SCIENTIFIC REPORTS

OPEN

One-pot synthesis of purple benzene-derived MnO_2 -carbon hybrids and synergistic enhancement for the removal of cationic dyes

Hyemin Kim¹ & Nagahiro Saito^{1,2}

MnO_2 -carbon hybrid (MnO_2 -C-PBz) was simultaneously synthesized by a one-step solution plasma process (SPP) using a single precursor referred to as “purple benzene”, which was derived from the K^+ (dicyclohexano-18-crown-6 ether) complex. To clarify the synergistic effects on the cationic dye removal, MnO_2 -free carbon and carbon-free MnO_2 samples were concurrently investigated. The results of adsorption for cationic dyes (methylene blue (MB) and rhodamine B (Rh B)) and anionic dye (methyl orange (MO)) revealed remarkably high affinity for cationic dyes. In particular, MnO_2 -C-PBz exhibited the highest adsorption capacity for MB, i.e., ~3 times greater than that of the others. In addition, MnO_2 -C-PBz exhibited a rapid, high decolorization ability at $C_0 = 10 \text{ mg L}^{-1}$ (within a few seconds, ~99%) and at $C_0 = 100 \text{ mg L}^{-1}$ (within 30 min, ~81%), and the theoretical maximum monolayer adsorption capacity was 357.14 mg g^{-1} as calculated from the Langmuir adsorption isotherm equation. Furthermore, compared with carbon-free MnO_2 , MnO_2 -C-PBz exhibited quite a good cyclic stability. We expect that our findings give rise to the understanding of the synergistic effects of MnO_2 -carbon hybrid, as well as role of each components for the cationic dye adsorption, and may open an innovative synthesis approach to inorganic-organic hybrid materials.

With the growth in the population and development of industries, there has been a considerable increase in the manufacture of food and products (including textiles, plastics, paper, and synthetic dyes), generating a large amount of effluent^{1,2}. The treatment of wastewater containing toxic heavy metals (e.g., Hg, Cd, Pb, and As) and various organic substances (e.g., dyestuffs, pesticides, and hydrocarbons), which threaten the health of humans and animals, has generated considerable concern^{3,4}. Among the different methods for the treatment of wastewater, adsorption has been attracting immense attention for its simplicity, cost-effectiveness, and reliability^{3,5}. Hence, extensive studies have been focused on the search for efficient adsorbents.

Among the different adsorbents available, recently, manganese dioxide (MnO_2) has been considered to be an effective adsorbent because of its environmental benignity, abundance, and cost-effectiveness^{6,7}. In particular, MnO_2 is highly suitable for the adsorption of cationic pollutants such as heavy metals and methylene blue (MB) because it exhibits a negatively charged surface over a wide range of pH (particularly high pH)^{8,9}. However, metal nanoparticle based adsorbent often limit a stability and reusability. The presence of various compounds in an aquatic environment, including ions, inorganic and organic pollutants, is known to lead to the self-aggregation of MnO_2 nanoparticles, thereby reducing the available active sites^{10–13}. To solve these issues, numerous studies have reported the formation of hybrid materials by the combination of various materials.

Recently, carbon materials (e.g., activated carbon (AC)^{14,15}, carbon nanotubes (CNTs)¹⁶, graphene¹⁷, graphene oxide¹⁸, and mesoporous carbon¹⁹) have been combined with various inorganic compounds (e.g., mesoporous silica^{15,20}, metal oxides²¹, and polymers²²) to enhance the adsorption performance and stability because of their high surface area, good conductivity, and thermal and mechanical stabilities. Meanwhile, the typical method

¹Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan. ²CREST-JST, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan. Correspondence and requests for materials should be addressed to N.S. (email: hiro@rd.numse.nagoya-u.ac.jp)

Figure 1. (a) XRD patterns, (b) Raman spectra, (c) N₂ adsorption/desorption isotherms and hysteresis loop (inset), and (d) pore size distributions of C-Bz, C-CE-Bz, and MnO₂-C-PBz.

to prepare MnO₂-carbon hybrid materials involves multi-step processes and a long processing time: (i) surface modification of carbon (e.g., CNTs and AC) by treatment in a strong acid, followed by (ii) deposition of MnO₂ on the carbon surface by an aging process (e.g., refluxing, water-bath heating, and hydrothermal aging) for several hours under relatively high-temperature conditions^{23–26}.

In our previous studies, nanostructured MnO₂ has been successfully synthesized by the application of plasma, referred to as the “solution plasma process (SPP),” in a potassium permanganate aqueous solution without any additional chemical agents²⁷ and with environmentally benign chemicals, i.e., sugar²⁸. In addition, various carbon-based materials^{29–31} have been synthesized by a single-step SPP from organic solvents, such as benzene, toluene, or pyridine, under ambient temperature and pressure within several minutes.

In this study, based on this background, inorganic oxide-organic carbon hybrid materials (i.e., the MnO₂-carbon hybrid) were synthesized by a single-step SPP. For the simultaneous synthesis of MnO₂-carbon hybrids, benzene and KMnO₄ were selected as the carbon and MnO₂ precursors, respectively, and dicyclohexano-18-crown-6 ether (hereafter referred to as DCH18C6) was used as the main chemical for preparing the single precursor, referred to as “purple benzene.” DCH18C6 is used because of its high solubility in benzene, related to its hydrophilic (interior) and hydrophobic (exterior) properties; particularly, it exhibits a high affinity for potassium ions (K⁺) because of its size selectivity for guest cations^{32–35}. Hence, MnO₄[−] is forcibly dissolved in benzene via the formation of a K⁺(DCH18C6) complex, affording “purple benzene” as the single precursor^{36–38}.

The adsorption studies were evaluated with cationic dyes, i.e., MB and Rh B. To clarify the synergistic effects on the enhancement of the dye removal ability, of the MnO₂-carbon hybrid, two types of MnO₂-free carbon-based samples, synthesized from benzene and crown-ether-added benzene, respectively, were also investigated. In addition, the potential of the MnO₂-carbon hybrid in comparison to carbon-free MnO₂ as a reusable adsorbent was investigated by recyclability tests. Furthermore, to better understand adsorption phenomena, adsorption kinetics and isotherms were also examined.

