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Chemical oxygen demand oxidation via sustained-release persulfate balls: a rate-compatibility study of flow velocity, releasing, and oxidation

Key words:

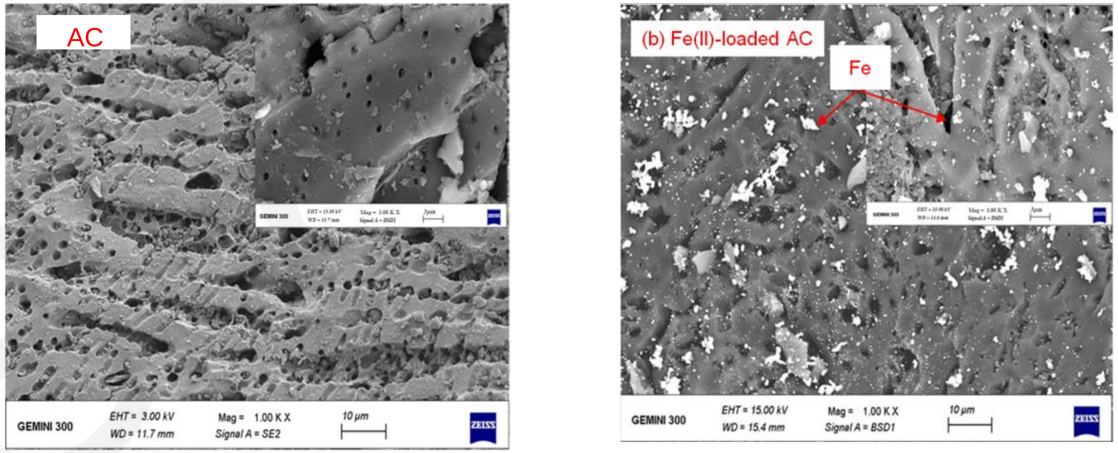
Chemical oxygen demand (COD); Sodium persulfate (PS); Sustained-release balls; Permeable reactive barrier (PRB); Fe(II)-loaded activated carbon (Fe-AC)

Introduction

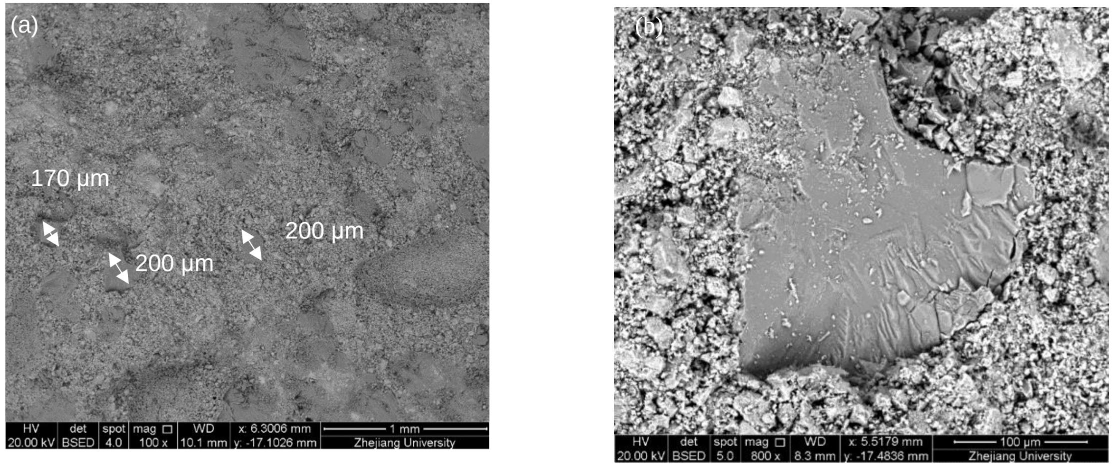
- Site removal of organic contaminants (chemical oxygen demand, or **COD**) from municipal solid wastes (MSW) by permeable reactive barrier (**PRB**) is popular
- Oxidation by **sustained-release persulfate (PS) balls** is adopted
- Release rate of PS balls, a function of **ball diameter**, should match chemical kinetics for maximal efficiency
- The compatibility of **flow velocity**, **oxidant-releasing rate** and **oxidation rates** is challenging

Materials

- Sustained-release persulfate balls, with weight ratio of **10.7:0.24:1.4:1** (**PS:cement:sand:water**), was manufactured
- COD removal rate maximal at **95%**
- SEM images of AC, Fe-AC revealed that **crystals of Fe(II) occupied and clogged AC micropores**
- PS ball diameter between **170 and 200 μm** in the sustained-release balls



