Modeling of pollutant removal by powdered activated carbon in a raw water aqueduct

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ABSTRACT

This study provides new parameters for the use of powdered activated carbon (PAC) in a raw water aqueduct under emergency response. Here, a coupled model was developed that dynamically predicts simultaneous PAC transport and pollutant removal in the water aqueduct. To calibrate the model, we have performed a Particle Image Velocimetry (PIV) settling experiment to determine the dynamic settling velocity, PAC deposition experiments in a rotating flume to quantify the bottom shearing effects, and jar tests to determine the dynamic pollutant adsorption rate. The model was validated against a field chemical oxygen demand experiment in a water aqueduct in Shanghai (China) and a laboratory nitrobenzene flume test. Then, given a certain pollution concentration arising from an accidental pollution event, the model could be used to predict the optimal flow rate and PAC dosage for establishing mitigation measures.

Keywords: water source pollution; risk management; mathematical model; rotating flume; PIV; nitrobenzene.

1. Introduction

Powdered activated carbon (PAC) treatment is a widely used and effective method of removing water pollutants, especially dissolved micro-organic contaminants (Loo et al., 2012). Its use for emergency responses in drinking water treatment plants (DWTPs), however, may be less efficient, because DWTPs usually have a low hydraulic retention time (HRT), so there is limited contact time during which the PAC can adsorb the pollutants from the water column. To enhance the efficiency, it has been proposed that the PAC be fed into the water aqueduct that connects the water source with the DWTP. These aqueducts are usually several kilometers long and there is a prolonged contact time during which the PAC can treat the pollutants. This idea has been implemented in some projects. For example, PAC was added to a raw water aqueduct as an emergency measure to treat the pollution released from the explosion of Jilin Petrochemical Plant in 2005, which resulted in a high nitrobenzene concentration, 3.5 times higher than the drinking water standard (Chen et al., 2006). Dedicated PAC feeding facilities were also built in Beijing and Shanghai in 2008 and 2009. The Beijing facility is located at the south-to-north diversion project of the Yangtze River and the Shanghai project is on the Huangpu River. These facilities will play an important role in treating future environmental pollution accidents.

For the effective operation of a PAC feeding facility, it is necessary to understand the interactions between the transport processes of PAC and the simultaneous pollutant removal in the water aqueduct. These interactive processes comprise PAC transport by advection and turbulent diffusion, sediment deposition, and PAC adsorption of pollutants. Although there is extensive literature on the PAC removal rates of a wide range of organic compounds using jar tests or pilot-scale experimental setups (e.g., Baeta et al., 2013; Ho et al., 2011; Kumar et al., 2010), little information is available on the dynamic behaviour of organic pollutant removal along an aqueduct while the water is flowing and PAC is distributed into the aqueduct by a controlled method. A computational fluid dynamics (CFD) model can offer a better representation of the water flow and PAC transport along with pollutant removal in a long-distance water aqueduct. Results from the CFD studies will provide information and guidance on PAC transport and settling as well as on feeding rates, making it possible to provide effective treatment under various conditions developed by water resource managers and engineers.

It is known that various aspects of sediment–pollutant transport modeling in a water environment have been studied. These studies concerned the modeling of sediment dynamics in water systems (Chen et al., 2014; Choi and Lee, 2014; Liu and Huang, 2009; Spencer et al., 2011; Sun et al., 2015; Xiao et al., 2014; Wang et al., 2014) and the association

of pollutants with suspended sediments and erosion of pollutants in association with bed sediments (Cheng et al., 2014; Droppo et al., 2011; Liang et al., 2013; Lick 2009; Wang et al., 2013; Yin et al., 2011). Software for the assessment of regional exposure (e.g., GREAT-ER) has also been developed to predict the spatially explicit exposure concentration of typical down-the-drain chemicals in river basins (Kehrein et al., 2015). However, these models are basically limited to uniform sediment-deposition as the sediments are transported from upstream to downstream reach rather than accounting for the dynamic nature of deposition related to sediment characteristics, local hydrodynamics, and so on. From this perspective, these modeling methods may be insufficient in the present problem, mainly because of potential variation in the PAC settling rate as well as the PAC adsorption rate through the water aqueduct. Therefore, a coupled PAC–pollutant removal model that incorporates dynamic PAC deposition and pollution adsorption rates is still needed to fully describe the relevant conditions and processes. In addition, dynamic transport and deposition differ from sediment to sediment, being influenced by the general properties of sediments, fluid shear stress, and so on; hence experimental data are also required to support the model to be developed.

To date, no study has been published with respect to modeling PAC transport and its efficiency in removing pollutants in a raw water

aqueduct. The purpose of this study is to develop a coupled PAC–pollutant removal model in conjunction with laboratory experiments and to provide a better understanding of how PAC works in a long-distance water aqueduct. The results of this study may reveal insights and indicate proper practice for PAC deployment in a water supply system for removal of water pollutants.

