the $MnO_x@CSAC$ had high reactivity 21 for the oxidative removal of dyes in water.

22 3.3. Oxidation products and degradation pathway of AR 73

1	Based on the data from the adsorption experiment of raw CSAC, it is clearly that
2	the dye was oxidized by using MnOx@CSAC. To further identify and establish the
3	degradation intermediates and products of AR 73, the pH 3 treatment was analyzed by
4	GC-MS (Detailed results are presented in Figure S6-8 of the Supporting Information).
5	Figure S9 shows that the intermediates and products were mostly acetic acid (1),
6	propionic acid (2), butyric acid (3), pentanoic acids (4), phthalic acid (5) and
7	4-(diphenyldiazenyl) phenol (6). The results indicated that the most detectable
8	degradation products were mainly low-molecular-weight organic acids, which are
9	known to be biologically degradable.
10	Based on the degradation products identified from the GC-MS analysis, a
11	reaction pathway scheme for the degradation of AR 73 by $MnO_x@CSAC$ is proposed
12	in Figure 5. First, electron transfer from the phenolic group of AR 73 to
13	$MnO_x@CSAC$ generates a phenoxy radical, which undergoes resonance
14	rearrangement and additional electron transfer to generate a carbocation on the C-1
15	carbon of the naphthol ring. Subsequently, nucleophilic attack by H ₂ O generates an
16	unstable tetrahedral complex, which breaks down to produce
17	1-(4-diazenylphenyl)-2-phenyldiazene and 1,2-naphthoquinone. One-electron
18	oxidation of 1-(4-diazenylphenyl)-2-phenyldiazene, an unstable intermediate product,
19	by O ₂ yields a 1-(4-diazenylphenyl)-2-phenyldiazene radical. Since this radical is also
20	unstable, it cleaves to produce a 1,2-diphenyldiazene radical and N_2 [29]. The
21	1,2-diphenyldiazene radical can undergo further oxidation followed by nucleophilic
22	attack by H ₂ O to generate 4-(diphenyldiazenyl) phenol. Another degradation pathway

is from 1,2-naphthoquinone to phthalic acid [30], which is also determined by GC-MS,
but not a final degradation product. Some of them can be further oxidized to
low-molecular-weight organic acids. This reaction mechanism suggests the
asymmetric cleavage of the azo bond [10].

5 *3.4. Oxidative degradation of other anionic dyes*

It is well known that different chemical structures with different functional 6 groups directly impact the degradation behaviors of dyes [31, 32]. The same reaction 7 8 conditions used for AR 73 were applied to the removal of a variety of other anionic dyes. Acid dyes, including C. I. Acid Red 1 (AR 1), C. I. Acid Blue 1 (AB 1), C. I. 9 Acid Blue 25 (AB 25), C. I. Acid Blue 40 (AB 40), C. I. Acid Blue 62 (AB 62) and C. 10 I. Acid Blue 193 (AB 193), as well as reactive dyes, including C. I. Reactive Red 11 11 (RR11), C. I. Reactive Blue 194 (RB 194) and C. I. Reactive Blue 74 (RB 74), were 12 13 chosen as typical dye pollutants. The removal rates of the nine dyes after reaction with 14 $MnO_x@CSAC$ for 10 minutes are presented in Table 1. The result suggested that the $MnO_x @CSAC$ could degrade both the acid and reactive dyes at pH 3. The anionic 15 dyes AR 1, AB 25, AB 40, AB 62, AB 193, RR 11 and RB74 all showed almost 16 17 complete degradation (>90%) after reaction with MnO_x@CSAC for 10 minutes. These nine dyes have different chemical structures with different functional groups 18 19 that influence the reactivity of the molecules in oxidative degradation processes.

20 *3.5. Stability test*

The stability is an important property for an effective oxidant in effluent treatment technologies. To evaluate the longevity of the oxidative degradation of

1	MnO _x @CSAC, it was examined through the recycling potential with 100 mL of dye
2	solution at 50 mg/L. At the first cycle use, the degradation rate of AR 73 using
3	MnO _x @CSAC was almost 100% after 10 minutes. However, some loss of Mn in the
4	remnant solution was observed (Figure 6a). In this particular case, we performed
5	synchrotron-based scanning transmission X-ray microscopy (STXM) imaging
6	analysis to determine Mn distribution on the MnOx@CSAC before and after reaction
7	(Figure 6b, 6c). This analysis suggested that MnO_x was successfully deposited on
8	both the surface and pores of the mesoporous CSAC treated by hydrothermal method,
9	but there was a slightly decrease of Mn from MnOx@CSAC sample. To determine the
10	contribution of adsorption by $MnO_x@CSAC$, the adsorption isotherms of the raw
11	CSAC were investigated. It can be observed from Figure 7a that the Langmuir
12	isotherm fits best with the experimental data (correlation coefficient $R^2=0.9906$),
13	while the low correlation coefficients ($R^2=0.8360$) show less agreement of Freundlich
14	isotherm with the experimental data. The adsorption capacity of the raw CSAC was
15	found to be 62.89 mg/g according to the fitted parameter of Langmuir equation
16	(Figure 7b). Therefore, under the above mentioned conditions, the raw CSAC
17	theoretically need to be reused thirteen continuous cycles to reach its maximum
18	adsorption capacity. Therefore, in order to determine the stability of MnOx@CSAC
19	and the oxidation degradation of AR 73 dye, the twenty continuous cycles of
20	MnO _x @CSAC were investigated (Figure 8). It is found that the oxidative degradation
21	of AR 73 by MnOx@CSAC was still strong after twenty usage cycles, with a
22	maximum removal rate of 99.1% and a minimum removal rate of 89.7% from the

1 same sample. The results indicated that the oxidation activity of the $MnO_x@CSAC$

2 was relatively stable and efficient.

