Research article

Removal of azo dye by a highly graphitized and heteroatom doped carbon derived from fish waste: Adsorption equilibrium and kinetics

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ABSTRACT

A highly graphitized and heteroatom doped porous carbon was prepared from fish waste in the present study. The morphology and chemical composition of the resultant porous carbon were characterized by SEM-EDS, TEM, BET, XRD and Raman measurement. The prepared porous carbon was employed as an adsorbent for acid orange 7, a typical azo dye, removal from aqueous solution. The results showed that the porous carbon had ultrahigh surface area of 2146 m²/g, a high degree of graphitization structure and naturally doped with nitrogen and phosphorous. The maximum adsorption capacity of acid orange 7 reached 285.71 mg/g due to unique property of the prepared porous carbon. In addition, acid orange 7 adsorption onto the porous carbon well followed pseudo-second-order kinetics model and acid orange 7 diffusion in micropores was the potential rate controlling step.

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1. Introduction

Dye-producing industries and dye-consuming industries generate large quantities of dye-containing wastewater that are discharged to local water resources (Yagub et al., 2014). The dyes not only deteriorate aesthetic properties of water by imparting significant color but also increase the biological oxygen demand, chemical oxygen demand, and dissolved and suspended solids (Ahmad et al., 2015). Azo dyes are one of most concerned dyes because of their potentiality to induce carcinogenicity or mutagenicity in humans and animals (Ahmad et al., 2015; Singh et al., 2015; Moussavi and Mahmoudi, 2009). Emissions standards are becoming increasingly stringent for azo dyes pollution and they are must be removed to minimize the environmental impact. Various processes and techniques have been developed for azo dyes removal from aqueous solution including adsorption (Goscianska et al., 2014, 2015a; Yagub et al., 2014), chemical coagulation (Zahrim et al., 2011), photodegradation (Davies et al., 2005) and biodegradation (Singh et al., 2015). Among them, adsorption onto porous materials is considered to be one of the most efficient

techniques for azo dyes removal from aqueous solution (Goscianska et al., 2014, 2015a,b; Yagub et al., 2014).

Porous carbon is of increasing importance in recent decades due to their potential applications such as catalyst supports, adsorbents, electrodes, sensors and energy storage media. In addition, heteroatom-doped porous carbons recently have become a hot area because of their expanded electric property originating from heteroatom-containing functional groups within carbon matrix (Daems et al., 2014; Shen and Fan, 2013; Chen et al., 2014). In general, high cost and stringent preparation conditions pose significant challenges for wide-scale application of the heteroatom-doped porous carbons. Biomass waste is a potential raw material for the synthesis of carbon material because it is abundant available and is an environmental friendly renewable resource. To date, many review papers have appeared about the production of porous carbons from different types of biomass resource (Abioye and Ani, 2015; Ahmed, 2016; Ding et al., 2013). However, most of prepared porous carbons are micro-porous materials and have wide pore size distribution, which significantly limit their application (Dias et al., 2007). Some biomass naturally contains nitrogen and other heteroatom, and therefore they are potentially to synthesize heteroatom doped carbon materials with the advantage of negligible cost. Several papers have been published about the production of heteroatom-doped porous carbon and their application in energy

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storage and supercapacitors (Daems et al., 2014; Shen and Fan, 2013). For instance, nitrogen and sulfur doped porous carbon material were prepared by carbonization of human hair and these doped carbon materials exhibited high charge storage capacity and good stability (Qian et al., 2014). In the case of dual-doped porous carbons prepared from the shell of broad beans, they showed a stable performance for lithium ion batteries and sodium ion batteries (Xu et al., 2015).

Huge amount of fish waste including fish scale, fish bone and fish dart and fish innards are generated from food industry every year. Besides high content of carbon, fish waste is rich of hydroxyapatite and protein, which are natural resource of phosphorous and nitrogen. In the present study, a nitrogen and phosphorous dual-doped porous carbon with highly porous structure and graphitization degree was prepared from fish waste. The physicochemical property of prepared porous carbon was characterized by multiple morphological and structural methods (SEM-EDS, TEM, BET and XRD). In addition, removal efficiency of acid orange 7 (AO7), a typical azo dye, from aqueous solution onto the prepared porous carbon was investigated.