2. Methodology and numerical model

2.1 Site description

The study area is a raw water aqueduct located in Shanghai, China. As shown in Fig. 1, surface water from Songpu Bridge station of Huangpu River is conveyed to the DWTPs through four parallel closed underground aqueducts, each 16.3 km long, 3.75 m wide, and 3.25 m deep, to Caohang, where the water aqueduct system diverges into two routes. The first route extends more than 20 km from Caohang to Linjiang and then connects to five DWTPs: Yangshupu, Yangsi, Pudong, Jujiqiao, and Nanshi; the second route guides water directly to the Changqiao DWTP. At Songpu, Linjiang, and Yanqiao, pumping stations and pressure surge tanks were installed to pressurize the flow within the long-distance trunk aqueduct. The peak flow rate of the raw water is $5.4 \times 10^6 \text{ m}^3/\text{d}$.

2.2 Numerical Model

108 To model the PAC transport in the aqueduct system, a numerical model
 109 that includes a PAC transport model and a PAC adsorption model has
 110 been developed.

111 *2.2.1 PAC transport model*

112 A one-dimensional advection-diffusion model has been developed to
 113 describe the PAC transport within the aqueducts. The conservation of
 114 PAC mass can be described by

$$115 \quad \frac{\partial A\theta}{\partial t} + \frac{\partial Q\theta}{\partial x} = \frac{\partial}{\partial x} \left(AD \frac{\partial \theta}{\partial x} \right) - WF_d, \quad (1)$$

116 where θ is the PAC concentration within the aqueduct, D is the
 117 dispersion coefficient in the longitudinal direction, W is the aqueduct
 118 width, and F_d is the deposition flux.

119 The deposition flux is given by the following equation (Krishnappan
 120 and Marsalek, 2002):

$$121 \quad F_d = pw_s\theta \quad (2)$$

122 where w_s is the PAC settling velocity in still water and p is the
 123 probability that PAC particles will settle to the aqueduct bed, which can
 124 be given by (Krishnappan and Marsalek, 2002; Liu and Huang, 2009)

$$125 \quad p = 1 - \frac{G}{G_{cr}} \quad (3)$$

126 where G_{cr} is the critical shear stress for PAC deposition, and G is the
 127 actual shear stressed defined by

$$G = \rho g \frac{U^2 n^2}{R^{1/3}} \quad (4)$$

where ρ is the water density, g is the acceleration of gravity, U is the cross-sectional averaged flow velocity, n is the bed roughness, and R is the hydraulic radius.

For each reach of the aqueduct, considering that the cross-sectional area of the aqueduct is constant along the longitudinal direction, Eq. (1) can be simplified to

$$\frac{\partial \theta}{\partial t} + U \frac{\partial \theta}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial \theta}{\partial x} \right) - p \frac{w_s \theta}{h} \quad (5)$$

where h is water depth in the aqueduct.

For Eq.(5), its boundary condition is

$$\theta(0, t) = \theta_0 \quad (6)$$

where θ_0 is PAC dose at the water aqueduct inlet. Assume the initial condition is zero everywhere.

Solving Eq. (6), one obtains

$$\theta(x, t) = \frac{\theta_0}{2} f(x, t) \quad \text{for } \theta \leq \theta_s \quad (7)$$

where θ_s is the PAC steady-state concentration within the water aqueduct, and $f(x, t)$ is

$$f(x, t) = e^{\frac{Ux}{2D}} \left[e^{-\sqrt{\frac{k'}{D}}x} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} - \sqrt{k't}\right) + e^{\sqrt{\frac{k'}{D}}x} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + \sqrt{k't}\right) \right] \quad (8)$$

and k' is

$$k' = pw_s' + \frac{U^2}{4D} \quad (9)$$

where $erfc(x,t)$ is the complementary error function, and $w_s' = w_s/h$.

The input variables to the PAC transport model are the PAC dose and the dynamic PAC settling rate, which are related to the PAC properties and water flow. To model the PAC transport with dynamic PAC deposition, the aqueduct was divided into a series of modeling grids or sub-reaches. For each sub-reach, the dynamic PAC settling rate was input based on physical experiments described in the following sections. The simulated PAC concentration from the previous reach is then defined as the upstream boundary of the next neighboring reach. The modeling scheme is shown in Fig. 2.

2.2.2 PAC adsorption model

On the water quality side, the PAC adsorption dynamics can be modeled by

$$\frac{dC}{dt} = -k_s \theta C \quad (10)$$

where C is the concentration of the dissolved pollutant and k_s is the adsorption rate of pollutant to PAC.

Similarly to the PAC transport equation, the transport equation of the dissolved pollutant can be given by

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - k_s \theta C \quad (11)$$

For Eq.(11), its boundary condition is

$$C(0,t) = C_0 \quad (12)$$

where C_0 is the pollutant concentration at the water aqueduct inlet, i.e., the pollution concentration of the water source.