Results and Discussion

The MnO₂-carbon hybrid (MnO₂-C-PBz) was successfully synthesized from purple benzene by SPP. To verify the effects of crown ethers or KMnO₄, reference samples, i.e., C-Bz and C-CE-Bz, were also prepared as described in the experimental section. From the XRD data (Fig. 1(a)), broad peaks at 2θ = ~23.7° and ~43.7°, corresponding to the 002 and 100/101 planes of graphitic carbon, were observed for all samples³⁹. C-Bz and C-CE-Bz exhibited almost the same XRD patterns, but the (002) peak of C-CE-Bz was slightly shifted toward a lower angle

Samples	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore size (nm)
C-Bz	148.67	1.57	42.18
C-CE-Bz	169.56	1.78	42.04
MnO ₂ -C-PBz	77.30	0.72	37.30

Table 1. Physical properties of SPP-synthesized adsorbents, C-Bz, C-CE-Bz, and MnO₂-C-PBz.

at $2\theta = \sim 23.4^\circ$. Crown ethers and/or decomposed oxygen-containing by-products are considered to be embedded in the carbon matrix. In contrast, compared with C-Bz and C-CE-Bz, MnO₂-C-PBz exhibited considerably weaker and broader peaks. In addition, new peaks at around $2\theta = 12.9^\circ$, 25.8° , 35.4° , and 66.1° were observed for MnO₂-C-PBz (inset: magnified XRD pattern). These peaks corresponded to potassium birnessite-type MnO₂ (JCPDS# 80-1098)⁴⁰. These results indicate the possibility that MnO₂ is formed and distributed on the surface of the carbon matrix. This can be deduced from the XRD results of MnO₂/C-Bz prepared by dispersing C-Bz in aqueous KMnO₄ solution (see supplementary information; Fig. S1[†]). The formation of the MnO₂-carbon hybrid was further confirmed by Raman spectroscopy. Two strong peaks corresponding to the D- and G-bands were observed at 1338 and 1588 cm^{-1} , respectively, for all samples, indicating the presence of carbon material (Fig. 1(b))⁴¹. Clear peaks were observed at 576 and 645 cm^{-1} , corresponding to the Mn-O stretching vibration in the MnO₆ octahedral layer and the symmetric stretching vibration in the MnO₆ octahedral framework, respectively⁴². These results confirmed the successful synthesis of the MnO₂-carbon hybrid by a single-step SPP.

The surface area and pore structure of the adsorbents were characterized by N₂ adsorption-desorption isotherm analysis. All samples exhibited type IV isotherms and a typical hysteresis loop of mesoporous materials (inset in Fig. 1(c))⁴³. The specific surface area (SSA_{BET}) values for C-Bz, C-CE-Bz, and MnO₂-C-PBz were 148.67, 169.56, and 77.3 $\text{m}^2 \text{g}^{-1}$, respectively. With the addition of crown ether (i.e., C-CE-Bz), SSA_{BET} slightly increased, whereas with the addition of KMnO₄ (i.e., MnO₂-C-PBz), it considerably decreased. Figure 1(d) shows the pore size distributions. All samples exhibited a hierarchical porous structure with mesopores or macropores ranging between ~ 5 and 100 nm. The total pore volume and average pore size of C-Bz and C-CE-Bz were similar, whereas considerably lower values were observed for MnO₂-C-PBz (Table 1). The effects of physical properties on adsorption capacity will be discussed in the section on adsorption studies.

XPS analysis was carried out to investigate the surface elemental composition of the products and the oxidation state of manganese in MnO₂-C-PBz. In comparison with MnO₂-free samples (i.e., C-Bz and C-CE-Bz), Mn, O, and K were observed for MnO₂-C-PBz (Fig. 2(a,b)), which clearly indicates that the MnO₂-carbon hybrid is successfully synthesized by SPP. Figure 2(c) shows the high-resolution XPS spectra of Mn 2p and Mn 3s. Two major peaks were observed at 653.74 and 642.07 eV, corresponding to the Mn 2p_{1/2} and Mn 2p_{3/2}, respectively, and a peak separation (ΔE) value of 11.67 eV was in good agreement with literature values^{44,45}. As shown in the bottom side of Fig. 2(c), the ΔE for Mn 3s was 5.09 eV, indicative of a mixture of trivalent (Mn³⁺) and tetravalent (Mn⁴⁺) states^{46,47}. This result is in agreement with the as described deconvolution peaks observed in the Mn 2p_{3/2} spectrum, which showed a mixture of Mn⁴⁺, Mn³⁺, and Mn²⁺. The O 1s spectra (Fig. 2(d)) provided clear evidence for the formation of MnO₂ because binding energy of metal oxide is different from those of the other oxygen species⁴⁸. Compared with MnO₂-free C-Bz and C-CE-Bz samples, MnO₂-C-PBz exhibited new peaks at around 531–529 eV. Two strong peaks were observed at binding energy values of 529.8 and 531.3 eV, corresponding to oxygen species in the MnO₂ lattice (O_{latt}, Mn-O-Mn) and adsorbed oxygen species (O_{ads}, Mn-OH), respectively⁴⁹.

FE-SEM and TEM were used to examine C-Bz, C-CE-Bz, and MnO₂-C-PBz. C-Bz exhibited relatively uniform spherical particles with a size of ~ 20 nm (Fig. 3(a,d)), and C-CE-Bz exhibited a slightly larger particle size of ~ 50 nm (Fig. 3(b,e)). On the contrary, MnO₂-C-PBz exhibited non-uniform flat particles in a wide particle size range from tens to hundreds of nanometers (Fig. 3(c,f)). The selected-area electron diffraction (SAED) patterns of samples (Fig. 3(d–f) inset images) exhibited three broad diffuse rings, corresponding to the 002, 100/101, and 110 planes of carbon materials from the inside diffraction ring, respectively⁵⁰. C-Bz and C-CE-Bz exhibited almost identical diffraction patterns, whereas MnO₂-C-PBz showed a weaker, broader diffraction pattern without any distinct diffraction patterns of MnO₂. This result indicated that amorphous MnO₂ is formed and loaded on the carbon surface, as evidenced from the weaker, broader SAED pattern compared with those of C-Bz and C-CE-Bz as well as the XRD results. In addition, the EDS spectrum (Fig. 3(g)) and elemental mapping results (Fig. 3(h)) clearly indicated that C, O, and Mn are present and that Mn and O are uniformly dispersed in MnO₂-C-PBz.