2. Material and methods

2.1. Materials

The fish waste (mainly contained fish scale) was collected from a local food market in Haidian District, Beijing. Potassium hydroxide, hydrochloric acid and AO7 were purchased from Beijing Chemical Reagents Co., Ltd.

2.2. Preparation of fish waste-derived porous carbon

The fish waste was thoroughly washed with de-ionized water and then was dried at 80 °C for 24 h in an oven. The dried fish waste was pre-carbonized at 300 °C for 1 h under nitrogen atmosphere. The pre-carbonized fish waste mixed with KOH (KOH weight/carbon weight = 1) and then activated in a quartz crucible at 700 °C for 1.5 h under nitrogen atmosphere. A heating rate of 5 °C/min was adopted for the pre-carbonization and activation experiments. The resultant dark solid was washed with 0.5 mol/L HCl solution thoroughly and then de-ionized water, followed by dried at 80 °C for 24 h. The obtained porous carbon was labeled as FWPC and stored in desiccator for use.

2.3. Characterization

The carbon, hydrogen, nitrogen and sulfur contents were determined on an EA3000 Elemental Analyzer (Italy). The porosity property was obtained from nitrogen adsorption isotherms at −196 °C using a Micromeritics ASAP 2010 analyzer (USA). Prior to N₂ sorption analysis, the porous carbon was degassed at 150 °C for 4 h. The surface morphology was examined by scanning electron microscopy (SEM) JSM 6010LA (Japan) equipped with energy dispersive spectroscopy (EDS). Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2100 microscope (Japan) operated at 200 kV acceleration voltages. The porous carbon for TEM measurements was suspended in ethanol and supported onto a holey carbon film on a Cu grid. The structure of was characterized by X-ray powder diffraction (XRD, Rigaku Ultima III, Japan) and Raman spectroscopy (Bruker VERTEX 70).

2.4. AO7 removal from aqueous solution

The batch adsorption experiments were performed by contacting AO7 solution with pre-set amount of porous carbon FWPC in

50-mL glass bottles placed in a water bath shaker at pre-determined temperatures. AO7 concentration after adsorption was determined by Shimadzu UV-2450 spectrophotometry (Japan) at 484 nm. Response surface methodology (RSM) was applied to investigate the effects of operating parameters and their interactions on AO7 adsorption efficiency. A face-centered central composite design (FCCCD) (Taymaz et al., 2011) was applied to design the adsorption experiments. The present study concerned the influences of temperature, initial AO7 concentration and contact time on AO7 adsorption onto the porous carbon. The levels of three parameters were investigated in the range of 10–50 °C, 60–300 mg/L and 2–18 min for adsorption temperature, initial concentration and contact time, respectively.

3. Results and discussion

3.1. Physicochemical property of porous carbon

Fig. 1 showed images of pre-carbonized fish waste and corresponding FWPC. As shown in Fig. 1a, the pre-carbonized fish waste has smooth surface and no clear porous structure is observed. In the case of FWPC, it exhibits a well developed alveolate morphology and the large amount of pores is present, forming a 3D connected porous structure (Fig. 1b and c). A closer view reveals that the FWPC has abundant large pores and these large pores originate from the removal of inorganic matters (main hydroxyapatite) in fish scale. As we know, fish scale is comprised of substantial amount of hydroxyapatite and the hydroxyapatite in fish scale acts as a natural template during preparation of FWPC in the present study. TEM images (Fig. 1d and e) indicate that abundant micropores about several nanometers in size and mesopores are present in the walls of the large pores, which they are introduced by KOH activation and partially by hydroxyapatite removal.