Eq. (12) can be solved by

$$C(x,t) = \frac{C_0}{2} g(x,t) \quad (13)$$

where $g(x,t)$ is given by

$$g(x,t) = e^{\frac{Ux}{2D}} \left[e^{-\sqrt{\frac{K}{D}}x} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} - \sqrt{Kt}\right) + e^{\sqrt{\frac{K}{D}}x} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + \sqrt{Kt}\right) \right] \quad (14)$$

and K is

$$K = k_s \theta + \frac{U^2}{4D} \quad (15)$$

Note that k_s could change dynamically during the PAC contact time, which has to be determined according to the laboratory jar test, as described in Section 2.3. The modeling scheme for the PAC adsorption model is the same as that of the PAC transport model described above.

2.3 Experimental approach

2.3.1 PAC settling experiment

Traditional direct settling speed measurement can be performed in a settling column, where water-PAC samples are collected from the side outlets at a fixed interval for the duration of the experiment. At each sample outlet, PAC concentration with time can be determined to

calculate the PAC settling speed. This method is suitable to measure the steady-state PAC settling speed, but inefficient to measure the dynamic PAC settling speed. Therefore, the Particle Image Velocimetry (PIV) measurement was employed, as shown in Fig. 3.

The experiment was performed in a plexiglass water column with an upper water tank ($0.4\text{ m} \times 0.4\text{ m} \times 0.3\text{ m}$) and a lower rectangular tube ($0.1\text{ m} \times 0.1\text{ m} \times 0.6\text{ m}$). The PIV measurement was conducted within the lower tube. The cross-section was illuminated by a New Wave Nd:YAG laser generator (TSI Inc.), and a digital Charge-Coupled Device (CCD) camera (TSI PowerViewPlus 4MP) was used to capture the images. A synchronizer (TSI 610035) was used to coordinate the measurement and was connected to a computer for data storage and analysis. The CCD camera was equipped with a Nikon lens with a focal length of 85 mm and an f/1.8 aperture. The double-pulsed laser had a power of 200 mJ/pulse at a wavelength of 532 nm. The thickness of the laser beam was tuned to less than 2 mm.

The measurement was conducted following the procedure described below. First, the settling column was filled with water. An iron block was installed on the base of the settling column to stabilize the platform. The camera was placed 20 cm above the settling column and was calibrated using a standard calibration board. Then, the water was kept still for approximately 24 h and the measured background velocity was found to

be less than 0.03 mm/s; no initial start-up effect of the device can be observed. Finally, the PAC particles were fed into the water tank through a sieve on the top of the upper water tank, and the measurement began after 15 min. The experiment was conducted at 20 °C.

2.3.2 PAC transport experiment

A PAC transport experiment was conducted using a rotating annular flume. In contrast with a straight flume, a rotating annular flume has a circulating water tunnel, so it has a long HRT to simulate the whole deposition process of the long aqueduct. The rotating annular flume in the current experiment was designed by the authors (Chinese Patent No. ZL 2013 2 0175169.1). Its diameter is 2.0 m, its width is 0.30 m, and its depth is 0.45 m. A counter-rotating top cover was installed inside the flume, making contact with the water surface of the flume to minimize secondary circulation (see Fig. 4(a)), which was proven by an Acoustic Doppler Velocimeter (ADV) test (Chinese Patent No. 201510093276.3).

A series of experiments was conducted to determine the PAC characteristics. Water was placed in the flume and a known amount of PAC was added to form a concentration corresponding to the data from the actual raw water aqueduct. First, the flume was rotated at high speed for about 20 min so that the PAC and water were thoroughly mixed mechanically; then the flume speed was reduced to a target rate and maintained for the duration of the experiment. During the experiment,

samples were taken from a side window of the flume, which was controlled by an automatic valve (Fig. 4(b)). The PAC concentration was measured by weighing the water and particle weights of the sample after filtering and drying. All the experiments were conducted at 20 °C.

2.3.3 PAC adsorption experiment

The temperature of the PAC adsorption experiment was the same as that of the PAC settling and transport experiments, that is, 20 °C. The water sample was collected directly from the water source of the study area.

To estimate the water pollution removal rate, a series of tests on the COD (Chemical Oxygen Demand) adsorbed to PAC was performed. The water sample collected was stored at 4 °C until use. Before the adsorption experiments, the PAC was dried in an oven at 105 °C for 24 hours and then cooled to room temperature in a desiccator prior to use. The PAC solution was prepared by mixing the required carbon dose with 1 L of ultrapure water. The PAC jar tests were conducted at room temperature (20 °C), and 13 jars, each containing 200 mL of sample, were tested. The PAC slurries were added at $t = 0$ and the samples were collected at $t = 5, 10, 15, 20, 30, 60, 90, 120, 180, 240, 300, \text{ and } 360$ min. The collected samples were immediately filtered through pre-rinsed 0.45- μm cellulose nitrate filters and then measured using potassium permanganate as the oxidant.