To observe the adsorption of MO and MB (pH = 6.5 ± 0.5) on the as-prepared samples, adsorption tests were carried out in MO and MB stock solutions. The adsorption behavior of MO and MB was clearly different (Fig. 4(a)). All samples exhibited a higher adsorption capacity for MB than MO, indicating that the as-synthesized samples are suitable for the adsorption of cationic dye molecules. Notably, (i) C-Bz and (ii) C-CE-Bz exhibited higher adsorption capacities than (iii) MnO₂-C-PBz in an MO solution, whereas the opposite tendency was observed in an MB solution. In particular, despite the fact that the SSA_{BET} values of C-Bz and C-CE-Bz were greater than that of MnO₂-C-PBz, MnO₂-C-PBz exhibited around three times higher adsorption capacity than the other samples, i.e., (i) C-Bz, 49.31 mg g^{-1} , (ii) C-CE-Bz, 54.04 mg g^{-1} , and (iii) MnO₂-C-PBz, 156.43 mg g^{-1} , under the same conditions for the MB solution. In addition, to investigate the effect of MnO₂ in the hybrid products, MB adsorption experiments were carried out using (iv) MnO₂-SP (synthesized by the same method, i.e., SPP²⁸, see supplementary information; Table S1[†]) and (v) commercial MnO₂. Compared with (iv) MnO₂-SP and (v) commercial MnO₂, the MnO₂-carbon hybrid exhibited higher adsorption capacity (Fig. 4(a)). The excellent adsorption ability of the MnO₂-carbon hybrid was clearly demonstrated by UV-visible spectra and MB dye

Figure 2. (a) XPS survey spectra and (b) XPS surface chemical composition of the as-prepared samples. High-resolution XPS spectra of (c) Mn 2p (upper side) and Mn 3s (bottom side) of MnO₂-C-PBz, and (d) O 1s of all samples.

solution color (inset image in Fig. 4(b)) after equilibrium adsorption (Fig. 4(b)). Additionally, Rh B adsorption behavior of MnO₂-carbon hybrid also exhibited good adsorption capacity and removal efficiency compared with anionic dye MO (see supplementary information; Fig. S2[†]). Therefore, these results suggest that the as-synthesized MnO₂-carbon hybrid is suitable for the removal of cationic dyes; particularly, the adsorption ability is enhanced using a hybrid with carbon materials. The adsorption behavior and effects of MnO₂ and carbon are investigated in detail in the following section on adsorption and isotherm studies.

Based on the above results, the adsorption ability of MnO₂-C-PBz with the best adsorption characteristics was investigated in detail. The dependence of MnO₂-C-PBz adsorption capacity on initial MB concentrations was evaluated to confirm the efficacy of the adsorbent. With the increase in initial MB concentrations from 10 to 300 mg L⁻¹, the adsorption capacity of MnO₂-C-PBz increased from 32.58 to 230.86 mg g⁻¹, whereas the dye removal efficiency decreased (Fig. 5(a)). The removal efficiency was observed to be greater than ~93% up to C₀ = 100 mg L⁻¹, and it dramatically decreased to ~33.5% at C₀ = 200 mg L⁻¹ and to ~22.3% at C₀ = 300 mg L⁻¹. In addition, with the immediate addition of a significantly low initial concentration (C₀ = 10 mg L⁻¹) of MnO₂-C-PBz, MB was rapidly removed within 10 s (~99%); hence, adsorption experiments are carried out at high concentrations of greater than 25 mg L⁻¹ to confirm the dependence of time on adsorption behavior. Removal efficiencies of greater than ~97% and ~92% within 10 min were observed for C₀ values of 25 and 50 mg L⁻¹, respectively, and a removal efficiency of greater than ~81% at a C₀ of 100 mg L⁻¹ was observed within 30 min (Fig. 5(b)). Moreover, MB was effectively decolorized. As can be observed in the inset images of Fig. 5(b), the blue solution color clearly disappeared at a low initial MB concentration (25 mg L⁻¹), indicative of the effective decolorization ability of MnO₂-C-PBz. Although the blue color did not completely disappear at higher initial concentrations (i.e., 50 and 100 mg L⁻¹), considerable decolorization was observed by comparison of the initial MB solution color. Thus far, the results indicate that MnO₂-C-PBz possesses the highly fast and effective MB removal abilities.

The effects of pH were investigated because solution pH is an important factor affecting the adsorption of dye molecules in an aqueous system. With the increase in pH from 2 to 12, the adsorption capacity of MnO₂-C-PBz for MB increased from around 111.6 to 151.8 mg g⁻¹ (Fig. 6). Murray⁸ and Fendorf *et al.*⁹ independently investigated the pH of the zero point of charge of MnO₂ (especially δ -phase MnO₂), which was verified to be around ~2.4 and 2.7. These values indicated that MnO₂ is negatively charged over a wide range of pH (pH > ~3). The MnO₂-C-PBz surface apparently became more negatively charged with increasing solution pH.

Figure 3. (a–c) FE-SEM images at 100 K magnification. (d–f) TEM images and SAED patterns (inset) of C-Bz (left), C-CE-Bz (middle), and MnO₂-C-PBz (right). (g) EDX spectra and (h) elemental maps of C, O, and Mn of MnO₂-C-PBz.

Figure 4. (a) Comparison of the equilibrium adsorption capacities of (i) C-Bz, (ii) C-CE-Bz, (iii) MnO₂-C-PBz, (iv) MnO₂-SP, and (v) commercial MnO₂ for the anionic dye (MO) and the cationic dye (MB). (b) UV-visible spectra and the MB dye solution after adsorption using each sample (inset images) (297 K, 0.6 g L⁻¹ of adsorbent, and natural pH (6.5 ± 0.5)).

Figure 5. (a) Adsorption capacity (bar graph) and removal efficiency (—□—) of MnO₂-C-PBz at different initial MB concentrations (C₀ = 10, 25, 100, 200, and 300 mg L⁻¹) at equilibrium. (b) Dependence of time on MB removal efficiency (C₀ = 25, 50, and 100 mg L⁻¹) and digital photographs (inset) showing the decolorization of MB by MnO₂-C-PBz (297 K, 0.6 g L⁻¹ of adsorbent, and natural pH (6.5 ± 0.5)).

Figure 6. Adsorption capacity of MnO₂-C-PBz at different pH values from 2 to 12 (297 K and 0.6 g L⁻¹ of adsorbent).

The adsorption mechanism in hybrid nanocomposite system, various interactions between adsorbent and adsorbate might have possibility to contribute adsorption capability. The possible interactions between MnO₂-carbon hybrid and MB molecules can be summarized as follows; (i) MnO₂: the strong electrostatic forces of attractions between negatively charged MnO₂ and positively charged MB⁺, (ii) π - π stacking interactions between bulk π -system of sp²-carbon and C=C or aromatic ring of MB molecules, and (iii) hydrogen bonding between oxygen-containing functional groups in carbon moieties derived from crown ether-containing precursor and MB molecules. Among these mechanism, we regard that electrostatic forces of attraction are main adsorption mechanism in our hybrid system based on the results of adsorption capability (Fig. 4) and pH-dependent of MB adsorption behavior (Fig. 6).