N₂ adsorption/desorption isotherm and the corresponding pore size distribution (PSD) curve of FWPC were shown in Fig. 2. The specific surface area and PSD were calculated using Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively. FWPC exhibits a type IV nitrogen adsorption/desorption isotherm according to the IUPAC classification. In detail, the fast adsorption at low relative pressure is ascribed to the sharp capillary condensation of N₂, indicating that the matrix of FWPC is rich in microporous structure. The presence of hysteresis loop at higher relative pressure ($P/P_0 = 0.40–0.95$) suggests the existence of abundant mesopores. Meanwhile, the slight upward tendency at high relative pressure ($P/P_0 = 0.95–1.00$) results from the adsorption of the macropores and accumulation of carbon particles. Therefore, FWPC has a highly developed hierarchical porosity network of micropores in combination of mesopores and macropores. The specific BET surface area and total pore volume of FWPC are 2146 m²/g and 0.42 cm³/g, respectively. The micropore surface area and external surface area calculated by t-plot method are 1554 and 592 m²/g, respectively. The PSD of FWPC was calculated by the DFT method from N₂ adsorption and the PSD data indicates that the size of majority of pores is about 2.4 nm in FWPC. Furthermore, the clear upward trend peak further confirms the presence of abundant micropores in FWPC. The ultrahigh surface area and hierarchical porous structure are well agreed with the SEM and TEM observations.

Table 1 summarized chemical composition of the FWPC determined by elemental analysis and energy-dispersive spectroscopy (EDS). The FWPC is comprised of C, H, N, O and P, and the contents of N and P are around 4.51 and 1.40%, respectively. The chemical analysis indicates that the N and P dual-doped porous carbon was prepared from fish waste in the present study.

Fig. 3A showed powder XRD pattern of the prepared porous

Fig. 1. Scanning electron microscopy (SEM) images of (a) fish waste pre-carbonized at 300 °C; SEM images (b and c) and TEM images (d and e) of prepared porous carbon at different viewing angles and magnifications.

Fig. 2. Nitrogen sorption isotherms of FWPC with corresponding pore size distribution (insert).

carbon in the wide-angle region. It can be seen that the porous carbon shows two broad peaks around 22.5° and 44.5°, corresponding to (002) and (100) spacing of the graphene stacks,

Table 1

Chemical composition of prepared porous carbon determined by elemental analysis and energy-dispersive X-ray spectroscopy (EDS).

FWPC	Elemental analysis				EDS analysis		
	C	H	N	S	N	P	S
	80.15	0.39	4.51	0.33	4.70	1.40	0.41

respectively. The XRD results implies that the FWPC possesses a well-developed graphitic structure and there is no impurities in it. The carbon material was further detected by Raman spectra (shown in Fig. 3B). The peaks located at around 1348 and 1593 are assigned to the characteristic D (defects and disorder) and G (graphitic) bands of carbon material, respectively. The D/G ratio of band intensity indicates the degree of structural order with respect to a perfect graphitic structure. Here the high ratio of 0.48 implies high graphitic degree of FWPC, which is consistent with XRD analysis. The higher graphitization degree is ascribed to the catalysis of metals in fish waste, especially Fe, which can promote the transformation of amorphous carbon to graphite during high temperature pyrolysis (Hoekstra et al., 2015; Liu et al., 2016; Maldonado-Hodar et al., 2000).

Besides the rich porous structure, nitrogen- and phosphorous containing groups can change surface basicity and the highly graphitized carbon can facilitate the formation of π - π interactions

Fig. 3. XRD and Raman pattern of the prepared porous carbon FWPC.

between graphene layers on carbon surface and aromatic rings of organic compounds, suggesting the potential application of porous carbon for acid azo dyes from aqueous solution.

Table 2
Independent parameters and response variables of FCCCD matrix.

Run no.	Operating parameters			Response variable
	Temperature (°C)	Initial concentration (mg/L)	Contact time (min)	AO7 adsorption (%)
T1	20	120	6	99.17
T2	30	180	10	99.10
T3	30	180	18	99.18
T4	30	180	10	98.50
T5	30	300	10	86.01
T6	30	180	10	98.90
T7	20	120	14	99.70
T8	40	240	6	90.12
T9	30	180	10	96.19
T10	30	180	10	98.55
T11	40	120	14	99.58
T12	30	180	2	87.21
T13	20	240	14	98.73
T14	20	240	6	89.02
T15	10	180	10	98.27
T16	30	180	10	98.89
T17	40	240	14	97.99
T18	50	180	10	98.76
T19	30	60	10	99.62
T20	40	120	6	99.10