As an open-channel water source, the upstream Huangpu River has a risk of high-concentration chemical pollution, for example, by

nitrobenzene, due to unexpected accidents. Therefore, an experiment on nitrobenzene adsorbed to PAC was conducted to characterize the interaction between the PAC and the nitrobenzene. The experimental procedure was the same as described above, with the COD replaced by nitrobenzene. The samples collected at $t = 5, 10, 15, 20, 30, 60, 90, 120, 180, 240, 300, \text{ and } 360$ min were filtered through pre-rinsed $0.45\text{-}\mu\text{m}$ cellulose nitrate filters and examined by a UV/VIS spectrophotometer (545 nm) using reduction and diazo-coupling reactions.

Similarly, the nitrobenzene experiment was also conducted in a rotating annular flume to quantify its transport dynamics: first, the raw water from the upstream Huangpu River was filled into the flume, and a known amount of nitrobenzene was introduced to prepare a fully mixed initial nitrobenzene solution; next, the flume was reduced to a speed lower than that at which the critical shear stress occurs, and then the PAC particles were added; finally, samples were taken in a time series from the opened window at the flume side wall. The samples were immediately filtered through pre-rinsed $0.45\text{-}\mu\text{m}$ cellulose nitrate filters and measured on a UV/VIS spectrophotometer (545 nm) using reduction and diazo-coupling reactions.

3. Results and discussion

3.1 Experimental results

3.1.1 PAC settling velocity

275 The commercially available bamboo charcoal used in Shanghai DWTPs
276 was tested in the present experiments. The PAC size distribution
277 measured using a laser particle size analyser (Mastersizer 3000, Malvern
278 Instruments Ltd., UK) is shown in Fig. 5. It can be seen that the PAC
279 employed in this study has a 50th-percentile diameter of approximately
280 25 μm and 90th-percentile diameter of approximately 88 μm . The
281 measured PAC settling speed is shown in Fig. 6. Since the PAC is black
282 in colour, it exhibits weak scattering of laser light compared to tracer
283 particles. However, by intensifying the laser light using an Nd:YAG laser,
284 PIV was able to discern and capture the PAC particles and produce a
285 satisfactory CCD image, as shown in the left panel of Fig. 6(a).
286 Furthermore, the post-processed velocity field is shown in the right panel
287 of Fig. 6(a). From the figure, we can see that the PAC settling velocity
288 was almost uniform within the measurement window, showing the good
289 performance of the designed experimental apparatus. The time series of
290 the measured PAC particle settling velocity obtained by averaging over
291 all vectors across the image is shown in Fig. 6(b) and was used as the
292 dynamic input of the numerical model. The time series shows that at the
293 beginning (i.e., 0~20 min) heavy and fast-settling PAC particles were
294 present in the measurement domain, which increased the settling velocity.
295 After the heavy particles had rained out, the PAC settling speed reached a
296 state with a balance of the gravitational, buoyancy, and drag forces.

We further compared the measured PAC settling velocity with the existing PIV measurement of settling velocity of fine sediments in Changjiang Estuary, which was reported to be a maximum value of 6.8×10^{-4} m/s and a steady-state value of 2.1×10^{-4} m/s (Jin and Wang, 2005). The two experimental results were of the same order of 10^{-4} m/s, but the measured settling velocity of fine sediments in Changjiang Estuary is greater than that of PAC. This can be explained as follows: the 50th-percentile diameter of measured fine sediments is about 8 μ m, which falls within the range that easily forms agglomerated flocs (i.e., <10 μ m) (Zhang, 1996); by comparison, the 50th-percentile diameter of PAC (i.e., 25 μ m) is greater than the critical size of fine sediments (i.e., <10 μ m), so the cohesiveness in the present study is negligible. For this reason, the settling speed of a flocculated sediment particle could be larger than that of a PAC particle. However, as the large flocs settled down, the settling speeds of fine-grained sediments gradually decreased to a value that was close to the measured PAC settling speed.

Based on the measured data, the general PAC density can also be obtained by using the Stokes equation for particle sedimentation. Throughout the duration of the experiment, the averaged PAC settling velocity is 1.55×10^{-4} m/s; hence the general PAC particle density is approximately $1.46 \text{ g}\cdot\text{cm}^{-3}$.

3.1.2 PAC deposition characteristics

319 China's *Technical Guideline on Emergency Water Purification Techniques*
320 *for Urban Drinking Water Supplies (Trial Implementation)* suggests that
321 the PAC dose at a DWTP should not usually exceed 30 mg/L due to
322 potential clogging of filters. However, if PAC is employed in a water
323 aqueduct, the maximum PAC dose can be up to 80 mg/L. The results of
324 the flume experiments are shown in Fig. 7 for PAC doses of 10 and 80
325 mg/L, **at various average flow velocities**. In this figure, the blue and red
326 lines represent experiments with PAC doses of 10 and 80 mg/L,
327 respectively.