Three initial concentrations of dye solution, 25, 50, and 100 mg L⁻¹, respectively, were selected to investigate the dependence of adsorption capacity on contact time. The equilibrium adsorption capacity increased with increase in the initial concentration (Fig. 7(a)). Rapid adsorption occurred at the initial stage (~10 min) and then attained equilibrium gradually. This result is related to the presence of a large number of active sites at the start of adsorption, followed by the decrease in the number of available active sites. To better understand the adsorption of MB on MnO₂-C-PBz, adsorption kinetics was further examined. The obtained experimental kinetic data were fitted by the linear forms of two kinetic models: the pseudo-first-order (PFO, eq. (1)) and pseudo-second-order (PSO, eq. (2)) models, respectively^{51,52}. These two linear forms can be described by eqs (1) and (2), respectively:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (1)$$

Figure 7. (a) Adsorption capacity as a function of contact time using the (b) pseudo-first-order, (c) pseudo-second-order, and (d) intraparticle diffusion models proposed by Weber and Morris for the adsorption of MB on $\text{MnO}_2\text{-C-PBz}$ at different initial concentrations (297 K, $C_0 = 25, 50$, and 100 mg L^{-1} , 0.6 g L^{-1} of adsorbent, and natural pH (6.5 ± 0.5)).

Experimental data		PFO model			PSO model			
$C_0 \text{ (mg L}^{-1}\text{)}$	$q_{e,exp} \text{ (mg g}^{-1}\text{)}$	$q_{e,cal} \text{ (mg g}^{-1}\text{)}$	$k_1 \text{ (min}^{-1}\text{)}$	R^2	$q_{e,cal} \text{ (mg g}^{-1}\text{)}$	$k_2 \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	$h \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	R^2
25	40.63	1.01	0.03938	0.6938	40.65	0.15925	263.1483	0.9999
50	81.07	10.15	0.04813	0.9532	81.30	0.02073	137.0189	0.9999
100	156.43	53.04	0.00299	0.8945	156.25	0.00186	45.4106	0.9997

Table 2. Parameters of the PFO and PSO kinetic models for the adsorption of MB on $\text{MnO}_2\text{-C-PBz}$.

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where q_e and q_t represent the adsorption capacities (mg g^{-1}) at equilibrium and contact time (t , min), respectively, and $k_1 \text{ (min}^{-1}\text{)}$ and $k_2 \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$ are the equilibrium rate constants for the PFO and PSO models, respectively. k_1 was determined from the slope of $\log(q_e - q_t)$ vs. t (Fig. 7(b)) obtained from the linear plots fitted using eq. (1), and k_2 and q_e were determined from the slope and intercept of t/q_t vs. t (see Fig. 7(c)) obtained from the linear plots fitted using eq. (2). In addition, the initial ($t \rightarrow 0$) adsorption rate $h \text{ (mg g}^{-1} \text{ min}^{-1}\text{)}$ was calculated by eq. (3)⁵¹:

$$h = k_2 q_e^2 \quad (3)$$

As summarized in Table 2, the correlation coefficient (R^2) values clearly indicated that the adsorption of MB on $\text{MnO}_2\text{-C-PBz}$ follows the PSO model ($R^2 > 0.9997$) compared with the PFO model ($R^2 > 0.6938$). The calculated values for the equilibrium adsorption capacity ($q_{e,cal}$) from the PSO model were 40.65, 81.30, and 156.25 mg g^{-1} at $C_0 = 25, 50$, and 100 mg L^{-1} , respectively. These values are almost same as those obtained from experiments ($q_{e,exp}$). This result indicates that the adsorption of $\text{MnO}_2\text{-C-PBz}$ follows the PSO model, with the rate-limiting step involving chemisorption between the adsorbate and adsorbent⁵². Therefore, the adsorption

Langmuir adsorption isotherm model		Freundlich adsorption isotherm model	
$q_{max,cal}$ (mg g ⁻¹)	357.14	$1/n$	0.6516
b (L mg ⁻¹)	0.4078	K_F	6.4353
R_L	0.00811–0.19693	R^2	0.9607
R^2	0.9104		

Table 3. Parameters for the Langmuir and Freundlich adsorption isotherm models for the adsorption of MB on MnO₂-C-PBz.

capacity of MnO₂-C-PBz is considered to be greater than those of the other reference samples (i.e., C-Bz and C-CE-Bz) despite its lower surface area (C-Bz: 148.67 m² g⁻¹; C-CE-Bz: 169.56 m² g⁻¹; MnO₂-C-PBz: 77.3 m² g⁻¹). In addition, the k_2 and h values decreased with the increase in initial MB concentrations, indicating that adsorption reaches a plateau more rapidly at a low initial concentration⁵³. However, it is difficult to determine the diffusion mechanism using only two previous kinetic models; hence, the linear form of the intraparticle diffusion kinetic model (proposed by Weber and Morris)⁵⁴ was also applied at different initial MB concentrations to further investigate sorption using the following equation:

$$q_t = k_{ip} t^{1/2} + C \quad (4)$$

The data obtained from eq. (4) exhibited two linear portions (Fig. 7(d)), indicating that adsorption can be described by a two-stage process: (i) the external surface adsorption stage, i.e., mass transfer through boundary-layer diffusion, and (ii) the gradual sorption stage, i.e., intraparticle diffusion⁵⁵. k_{ip} represents the adsorption rate (mg g⁻¹ min^{-1/2}), and C (mg g⁻¹) is the value related to boundary thickness. Steep slopes were observed at the initial portion, and plateau slopes were observed at the second stage (Fig. 7(d)). Initially, rapid adsorption was observed, which slowly attained equilibrium. This result suggests that the adsorption of MB on MnO₂-C-PBz is controlled by external surface adsorption, followed by intraparticle diffusion⁵⁶. In addition, the rate constants (k_{ip}) increased with the increase in initial MB concentrations (k_{ip} : 9.05 (at 25 mg L⁻¹) < 12.60 (at 50 mg L⁻¹) < 15.45 (at 100 mg L⁻¹)) because a high initial MB concentration provides a high driving force to overcome the mass-transfer resistance of MB between the aqueous and solid phases, leading to a high rate for the adsorption of MB molecules on the MnO₂-C-PBz adsorbent⁵⁷.