3.2. AO7 adsorption onto FWPC

3.2.1. AO7 adsorption analysis by RSM

FCCCD matrix and AO7 adsorption results were presented in Table 2. It can be seen that AO7 adsorption efficiency ranged from 86.01 to 99.70% under tested operation conditions. The experimental results were fitted to second-order polynomial regression equation, which is expressed as the following Eq. (1):

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j \quad (1)$$

where y is the predicted response variable; β_0 is the constant coefficient; β_i is the linear coefficients; β_{ii} is the quadratic coefficients; β_{ij} is the linear coefficients for the interaction between independent variables i and j ; x_i and x_j are the coded independent parameters, which are calculated by the following Eq. (2).

$$X_{\text{code},i} = \frac{2X_{\text{actual},i} - X_{\text{actual},\max} - X_{\text{actual},\min}}{X_{\text{actual},\max} - X_{\text{actual},\min}} \quad (2)$$

where X_{actual} and X_{code} are the actual and coded forms of the independent parameters.

Table S1 illustrated the actual and coded forms of temperature, initial concentration and contact time. Based on these three coded parameters, the developed model for AO7 adsorption was given in Eq. (3), where X_{TE} , X_{IC} , and X_{CT} represent temperature, initial AO7 concentration and contact time, respectively.

$$\begin{aligned} \text{Adsorption efficiency (\%)} = & 98.53 + 0.073 \times X_{\text{TE}} - 3.06 \times X_{\text{IC}} \\ & + 2.66 \times X_{\text{CT}} + 0.068 \times X_{\text{TE}} \times X_{\text{IC}} \\ & - 0.24 \times X_{\text{TE}} \times X_{\text{CT}} + 2.07 \times X_{\text{IC}} \\ & \times X_{\text{CT}} + 0.13 \times X_{\text{TE}}^2 - 1.3 \times X_{\text{IC}}^2 \\ & - 1.2 \times X_{\text{CT}}^2 \end{aligned} \quad (3)$$

The reliability of the developed model was evaluated using analysis of variance (ANOVA), including the test of significance of model and terms and the test of lack of fit (shown in Table 3). In the test of significance, values of p -value less than 0.05 mean the

Table 3

Significance of regression coefficients for AO7 removal onto prepared porous carbon.

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	371.06	9	41.23	29.38	<0.0001
X_{TE}	0.086	1	0.086	0.061	0.8097
X_{IC}	149.48	1	149.48	106.51	<0.0001
X_{CT}	113.02	1	113.02	80.53	<0.0001
X_{TE}^2	0.41	1	0.41	0.29	0.6011
X_{IC}^2	42.39	1	42.39	30.21	0.0003
X_{CT}^2	36.35	1	36.35	25.90	0.0005
$X_{TE}X_{IC}$	0.037	1	0.037	0.027	0.8739
$X_{TE}X_{CT}$	0.44	1	0.44	0.32	0.5860
$X_{IC}X_{CT}$	34.29	1	34.29	24.43	0.0006
Residual	14.03	10	1.40	—	—
Lack-of-fit	8.14	5	1.63	1.38	0.3657

model/term is significant. As can be seen from Table 3, the model for AO7 adsorption and terms of X_{IC} , X_{CT} , X_{IC}^2 , X_{CT}^2 and $X_{IC}X_{CT}$ are significant, indicating that AO7 adsorption efficiency is mainly affected by initial AO7 concentration, contact time and their interactions instead of temperature. In addition, the p-value of “lack of fit” was 0.3657, suggesting that lack of fit for the model is not significant for the noise. Consequently, the model for AO7

adsorption is adequate and reliable, and the effect of operating parameters and their interactions on AO7 adsorption efficiency can be properly evaluated with the developed model.

Fig. 4a showed the interactions between initial concentration and contact time for AO7 adsorption efficiency onto FWPC. A convex surface was obtained, indicating that the effect of initial AO7 concentration closely relates with contact time. Specifically,

Fig. 4. Response surface (a) and corresponding contour plot (b) of AO7 adsorption efficiency as a function of initial AO7 concentration and contact time.