328 It was found that at a lower fluid shear stress, the PAC concentration
329 started decreasing initially and then reached a steady-state concentration.
330 The decreasing trend of the concentration can be explained by the balance
331 of the shear stress and the gravity. For each case that started from a fully
332 mixed state, the shear stress induced by the flume flow could not support
333 the suspension of the heavy particles in the mixture, which finally settled
334 to the flume bottom. Meanwhile, the turbulence and shear stress could
335 still hold the light particles in the water column, so a steady-state
336 concentration could be finally maintained. Since stronger shear stress and
337 turbulence induced by higher mean flow rates can sustain heavier
338 particles, a larger fraction of the mixture will be kept in the steady state
339 when the mean flow rate is higher. This also explains why the relative

steady-state concentration only depends on the shear stress in spite of the difference in the initial PAC dose (Fig. 7).

Published literatures reported that the fraction of the deposited sediment can be fitted as a function of bed shear stress, for example, a power law type relationship (Droppo et al., 2011; Milburn and Krishnappan, 2003; Skafel and Krishnappan, 1999; Stonen and Krishnappan, 1997). Adopting this equation form, our experiment determines that the PAC steady-state concentration is:

$$\theta_s = 0.245 \theta_0 \left(\frac{G}{0.02} - 1 \right)^{0.492} \quad (16)$$

The goodness of the fit can be seen in Fig. 8. Based on Eq. (16), it can be further concluded that the critical fluid shear for PAC deposition (i.e., G_{cr} in Eq. (3)) is 0.37 Pa.

3.1.3 PAC adsorption rate

Fig. 9(a) shows the experimental results of the COD over time in the jar test, and hence the adsorption rate of k_s can be determined from the following equation:

$$\frac{dC}{dt} = -k_s \theta C \quad (17)$$

Eq. (17) gives the analytical solution of the form

$$k_s = \frac{\ln C_2 - \ln C_1}{\theta(t_1 - t_2)} \quad (18)$$

where C_1 and C_2 are the measured values of COD at different sampling times in the jar test.

The rate of COD adsorbed to PAC over time obtained using Eq. (18) is shown in Fig. 9(b). Similarly, the rate of nitrobenzene adsorbed to PAC could be determined using the same method. In this case, three initial nitrobenzene concentrations of 0.05, 0.10, and 0.20 mg/L were tested (see Fig. 10). It was found that as nitrobenzene was adsorbed, its concentration decreased rapidly within the first 30 min but more slowly as the experiment proceeded to the equilibrium concentration at approximately 180 min. At the PAC contact time of 30 min, the PAC was able to remove 75.8, 66.7, or 55.3% of the nitrobenzene when the initial nitrobenzene concentration was 0.05, 0.10, or 0.20 mg/L, respectively. In addition, it can be seen that adsorption rate of the nitrobenzene is much faster than that of COD. This can be explained by the fact that nitrobenzene has a broad pore size distribution. By comparison, the components in the COD of the water source are mainly hydrophilic (i.e. 68%) and are less easily removed by PAC.

Therefore, for organic pollutant removal in the water aqueduct, considering that both PAC deposition rate and pollutant removal rate vary significantly during the initial period of PAC advection and transport (i.e., approximately 0~30 min in this case), attention should be paid to the dynamics of PAC–organic pollutants. Modeling reliability depends on the

accurate measurement of the dynamic PAC settling velocity and pollutant removal rates. Note that the organic pollutant removal by PAC differs from place to place due to the competitive adsorption among the organic pollutants in the water sample, so the dynamic pollutant removal rate has to be determined for each studied system.

3.2 Modeling results of the PAC transport in the raw water aqueduct

Our targeted system has been described in Section 2.1. As depicted in Fig. 1, this city has two major drinking water sources from the upstream of Huangpu River and Yangtze River, which secure the water supply to the urban area and allow adjustment of the raw water extraction ratio between these two sources. For the targeted system, we have modeled a series of PAC transport scenarios along the aqueducts with water supply discharges of 5, 10, 15, 20, 25, 30, and 40% of the peak flow. Considering that the aqueduct is full of water and exhibits pressurized flow, we can derive the flow velocity by using

$$U = Q/A \quad (19)$$

where Q is the flow discharge and A is the cross-sectional area. The peak flow rate for the aqueduct is $62.5 \text{ m}^3/\text{s}$ and the cross-sectional areas are given in Section 2.1, so the mean flow rate can be obtained and is shown in Table 1.