The study of adsorption isotherms can provide insights into adsorption behavior, and efficient adsorbents can be designed on the basis of the obtained parameters. Hence, equilibrium adsorption data are analyzed using the linear form of the Langmuir adsorption isotherm model, which is based on the hypothesis of monolayer adsorption using a homogeneous adsorbent surface, and the Freundlich adsorption isotherm model, which is based on the hypothesis of multilayer adsorption on a heterogeneous adsorbent surface⁵⁸. The linear form of the Langmuir adsorption isotherm model is described as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_e} \quad (5)$$

where C_e , q_e , and q_{max} represent the concentrations of the dye solution at equilibrium (mg L⁻¹), adsorption capacity at equilibrium (mg g⁻¹), and the theoretical maximum monolayer adsorption capacity of the adsorbent (mg g⁻¹), respectively, and b is the Langmuir constant (L mg⁻¹). The q_{max} and b values were determined from the slope and intercept of the linear fitted plot of C_e/q_e vs. C_e (Fig. S3(a)[†]). Furthermore, the separation factor R_L (also known as the equilibrium parameter), providing information about the favorability of adsorption in the adsorbate/adsorbent system, was calculated using eq. (6)⁵⁹:

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

R_L represents the shape of the isotherm: (i) $R_L > 1$ (unfavorable), (ii) $R_L = 1$ (linear), (iii) $0 < R_L < 1$ (favorable), and (iv) $R_L = 0$ (irreversible)^{59,60}.

The linear form of the Freundlich isotherm model is described as follows⁶¹:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \quad (7)$$

where K_F is the Freundlich constant (mg g⁻¹), related to the adsorption capacity, and $1/n$ is the heterogeneity parameter: (i) $1/n < 1$ (favorable, heterogeneous adsorption) and (ii) $1/n > 1$ (unfavorable)⁶². These factors can be used to describe the multilayer adsorption on a heterogeneous adsorbent surface^{58,62}.

Table 3 shows the calculated isotherm parameters from the linear forms of the Langmuir and Freundlich adsorption models and fitted lines presents in Fig. S3(b)[†]. The high R^2 values indicate that the two models successfully explain the favorable adsorption of MB on MnO₂-C-PBz. The theoretical maximum monolayer adsorption capacity (q_{max}) was 357.14 mg g⁻¹ as calculated from the Langmuir adsorption isotherm model. Compared with various adsorbents, including carbon, metal oxide, and metal-oxide-carbon hybrid adsorbents reported in literatures as shown in Table S2, MnO₂-C-PBz exhibited a significantly high adsorption capacity. In particular, our MnO₂-C-PBz showed very high adsorption capacity for MB compared with other similar metal oxide-carbon

Figure 8. Reusability tests of MnO₂-C-PBz and MnO₂-SP for the removal of MB (bar graph = adsorption capacity (mg g⁻¹), symbol-line graph = removal efficiency (%), C₀ = 100 mg L⁻¹, adsorbent dosage = 0.6 g L⁻¹, and contact time = 180 min).

hybrid adsorbents, suggesting that it could be a promising adsorbent for application of cationic pollutants removal. The R_L values (0.00811–0.19693) in the range of 0–1 (Table 3) indicated the favorable adsorption of MB on MnO₂-C-PBz. In addition, a higher correlation coefficient for the Freundlich model ($R^2 = 0.9607 > 0.9104$) indicated that the adsorption of MB on MnO₂-C-PBz is not restricted only to monolayer adsorption⁶². A $1/n$ value of 0.6516 reflected that the adsorption of MB is favorable on the heterogeneous sites of MnO₂-C-PBz.

To confirm the reusability of the MnO₂-carbon hybrid adsorbent, multi-recycle tests were performed and compared to the carbon-free MnO₂-SP synthesized by SPP. As can be seen in Fig. 8, in the first cycle, MnO₂-C-PBz and MnO₂-SP exhibited similar adsorption capacities (~149.66 and ~149.83 mg g⁻¹) and removal efficiencies (~89.78% and ~89.81%). In the second cycle, however, the removal efficiency of MnO₂-SP dramatically decreased from 89.8% to 49.2%, whereas that of MnO₂-C-PBz slightly decreased to around 0.49%. As the cycle repeats, the removal efficiency of MnO₂-SP gradually decreased, but that of MnO₂-C-PBz remained stable. Consequently, after seven cycles, the MnO₂-C-PBz still maintained considerable dye removal performance and stability as compared with those of MnO₂-SP. Although large SSA of MnO₂-SP provides high adsorption capacity and removal efficiency in the first cycle, MB molecules could be blocked in the micropores or small mesopores; therefore, the efficient desorption of MB molecules from the adsorbent does not occur. Meanwhile, MnO₂-C-PBz shows no obvious degrading after cycle tests (see Fig. S4[†]), which demonstrates immense potential for reusable adsorbent. From the results obtained thus far, the synergistic effects related to the presence of MnO₂ and the high stability of carbon for the removal of cationic dyes have been clearly confirmed.

Conclusion

In this study, we first report a one-pot synthesis of MnO₂-carbon hybrid (MnO₂-C-PBz) by applying plasma in single-precursor “purple benzene” derived from K⁺(DCH18C6) complex formation, and its performance for the adsorption of cationic dye (i.e., MB) was investigated. The MnO₂-C-PBz showed around 3 times greater adsorption capacity than those of MnO₂-free carbon (C-Bz and CE-Bz), and exhibited quite a good cyclic stability than carbon-free MnO₂ (MnO₂-SP). In addition, the adsorption kinetics and isotherm studies demonstrated that MnO₂-C-PBz is a heterogeneous adsorbent, which is accompanied by complex adsorption, with both chemisorption and physisorption. From the results obtained thus far, the MnO₂-carbon hybrid is an efficient and reusable adsorbent for the removal of cationic dyes, which attributed to adsorption properties of both MnO₂ and carbon. This finding will be useful for understanding the synergistic effects of the MnO₂-carbon hybrid for the adsorption of cationic dye and contributing an innovative single-step synthetic approach for inorganic oxide-organic carbon hybrid materials.