Fig. 5. Langmuir (a) and Freundlich (b) adsorption isotherms of AO7 onto FWPC (0.01 g FWPC; AO7 concentration 55–280 mg/L; 200 rpm agitation; 30 min contact time).

AO7 adsorption efficiency gradually decreased with the increasing initial concentration at shorter contact time (2–6 min). However, a reverse trend of adsorption efficiency (initially increased and then decreased) was observed at longer contact time (14–18 min). At lower initial AO7 concentration (60–120 mg/L), the adsorption efficiency underwent a fall after a rise with increasing contact time. In the case of higher AO7 initial concentrations (240–300 mg/L), the adsorption efficiency increased continuously with the prolonging contact time. A possible explanation for low adsorption efficiency at short time is that the contact time is shorter than the equilibrium time required for AO7 molecules from solution to the adsorption sites of FWPC. While with increased contact time, AO7 molecules can reach all the adsorption sites of FWPC until saturation. A previous report is well agreed with the observation in the present study, in which high level of AO7 removal onto acid hydrolysed spent brewery grains was achieved at high initial concentrations and increased contact time (Silva et al., 2004a).

Contour figure of AO7 adsorption efficiency was plotted (shown in Fig. 4b) to determine the optimal initial concentration and contact time in the present study. It is clear that high removal rate of AO7 (higher than 99%) was achieved with optimized range of initial AO7 concentration of 66–181 mg/L and contact time of 7–15 min. By comparing, the AO7 adsorption capacity onto FWPC is higher than those onto reported adsorbents in the literature (Aber

et al., 2007; Elizalde-González and Hernández-Montoya, 2009; Hamzeh et al., 2012; Hsiu-Mei et al., 2009; Silva et al., 2004a, 2004b; Padmesh et al., 2005). In addition, it is worth noting that the optimal contact time of AO7 adsorption onto FWPC in the present study is far shorter than that of other adsorbents (Aber et al., 2007; Elizalde-González and Hernández-Montoya, 2009; Hamzeh et al., 2012; Hsiu-Mei et al., 2009; Silva et al., 2004a, 2004b; Padmesh et al., 2005), confirming that FWPC is very efficient for AO7 removal from aqueous solution.

3.2.2. Adsorption isotherms

To estimate the maximum adsorption capacity and evaluate the adsorption intensity of AO7 onto FWPC, Langmuir and Freundlich models were used to fit the experimental data. The two models' linear forms are:

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{b} \quad \text{Langmuir model} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Freundlich model} \quad (5)$$

where C_e (mg/L) is the equilibrium concentration in the solution, q_e (mg/g) is the AO7 adsorbed at equilibrium, b (mg/g) is the

Table 4

Constants and correlation coefficients of isotherm, kinetics and intra-particle diffusion model.

Adsorption isotherm	Langmuir model			Freundlich model		
	a	b	R ²	K _F	n	R ²
	3.89	285.71	0.9993	186.31	2.98	0.7981
Kinetics model	Pseudo-first-order kinetics model			Pseudo-first-order kinetics model		
	q _e	K ₁	R ²	q _e	K ₂	R ²
	21.43	10.00	0.8036	243.90	1.68	0.9999
Intra-particle diffusion model	First proportion			Second proportion		
	K _d	C	R ²	K _d	C	R ²
	10.06	233.22	0.7032	434.76	137.80	0.9241

Fig. 6. Kinetics patterns of pseudo-first-order (a) and pseudo-second-order (b) of AO7 onto FWPC (120 mg/L initial concentration; 0.06 g FWPC; 200 rpm agitation; Temperature 20 °C).

maximum adsorption capacity, n Freundlich constant related to adsorption intensity, and a (L/mg) and $K_F ((\text{mg/g}) (\text{L/mg})^{1/n})$ are the adsorption constants for Langmuir and Freundlich model, respectively.