The PAC transport results from our modeling of the aqueducts are presented in Fig. 11 for water supply discharge ranging from 5 to 40% of

the peak flow, where relative PAC concentrations along the two routes are shown against the aqueduct distance. As shown in Fig. 11(a), along the Changqiao DWTP branch, the PAC deposition occurred in two segments: the first was the reach between Songpu and Caohang and the second was between Caohang and Changqiao. The concentration remained constant over the other aqueduct sections. Similar results can be seen in Fig. 11(b), where it can be noted that a quick drop of the PAC concentration occurred from Caohang to Linjiang. The reason for the concentration decrease is that the shear stress cannot sustain the PAC suspension when the hydrodynamic environment changes at the beginning of a new reach. As shown in Eq. (4), the actual shear stress is proportional to the water flow within the aqueduct. As the raw water is conveyed to the DWTP (see Fig. 1), the water discharge down the aqueduct decreases. Therefore, a weaker stress may occur within the downstream aqueduct reach, and a certain quantity of the PAC transported from the upstream segment will be deposited. However, if the fluid shear in the downstream control segment is equal to or greater than that in the upstream segment due to the decreased hydraulic radius, then the PAC arriving from the upstream segment will have gone through the deposition process already and will have reached the steady-state concentration. This explains why the PAC concentration over the aqueduct remains unchanged down the Changqiao in Fig. 11(a) and Linjiang in Fig. 11(b). Furthermore, if the water supply

is up to 50% of the peak flow, the actual fluid shear throughout the aqueduct reaches will be above the critical fluid shear and PAC deposition will not occur within the whole aqueduct.

3.3 Model validation and application in the field

3.3.1 Validation of the numerical model

Before applying the present model to the field, a model validation has been conducted by comparing the results with field observations and the flume test.

A field measurement conducted in September 2009 at the study site can be used to validate the numerical model. During this period, the average water temperature was 22 °C, which was comparable to the temperature of laboratory experiments described above. The actual water flow rate was $3.5 \times 10^6 \text{ m}^3/\text{d}$ for the modeling calibration scenario. The PAC was injected into the water source at a concentration of 20 mg/L. The COD concentration was measured at the Linjiang and Yangshupu DWTPs to assess the pollutant removal by PAC. The background dissolved COD concentration at the water source was approximately 4.5 mg/L. Using the estimated k_s value derived from Fig. 9, we can predict the COD concentration along the aqueduct, as shown in Fig. 12. This result is comparable with the measured COD at two DWTPs (see Table 2).

In the laboratory jar tests or pilot-scale experimental setup, the dynamic behaviour of organic pollutant removal is a pure adsorption process; by contrast, the organic pollutant removal along an actual aqueduct incorporates pollutant advection–dispersion and a dynamic adsorption process. Therefore, pollutant transport and removal may differ between the laboratory jar and actual water aqueduct, due to the effect of shear flow dispersion in the actual aqueduct. In this case, the dispersion coefficient D is calibrated to be $1.0 \text{ m}^2/\text{s}$. Theoretically, the dispersion coefficient is very dependent on the mean flow velocity of the channel; that is, the higher the mean flow velocity, the greater the advection–dispersion effect.

From a general perspective, the dispersion coefficient can be estimated by the equation (Fisher et al., 1979)

$$D = \frac{aU^2W^2}{hu_*} \quad (20)$$

where a is an empirical coefficient and u_* is the bottom shear velocity.

Eq. (20) shows that the dispersion coefficient is proportional to the square of the mean flow velocity in the water aqueduct. Consequently, the estimated dispersion coefficient is $0.1\text{--}2.4 \text{ m}^2/\text{s}$ for a water supply ranging from 5 to 100% of the peak flow.

Since the nitrobenzene cannot be delivered in the field test for safety concerns, the model validation of the nitrobenzene transport and removal

test could only be performed in the laboratory using the annular flume adsorption experiments described above. Specifically, for two initial nitrobenzene concentrations of 0.10 and 0.20 mg/L, the modeled results were compared with the measured ones from the rotating annular flume at the shear stress of 0.10 Pa, as shown in Fig. 13. The mean relative error was found to be 5%, which further validated our developed model.

3.3.2 Assessment of nitrobenzene removal in the raw water aqueduct

After model validation, the model was used to assess the PAC operation strategy in the aqueduct system. Our modeling scenario is the removal from the water source of nitrobenzene at concentrations of 0.10 and 0.20 mg/L, which exceed the standard for drinking water use (i.e., 0.017 mg/L) by factors of approximately 5 and 11.

As discussed above, the critical shear stress without deposition is 0.37 Pa, corresponding to a water discharge of 24.38 m³/s or 39% of the peak flow. Therefore, at a water supply above 39% of the peak discharge, no deposition will occur within the PAC adsorption time (i.e., approximately 180 min) and the minimum PAC dose remains unchanged. However, if the water supply falls below 39% of peak flow, an increased PAC dose should be used to compensate for the reduction of the nitrobenzene removal rate due to the PAC settling.