Methods

Chemicals and materials. Benzene (C₆H₆, >99.5% purity, Kanto Chemical Co., Inc., Japan) and potassium permanganate (KMnO₄, >99.3% purity, Wako Pure Chemical Industries Ltd., Japan) were selected as the carbon and manganese oxide precursors, respectively. DCH18C6 (C₂₀H₃₆O₆, >98.0%, Tokyo Chemical Industry Co., Ltd., Japan) was used as the main chemical agent for preparing purple benzene. Manganese(IV) oxide powder (85% purity, Kanto Chemical Co., Inc., Japan) was used as a commercial MnO₂ sample for comparing the dye removal performance with the as-prepared adsorbents. Ethanol (C₂H₅OH, >99.5%), hydrochloric acid (HCl, 35–37%), and a sodium hydroxide solution (NaOH, 48–50%) were purchased from Kanto Chemical Co., Inc., Japan. MB (C₁₆H₁₈ClN₃S·3H₂O, 98.5% purity, Kishida Chemical Co., Ltd., Japan), Rh B (C₂₈H₃₁ClN₂O₃, Guaranteed reagent, Wako Pure Chemical Industries Ltd., Japan) and MO (C₁₄H₁₄N₃NaO₃S, ACS reagent, dye content 85%, Sigma-Aldrich, Japan) were selected as typical cationic and anionic organic dyes. Distilled water was obtained from an Aquarius water distillation apparatus (RFD250NB, Advantec, Japan) with a resistivity of 18.2 MΩ cm at 25 °C. All chemicals were used without further purification.

Synthesis of the MnO₂-carbon hybrid by SPP. The MnO₂-carbon hybrid was successfully synthesized by a one-pot SPP in purple benzene derived from the K⁺ (DCH18C6) complex. Purple benzene was prepared as

Figure 9. Schematic for the synthesis of the MnO_2 -carbon hybrid from purple benzene by SPP: (a) benzene solvent, (b) dicyclohexano-18-crown-6 ether-added benzene, (c) purple benzene, and (d) MnO_2 -carbon hybrids synthesized from purple benzene by SPP.

follows (Fig. 9). DCH18C6 (50 mM) was added to benzene (100 mL). After vigorous stirring for a few minutes, KMnO_4 (5 mM) was added and sufficiently mixed until a homogeneous purple solution was obtained without the remaining solid KMnO_4 . As-prepared purple benzene was transferred into a glass reactor with a volume of 100 mL, consisting of a pair of tungsten electrodes ($\varnothing$ 1 mm, 99.5% purity, Nilaco, Japan) insulated with ceramic tubes and connected to a bipolar pulse power supply (Kurita, Japan) for generating plasma in the liquid-phase precursor. The plasma discharging conditions for frequency, pulse width, voltage, and gap distance of the metal electrode were maintained constant at 25 kHz, 0.8 μs , 1.4–1.6 kV, and 1 mm, respectively. Figure S5[†] shows the photograph of the purple benzene precursor and the schematic of the SP apparatus in detail. SP was allowed to proceed at ambient temperature and pressure for 10 min under constant stirring during operation to ensure a homogeneous chemical reaction. The resulting MnO_2 -carbon hybrid obtained from SPP was collected by vacuum filtration and rinsed several times with ethanol, followed by air drying in an oven at 85 °C for 12 h. The production rate of MnO_2 -carbon hybrid was approx. 20 mg min^{-1} in the purple benzene during discharging. In addition, to demonstrate the effect of the MnO_2 -carbon hybrid, reference samples were prepared from pure benzene and benzene with DCH18C6 ethers without KMnO_4 under the same SP conditions as stated above. The resulting products obtained using pure benzene, benzene with crown ether (DCH18C6), and purple benzene precursors were designated as C-Bz (carbon synthesized from benzene), C-CE-Bz (carbon synthesized from crown ether-benzene), and MnO_2 -C-PBz (MnO_2 -carbon hybrid synthesized from purple benzene), respectively.

Material characterization. The fabricated samples were characterized by X-ray diffraction (XRD, SmartLab, Rigaku Co., Ltd., Japan) with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation operating at 45 kV and 200 mA and by Raman spectroscopy (inVia Raman Microscope, Renishaw Co. Ltd., UK) with a solid-state laser operating at 532 nm to examine the structural features. N_2 adsorption/desorption isotherms were recorded on a BELSORP mini II analyzer (MicrotracBEL Corp.) at 77 K in liquid nitrogen to characterize the surface area and pore structure of the adsorbents. The specific surface area (SSA) was determined by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated from the Barrett–Joyner–Halenda analysis. Morphologies were observed by field-emission scanning electron microscopy (FE-SEM, S-4800, HITACHI High Technologies Co., Ltd., Japan) at an accelerating voltage of 10 kV and by transmission electron microscopy (TEM, JEM-2500SE, JEOL, Japan) at an accelerating voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDS) and elemental mapping images were obtained on an FE-SEM system equipped with an EDS system (EMAX Energy, Horiba Ltd., Japan). X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5000 VersaProbe II (ULVAC-PHI, Inc., Japan) with $\text{Mg K}\alpha$ radiation to examine the surface chemistry of materials.

Adsorption studies. Adsorption capacities for MB from aqueous solutions were analyzed by batch experiments. To observe the adsorption of anionic and cationic organic dyes on the as-prepared samples, MO, MB and Rh B were selected. Adsorption kinetic experiments were carried out under different conditions of initial dye concentration (10, 25, 50, 100, 200, and 300 mg L^{-1}), solution pH (2, 4, 6.5, 8, 10, and 12), and contact time

(0–240 min). The pH was adjusted using a 0.1 M HCl or 0.1 M NaOH solution, and adsorption experiments were carried out at room temperature (297 K) and under natural pH. The adsorbent dose was maintained constant at 0.6 g L^{-1} , and adsorption experiments were carried out in a 150 mL conical flask with 60 mg of the adsorbent and 100 mL of the dye stock solution. During the tests, the conical flasks were wrapped in aluminum foil to intercept surrounding light so as to minimize other effects. UV-visible spectroscopy (Shimadzu UV-3600, Japan) was utilized to determine dye removal efficiency and adsorption capacity. The solution was filtered using a $0.45 \text{ }\mu\text{m}$ membrane filter (PTFE, ADVANTEC, Japan) before characterization. The dye removal efficiency (R) and adsorption capacity at equilibrium (q_e) were evaluated from the UV-visible spectra using the following equations:

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (8)$$

$$q_e = \frac{(C_0 - C_e)}{W} \times V \quad (9)$$

where C_0 , C_t , and C_e represent initial dye concentration, dye concentration at contact time (t), and dye concentration at equilibrium (mg L^{-1}), respectively. W and V represent adsorbent dosage (mg) and dye solution volume (L), respectively.