The linearity test of two models for the adsorption of AO7 onto FWPC was plotted and the experimental results were illustrated in Fig. 5 and Table 4. Correlation coefficients suggests that the better fitting of experimental data is Langmuir model isotherm ($R^2 = 0.9993$) rather than Freundlich isotherm ($R^2 = 0.7981$) with maximum adsorption capacity 285.71 mg/g onto FWPC at 20 °C. The reason for the worse fitness by Freundlich model is that the supply of adsorption site is not infinite on FWPC surface. In

addition, the parameter a relates to the energy of adsorption and it can be seen that AO7 adsorption onto FWPC has high bond energy ($a = 3.89$ L/mg). By comparing, the adsorption capacity of AO7 onto FWPC is higher than other adsorbents reported in literature (Aber et al., 2007; Elizalde-González and Hernández-Montoya, 2009; Hamzeh et al., 2012; Hsiu-Mei et al., 2009; Silva et al., 2004a, 2004b; Padmesh et al., 2005).

3.2.3. Adsorption kinetics

Pseudo-first-order (Eq. (6)) and pseudo-second-order (Eq. (7)) were employed to study AO7 adsorption mechanism onto FWPC.

Fig. 7. Intra-particle diffusion kinetics for AO7 adsorption onto FWPC.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where q_t and q_e (mg/g) are the amount of AO7 adsorbed at time t (h) and equilibrium, k_1 (1/h) and k_2 (g/(mgh)) are the rate constants for the pseudo-first-order and pseudo-second-order adsorption kinetics, respectively.

Fig. 6 and Table 4 showed the regression analysis based on pseudo-first-order and pseudo-second-order kinetics for AO7 adsorption onto FWPC. As can be seen from Fig. 6a, the correlation coefficient of pseudo-first-order kinetics model is low ($R^2 = 0.8036$) and q_e value calculated from the plot (21.43 mg/g) is far lower than the experimental data, indicating AO7 adsorption onto FWPC does not follow pseudo-first-order equation. In the case of pseudo-second-order model (Fig. 6b), the calculated q_e value (243.90 mg/g) is close to the experimental data (239.70 mg/g) and the high correlation coefficient ($R^2 = 0.9999$) confirms that adsorption behavior of AO7 onto FWPC well fits pseudo-second-order model.

To identify the diffusion mechanism, kinetic data was analyzed by the intra-particle diffusion kinetic model (Eq. (8)).

$$q_t = K_d t^{1/2} + C \quad (8)$$

Where K_d (mg/(gh^{1/2})) is the intra-particle diffusion rate constant, C (mg/g) and q_t (mg/g) are the adsorption constant and adsorbed AO7 at time t (h), respectively.

According to intra-particle diffusion model, a plot of q_t versus $t^{1/2}$ should be linear if intra-particle diffusion is rate-limiting step of adsorption process, and if this line passes through the origin the intra-particle diffusion is the only rate-controlling step (Liu and Zhang, 2009). In the present study, the plot of q_t against $t^{1/2}$ (shown in Fig. 7) did not pass through the origin and were not linear over the whole time range, indicating that the intra-particle diffusion is not the only rate controlling step for AO7 adsorption onto FWPC. The linearity was evaluated separately within the whole time range. The first proportion and second proportion corresponds to AO7 transfer across the bulk solution to the solution around carbon surface and the diffusion into surface pores of FWPC, respectively. The higher slope (shown in Table 4) for the first proportion implies that AO7 transfer from bulk solution to carbon surface is faster. The lower slope of the second proportion suggests intra-particle diffusion is rate-controlling step after a certain contact time.

4. Conclusions

A highly graphitized nanostructure carbon with nitrogen and phosphorous doping was prepared from fish waste. The macropores and mesopores of the porous carbon facilitated mass transportation, and high surface area and heteroatom-doped elements provided sufficient active sites, resulting in high adsorption capacity and fast adsorption rate of AO7 from aqueous solution. Langmuir isotherm and pseudo-second-order kinetics model well described AO7 adsorption onto the porous carbon. The present study provided a low cost, simple route to prepare highly effective porous carbon towards azo dye contaminated wastewater treatment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2016.08.008>.

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