3 4. Conclusions

In this study, a facile and convenient method was proposed for the in situ 4 synthesis of nanostructured MnOx on raw CSAC. MnOx@CSAC obtained via a 5 hydrothermal method could efficiently and rapidly degrade AR 73 at pH 3 with a 6 maximum decolorization efficiency of 99.1% after just 10 minutes of contact. The 7 8 degradation intermediates and products were identified by GC-MS analysis. The MnO_x@CSAC also could efficiently degrade other anionic dyes. Additionally, after 9 10 twenty continuous cycles 89.7% decolorization was still being achieved illustrating the longevity of the $MnO_x@CSAC$ oxidative capacity. 11

12 Acknowledgments

The authors acknowledge financial support from Zhejiang University-Focused
Photonics United Foundation, Zhejiang Provincial Natural Science Foundation of
China under Grant No. LY12B07006 and Intercross-Science Research Seed
Foundation for the Youth Scholars of Zhejiang University.

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Dye	Removal Rate (%)	Pictures of Experiment
AR1	98.8	Control
RB194	72.0	المتكافية المتحدادي
RB74	98.2	
AB40	95.4	
AB62	99.7	MnO _x @CSAC
AB193	96.8	
AB25	90.1	
AB1	79.4	
RR11	92.0	

Table 1Degradation efficiencies of common anionic dyes

The initial concentration of anionic dyes is 50 mg/L, volume is 10 mL, pH=3, T=25

°C, and the dosage of $MnO_x@CSAC$ is 0.01 g, and the reaction time is 10 minutes.

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Figure legends

Figure 1. (a) SEM image of the raw CSAC. (b) SEM image of $MnO_x@CSAC$ (the nanostructured MnO_x -loaded CSAC through a hydrothermal route). (c) SEM image of the HT-CSAC (the raw CSAC treated by a hydrothermal method). (d) TEM image of MnO_2 nanowires. (e) TEM image of the raw CSAC. (f) TEM image of $MnO_x@CSAC$: the green arrows designate the MnO_x nanowires.

Figure 2. XRD patterns of the raw CSAC, MnO₂ and MnO_x@CSAC.

Figure 3. Decolorization of AR 73 with different materials (Initial concentration 50 mg/L, 10 mL, pH 3, T=25 °C, product dosage 0.01 g, including MnO_x@CSAC: the nanostructured MnO_x-loaded CSAC by a hydrothermal method; N₂-MnO_x@CSAC: the MnO_x-loaded CSAC by calcination under a nitrogen atmosphere; Air-MnO_x@CSAC: the MnO_x-loaded CSAC by calcination under an air atmosphere; N₂-CSAC obtained by calcination under a nitrogen atmosphere).

Figure 4. (a) pH sensitivity of $MnO_x@CSAC$ (Initial concentration 50 mg/L, 100 mL, T=25 °C, the $MnO_x@CSAC$ dosage 0.1 g). (b) UV-Vis spectra of $MnO_x@CSAC$ in pH 3 treatment. (c) pH sensitivity of the raw CSAC (Initial concentration 50 mg/L, 100 mL, T=25 °C, the raw CSAC dosage 0.1 g).

Figure 5. Proposed pathway of AR 73 degradation under MnO_x@CSAC system.

Figure 6. (a) Soluble Mn measured for pH 3 after 10 minutes in the decolorized dye and blank solutions. (b) The qualitative distribution of Mn in $MnO_x@CSAC$ before reaction in a STXM image. (c) The qualitative distribution of Mn in $MnO_x@CSAC$

after reaction in a STXM image.

Figure 7. (a) Adsorption isotherms fitted to Langmuir model and Freundlich model

for the raw CSAC. (b) The linear fitting curve of Langmuir model for the raw CSAC.

Figure 8. Degradation of AR 73 in the recycle experiment (Initial concentration 50

mg/L, 10 mL, pH 3, T=25 °C, MnO_x@CSAC dosage 0.01 g)

A certain and a certain a



Figure 1



Figure 2



Figure 3



Figure 4





Figure 6



Figure 7



Figure 8

Nano-MnO_x on activated carbon prepared by hydrothermal process for fast and highly efficient degradation of azo dyes

Lili Xu, Xingfa Li, Yuezhong Wen, Jianqing Ma, Weiping Liu

By facile and green hydrothermal method, a novel, low-cost and highly active nano- MnO_x on activated carbon was prepared for the fast and highly efficient removal of azo dyes from wastewater.