Reusability tests. Reusability tests were carried out to evaluate the stability and reusability of adsorbents. A total of 60 mg of adsorbents was added in 100 mL of an MB solution with a C_0 of 100 mg L^{-1} at natural pH (6.5 ± 0.5) for 180 min. After the adsorption of MB on the adsorbent, the solution phase was obtained by filtration using a $0.45 \text{ }\mu\text{m}$ membrane filter, and the solid phase (adsorbent) was collected by centrifugation, followed by washing two times using ethanol with 0.1 M NaOH (1 wt%). The washed adsorbent was dried at 65°C for 2 hrs, and recyclability tests were carried out seven times under the same conditions and procedures as stated above.

References

- Vandevivere, P. C., Bianchi, R. & Verstraete, W. Review: Treatment and reuse of wastewater from the textile wet-processing industry: Review of emerging technologies. *J. Chem. Technol. Biotechnol.* **72**, 289–302 (1998).
- Geissen, V. *et al.* Emerging pollutants in the environment: a challenge for water resource management. *J. Soil. Water. Conserv.* **3**, 57–65 (2015).
- Ali, I. New generation adsorbents for water treatment. *Chem. Rev.* **112**, 5073–5091 (2012).
- Ponder, S. M., Darab, J. G. & Mallouk, T. E. Remediation of Cr (VI) and Pb (II) aqueous solutions using supported, nanoscale zero-valent iron. *Environ. Sci. Technol.* **34**, 2564–2569 (2000).
- Worch, E. Adsorption technology in water treatment: fundamentals, processes, and modeling. Gruyter, W. d. (2012).
- Xu, M. *et al.* Hydrothermal synthesis and pseudocapacitance properties of $\alpha\text{-MnO}_2$ hollow spheres and hollow urchins. *J. Phys. Chem. C* **111**, 19141–19147 (2007).
- Toupin, M., Brousse, T. & Bélanger, D. Influence of microstructure on the charge storage properties of chemically synthesized manganese dioxide. *Chem. Mater.* **14**, 3946–3952 (2002).
- Murray, J. W. The surface chemistry of hydrous manganese dioxide. *J. Colloid Interface Sci.* **46**, 357–371 (1974).
- Fendorf, S. E. & Zasoski, R. J. Chromium (III) oxidation by delta-manganese oxide (MnO_2). 1. Characterization. *Environ. Sci. Technol.* **26**, 79–85 (1992).
- Wang, N. *et al.* Fabrication of a compressible PU@ RGO@ MnO_2 hybrid sponge for efficient removal of methylene blue with an excellent recyclability. *RSC Adv.* **6**, 88897–88903 (2016).
- Gilbert, B., Ono, R. K., Ching, K. A. & Kim, C. S. The effects of nanoparticle aggregation processes on aggregate structure and metal uptake. *J. Colloid Interface Sci.* **339**, 285–295 (2009).
- Kim, E. J., Kim, J., Choi, S. C. & Chang, Y. S. Sorption behavior of heavy metals on poorly crystalline manganese oxides: roles of water conditions and light. *Env. Sci. Process. Impact.* **16**, 1519–1525 (2014).
- Maliyekkal, S. M., Lisha, K. P. & Pradeep, T. A novel cellulose–manganese oxide hybrid material by *in situ* soft chemical synthesis and its application for the removal of Pb (II) from water. *J. Hazard. Mater.* **181**, 986–995 (2010).
- Namasivayam, C. & Kavitha, D. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigm.* **54**, 47–58 (2002).
- Wu, Z. & Zhao, D. Ordered mesoporous materials as adsorbents. *Chem. Commun.* **47**, 3332–3338 (2011).
- Li, Y. *et al.* Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. *Chem. Eng. Res. Des.* **91**, 361–368 (2013).
- Shen, Y. & Chen, B. Sulfonated graphene nanosheets as a superb adsorbent for various environmental pollutants in water. *Environ. Sci. Technol.* **49**, 7364–7372 (2015).
- Yan, H. *et al.* Influence of the surface structure of graphene oxide on the adsorption of aromatic organic compounds from water. *ACS Appl. Mater. Interfaces* **7**, 6690–6697 (2015).
- Chen, L. *et al.* Facile synthesis of mesoporous carbon nanocomposites from natural biomass for efficient dye adsorption and selective heavy metal removal. *RSC Adv.* **6**, 2259–2269 (2016).
- Yang, W. *et al.* Preparation of diamine modified mesoporous silica on multi-walled carbon nanotubes for the adsorption of heavy metals in aqueous solution. *Appl. Surf. Sci.* **282**, 38–45 (2013).
- Gupta, V. & Saleh, T. A. Syntheses of Carbon Nanotube-Metal Oxides Composites; Adsorption and Photo-degradation. In *Carbon Nanotubes-From Research to Applications* (Intech, 2011).
- Pan, B. *et al.* Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chem. Eng. J.* **151**, 19–29 (2009).
- Wang, J.-W., Chen, Y. & Chen, B.-Z. A synthesis method of MnO_2 /activated carbon composite for electrochemical supercapacitors. *J. Electrochem. Soc.* **162**, A1654–A1661 (2015).
- Safieh, K. A. A., Al-Degs, Y. S., Sunjuk, M. S., Saleh, A. I. & Al-Ghouti, M. A. Selective removal of dibenzothiophene from commercial diesel using manganese dioxide-modified activated carbon: a kinetic study. *Environ. Technol.* **36**, 98–105 (2015).
- Chen, Y. *et al.* One-pot synthesis of MnO_2 /graphene/carbon nanotube hybrid by chemical method. *Carbon* **49**, 4434–4442 (2011).
- Wang, G., Xu, H., Lu, L. & Zhao, H. One-step synthesis of mesoporous MnO_2 /carbon sphere composites for asymmetric electrochemical capacitors. *J. Mater. Chem. A* **3**, 1127–1132 (2015).
- Kim, H., Watthanaphanit, A. & Saito, N. Synthesis of colloidal MnO_2 with a sheet-like structure by one-pot plasma discharge in permanganate aqueous solution. *RSC Adv.* **6**, 2826–2834 (2016).