Specifically, the minimum PAC doses for the flow rates of 5 to 40% of the peak discharge are listed in Table 3 and correspond to fluid shear of

0.01 to 0.39 Pa. For the initial nitrobenzene concentration of 0.10 mg/L, the minimum PAC dose lies between 36 and 41 mg/L, and for the initial nitrobenzene concentration of 0.20 mg/L, the minimum PAC dose is 58–65 mg/L.

Fig. 14 shows the simulated distribution of the nitrobenzene concentration over the water aqueduct. Note that the PAC contact time required to reach a steady nitrobenzene concentration is ~180 min, which corresponds to a distance of 769–4614 m along the aqueduct. Therefore, PAC removal only occurs within the first reach of the aqueduct and there is no need to specify the PAC dose for different DWTPs.

It is important to point out that in the scenario of serious water-source pollution (e.g., a nitrobenzene concentration of 0.20 mg/L in this case), the water aqueduct cannot be operated at full peak discharge. The reason is that a high PAC dose that is not deposited in the aqueduct could disrupt the DWTP, that is, by clogging the filter system. According to our survey, the PAC concentration at the DWTP should not exceed 30 mg/L. Therefore, if the PAC dose at the water source is above 30 mg/L, the actual fluid shear within the aqueduct should be below the critical fluid shear (i.e., 0.37 Pa in this case), so that a certain portion of the PAC can settle along the aqueduct bed before reaching the DWTP. To address this issue, a series of simulations were performed and the results are shown in Table 4, including the cases with different flow rates. In this table, the

suspended PAC concentration entering the DWTPs remains constant, except for Changqiao DWTP, because the PAC concentration has reached the steady state at Linjiang station, as discussed above. Specifically, in this case, the fluid shear cannot exceed 0.40 Pa (i.e. the flow rate of 25.4 m³/s) or 0.18 Pa (i.e. the flow rate of 17.1 m³/s) in treating the initial nitrobenzene concentrations of 0.10 and 0.20 mg/L, to avoid the clogging issue.

Theoretically, the actual fluid shear is proportional to the water flow velocity and inversely proportional to the hydraulic radius (see Eq. (4)). Therefore, if we want to increase the emergent water-supply flow under a given fluid shear, the aqueduct hydraulic radius should be enlarged. An aqueduct with a relatively large hydraulic radius may be characterized as having a large width-to-depth ratio. The lower aqueduct depth could further accelerate PAC deposition on the aqueduct bed (see Eq. (9)). Based on the above discussion, this study also provides insights for future aqueduct geometry design that would enable emergent water supply operation to be optimized from a wider perspective.

4. Conclusion

The dynamics of PAC and organic pollutants within aqueducts are determined by the flow discharge, PAC properties and concentration, and pollutant characteristics. The interactions of the domains are related to: (1) PAC properties relative to the PAC settling rate, which dictates PAC

deposition on the bed; (2) flow regimes relative to fluid shear stress, which also dictates PAC deposition on the bed; (3) initial PAC dose relative to PAC concentration along the aqueduct, which dictates the potential efficiency of pollutant removal; (4) pollutant behaviour relative to sorption parameters, which also dictates the removal degree. A combination of the PIV-based PAC settling test, rotating annular flume-based PAC transport test, and laboratory-jar-based PAC adsorption test has been proven effective in understanding the dynamics of the above PAC–organic pollutants, and a coupled dynamic PAC–pollutant removal model is developed to guide the PAC operation strategy within the aqueduct.

For scenarios of serious water-source pollution, a high PAC dose should be used but the actual fluid shear within the aqueduct must be lower than the critical fluid shear (e.g., 0.37 Pa in this case). As a result, a portion of the PAC is deposited on the aqueduct bed to prevent excessive PAC to clog the DWTPs. Our study can also outline the design of the new raw water aqueduct: at a given fluid shear, the larger the aqueduct hydraulic radius, the bigger the actual water supply discharge should be. An aqueduct exhibiting a relatively large width-to-depth ratio is more effective in enhancing the emergent water-supply flow.

The modeling framework is useful for assessing emergency management protocols for PAC deployment within the aqueduct to

safeguard the drinking water supply, and the developed algorithms and approaches can be used for similar problems. Future studies will focus on developing a database as the knowledge for response scenarios of water source disruptions.

Acknowledgements

This work was supported by the National Science Foundation of China (Grant No. 11102137) and the research project funded by Shanghai Science and Technology Commission (Grant No. 13210701001).

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Fig. 1. The raw water aqueduct system of the upstream Huangpu River in Shanghai, China.

w_0 : measured PAC settling velocity at initial time t_0 ; p_0 : PAC deposition
fraction at initial time t_0 ; w_1 : measured PAC settling velocity at time t_1 ; p_1 : PAC
deposition fraction at time t_1 ; w_n : measured PAC settling velocity related to time t_n ;
 p_n : PAC deposition fraction at time t_n .

Fig. 2 - Schematic representation of dynamic PAC transport modeling.

(a) Experimental set-up of the PIV

(b) Photo of the experimental set-up

Fig. 3 Experimental set-up for the PIV test on the PAC particle settling.

(a) The experimental set-up of the rotating annular flume

(b) Photos of the experimental set-up and the sampling outlets

Fig. 4 The annular circular flume for the PAC transport experiment.

Fig.5 Distribution of measured PAC particles.

(a) A typical CCD image of the PAC particles and the post-processed settling velocity of the test window (uncertainty of PAC settling velocity across the captured image was less than 0.5%)

(b) The time series of the averaged PAC settling velocity

Fig.6 The PIV experiments on the PAC particle settling.

Fig. 7. Results from the PAC deposition experiments as a function of the PAC doses of 10 mg/L (blue) and 80 mg/L (red) at various average flow velocities.

Fig.8 The PAC steady-state concentration at different flume velocities.

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(a)

(b)

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Fig. 9 The experimental results of the COD removal experiments with a PAC dose

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of 10 mg/L: (a) the COD reduction in the lab jar test; and (b) k_s as a function of time.

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(b) (b)

Fig. 10 The experimental results of the nitrobenzene removal by the PAC dose of 30 mg/L: (a) The nitrobenzene reduction in the lab jar test; and (b) k_s as a function of time.

(a) Changqiao DWTP branch

(b) Yangshupu DWTP branch

Fig.11 The modeled PAC concentration over the aqueducts.

Fig. 12 The predicted COD concentration along the aqueduct at PAC dose of 20 mg/L and water flow discharge of $3.5 \times 10^6 \text{ m}^3/\text{d}$.

(a) Result with the initial nitrobenzene concentration of 0.10 mg/L

(b) Result of the initial nitrobenzene concentration of 0.20 mg/L

Fig.13. Comparison between the simulated and the measured nitrobenzene concentrations in the flume with a shear stress of 0.10 Pa.

(a) initial nitrobenzene concentration of 0.10 mg/L

(b) initial nitrobenzene concentration of 0.20 mg/L

Fig. 14 The predicted nitrobenzene removal over the aqueduct with different shear stress and initial nitrobenzene concentrations.

Table 1 Mean flowing velocity in the aqueduct reach for different water supply discharges

Water discharge (% of the peak flow)	Mean flowing velocity at different aqueduct reaches (m/s)				
	Songpu-Caohang	Caohang-Changqiao	Changqiao-Changqiao DWTP	Caohang-Linjiang	Linjiang
5	0.06	0.04	0.10	0.05	0.07
10	0.13	0.07	0.19	0.09	0.14
15	0.19	0.11	0.29	0.14	0.22
20	0.26	0.15	0.39	0.19	0.29
25	0.32	0.18	0.48	0.23	0.36
30	0.38	0.22	0.58	0.28	0.43
40	0.51	0.29	0.77	0.38	0.58

756 **Table 2** Comparison between simulated and modeled COD removal by PAC in the aqueduct

Location	Operating time		Comparison			
	Starting time	Ending time	Raw water COD (mg/L)	Measured COD (mg/L)	Simulated COD (mg/L)	Relative error (%)
Songpu water source	2009/9/21 10:00	2009/9/22 22:00	4.5			
Linjiang DWTP	2009/9/21 18:00	2009/9/23 6:00		3.65	3.62	0.8
Yangshupu DWTP	2009/9/22 0:00	2009/9/23 12:00		3.68	3.62	1.6

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Table 3 Critical PAC dose (mg/L) to remove nitrobenzene at different shear stresses

Initial nitrobenzene concentration (mg/L)	Shear Stress (Pa)						
	0.0 1	0.0 2	0.0 5	0.1 0	0.1 5	0.2 2	0.39
0.10	41	40	40	39	39	38	36
0.20	65	64	64	63	62	60	58

Table 4 Simulated PAC concentrations reaching the DWTPs at different shear stresses and initial nitrobenzene concentrations

Initial		Fluid shear (Pa)							
nitrobenzene concentration (mg/L)	PAC concentration (mg/L)	0.01	0.02	0.05	0.10	0.15	0.22	0.39	0.61
0.10	PAC concentration at starting point	1	0	0	9	9	8	6	6
	Suspended PAC reaching Changqiao DWTP	0	0.1	0.7	0.6	2.0	7.8	6.2	0.3
	Suspended PAC reaching other DWTPs	0	0.1	0.8	2.2	7.0	0.4	8.9	5.0
0.20	PAC concentration at starting point	5	4	4	3	2	0	8	8
	Suspended PAC reaching Changqiao DWTP	0	0.1	0.9	2.2	9.0	6.7	2.2	8.8
	Suspended PAC reaching other DWTPs	0	0.2	0.8	9.7	7.0	2.2	6.5	6.4