28. Kim, H., Watthanaphanit, A. & Saito, N. Simple Solution Plasma Synthesis of Hierarchical Nanoporous MnO₂ for Organic Dye Removal. *ACS Sustain. Chem. Eng.* **5**, 5842–5851 (2017).
29. Kang, J., Li, O. L. & Saito, N. Synthesis of structure-controlled carbon nano spheres by solution plasma process. *Carbon* **60**, 292–298 (2013).
30. Kim, D.-w, Li, O. L. & Saito, N. Enhancement of ORR catalytic activity by multiple heteroatom-doped carbon materials. *Phys. Chem. Chem. Phys.* **17**, 407–413 (2015).
31. Hyun, K., Ueno, T., Li, O. L. & Saito, N. Synthesis of heteroatom-carbon nanosheets by solution plasma processing using N-methyl-2-pyrrolidone as precursor. *RSC Adv.* **6**, 6990–6996 (2016).
32. Pedersen, C. J. The discovery of crown ethers (Noble Lecture). *Angew. Chem. Int. Ed.* **27**, 1021–1027 (1988).
33. Visser, A. E., Swatloski, R. P., Reichert, W. M., Griffin, S. T. & Rogers, R. D. Traditional extractants in nontraditional solvents: Groups 1 and 2 extraction by crown ethers in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **39**, 3596–3604 (2000).
34. Pedersen, C. J. Cyclic polyethers and their complexes with metal salts. *J. Am. Chem. Soc.* **89**, 7017–7036 (1967).
35. Gokel, G. W., Leevy, W. M. & Weber, M. E. Crown ethers: sensors for ions and molecular scaffolds for materials and biological models. *Chem. Rev.* **104**, 2723–2750 (2004).
36. Sam, D. J. & Simmons, H. E. Crown polyether chemistry. Potassium permanganate oxidations in benzene. *J. Am. Chem. Soc.* **94**, 4024–4025 (1972).
37. Doheny, A. J. Jr. & Ganem, B. Purple benzene revisited. *J. Chem. Educ.* **57**, 308 (1980).
38. Steed, J. W. First- and second-sphere coordination chemistry of alkali metal crown ether complexes. *Coord. Chem. Rev.* **215**, 171–221 (2001).
39. Manoj, B. & Kunjomana, A. Study of stacking structure of amorphous carbon by X-ray diffraction technique. *Int. J. Electrochem. Sci.* **7**, 3127–3134 (2012).
40. Huang, M. *et al.* Self-assembly of mesoporous nanotubes assembled from interwoven ultrathin birnessite-type MnO₂ nanosheets for asymmetric supercapacitors. *Sci. Rep.* **4** (2014).
41. Wang, Y., Alsmeyer, D. C. & McCreery, R. L. Raman spectroscopy of carbon materials: structural basis of observed spectra. *Chem. Mater.* **2**, 557–563 (1990).
42. Julien, C. *et al.* Raman spectra of birnessite manganese dioxides. *Solid State Ionics* **159**, 345–356 (2003).
43. Thommes, M. *et al.* Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **87**, 1051–1069 (2015).
44. Xu, B. *et al.* One-pot hydrothermal synthesis of novel 3D starfish-like δ-MnO₂ nanosheets on carbon fiber paper for high-performance supercapacitors. *RSC Adv.* **7**, 14910–14916 (2017).
45. Ren, Z. *et al.* Large-scale synthesis of hybrid metal oxides through metal redox mechanism for high-performance pseudocapacitors. *Sci. Rep.* **6**, 20021 (2016).
46. Junta, J. L. & Hochella, M. F. Manganese (II) oxidation at mineral surfaces: A microscopic and spectroscopic study. *Geochim. Cosmochim. Acta* **58**, 4985–4999 (1994).
47. Jadhav, P. R. *et al.* Design and electro-synthesis of 3-D nanofibers of MnO₂ thin films and their application in high performance supercapacitor. *Electrochim. Acta* **176**, 523–532 (2015).
48. Dupin, J.-C., Gonbeau, D., Vinatier, P. & Levasseur, A. Systematic XPS studies of metal oxides, hydroxides and peroxides. *Phys. Chem. Chem. Phys.* **2**, 1319–1324 (2000).
49. Tang, W. *et al.* Oxalate route for promoting activity of manganese oxide catalysts in total VOCs' oxidation: effect of calcination temperature and preparation method. *J. Mater. Chem. A* **2**, 2544–2554 (2014).
50. Parent, P. *et al.* Nanoscale characterization of aircraft soot: a high-resolution transmission electron microscopy, Raman spectroscopy, X-ray photoelectron and near-edge X-ray absorption spectroscopy study. *Carbon* **101**, 86–100 (2016).
51. Ho, Y. & McKay, G. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Saf. Environ.* **76**, 332–340 (1998).
52. Ho, Y.-S. & McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **34**, 451–465 (1999).
53. Chen, D., Zhang, J. & Chen, J. Adsorption of methyl tert-butyl ether using granular activated carbon: Equilibrium and kinetic analysis. *Int. J. Environ. Sci. Te.* **7**, 235–242 (2010).
54. Weber, W. & Morris, G. Removal of biologically-resistant pollutants from waste waters by adsorption. *Adv. Water Resour.* **2**, 231–266 (1962).
55. Yiacoumi, S. & Tien, C. Kinetics of metal ion adsorption from aqueous solutions: models, algorithms, and applications. (Springer Science & Business Media, (2013).
56. Ramaraju, B., Manoj Kumar Reddy, P. & Subrahmanyam, C. Low cost adsorbents from agricultural waste for removal of dyes. *Environ. Prog. Sustain. Energy* **33**, 38–46 (2014).
57. Hameed, B., Mahmoud, D. & Ahmad, A. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste. *J. Hazard. Mater.* **158**, 65–72 (2008).
58. Allen, S., McKay, G. & Porter, J. F. Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *J. Colloid Interface Sci.* **280**, 322–333 (2004).
59. Weber, T. W. & Chakravorty, R. K. Pore and solid diffusion models for fixed-bed adsorbents. *AIChE J.* **20**, 228–238 (1974).
60. Hall, K. R., Eagleton, L. C., Acrivos, A. & Vermeulen, T. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Ind. Eng. Chem. Fund.* **5**, 212–223 (1966).
61. Allen, S. J., McKay, G. & Khader, K. Equilibrium adsorption isotherms for basic dyes onto lignite. *J. Chem. Technol. Biotechnol.* **45**, 291–302 (1989).
62. Özcan, A. S., Erdem, B. & Özcan, A. Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. *J. Colloid Interface Sci.* **280**, 44–54 (2004).

Acknowledgements

We appreciate the financial support from the Core Research for Evolutional Science and Technology of Japan Science and Technology (JST) Agency. Grant JPMJCR12L1.

Author Contributions

H.M. Kim designed research and performed the experiments, data analysis and wrote manuscript; N. Saito and H.M. Kim discussed the results and contributed to manuscript preparation.

Additional Information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s41598-018-22203-1>.

Competing Interests: The authors declare no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2018