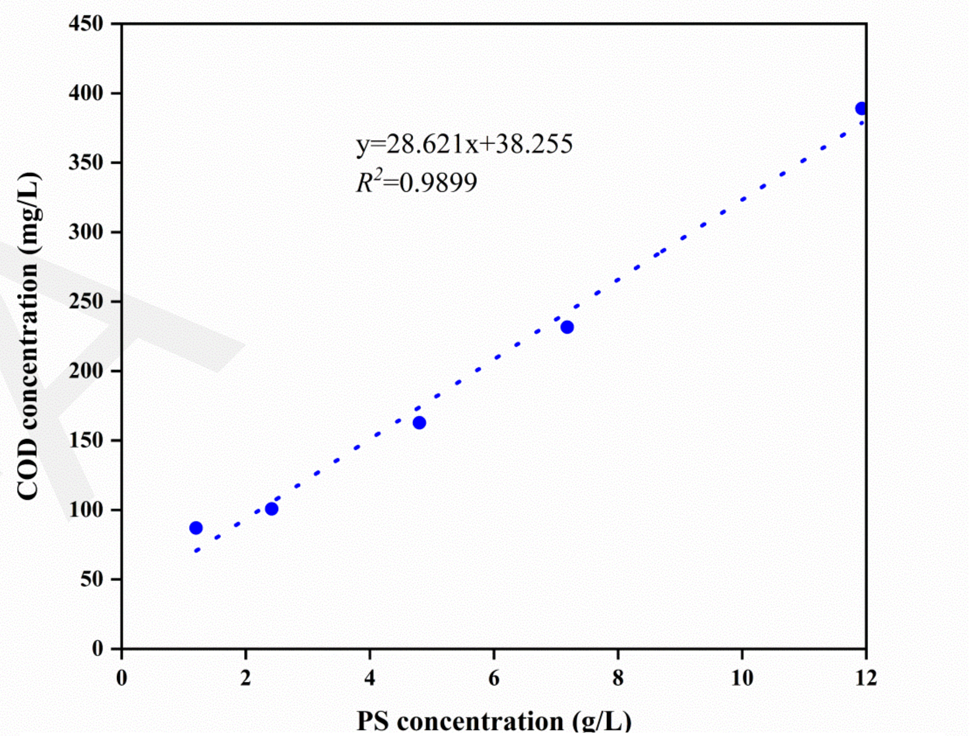
SEM images of AC before and after Fe(II) loading

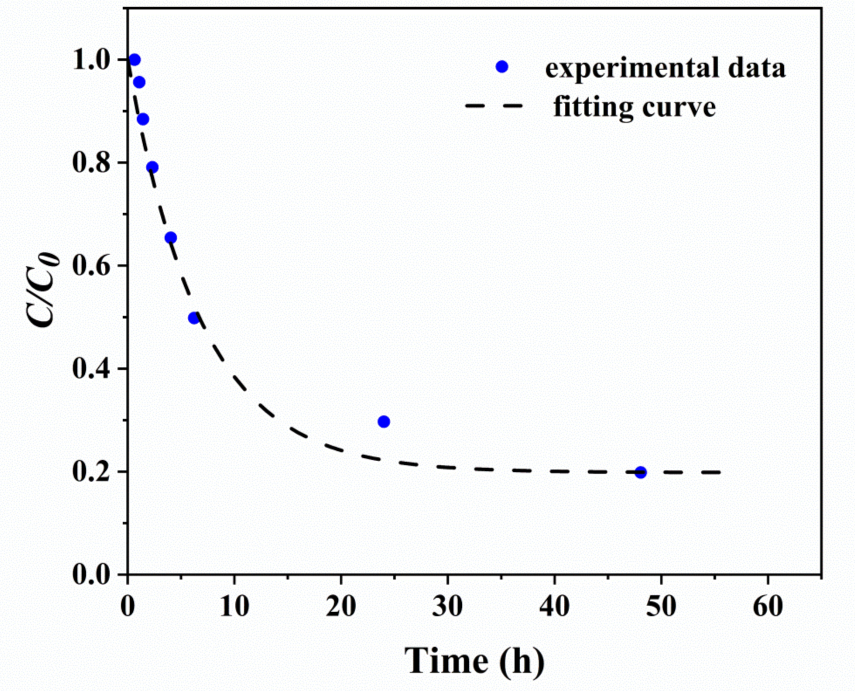


SEM images of sustained-release PS balls

COD Oxidation Kinetics

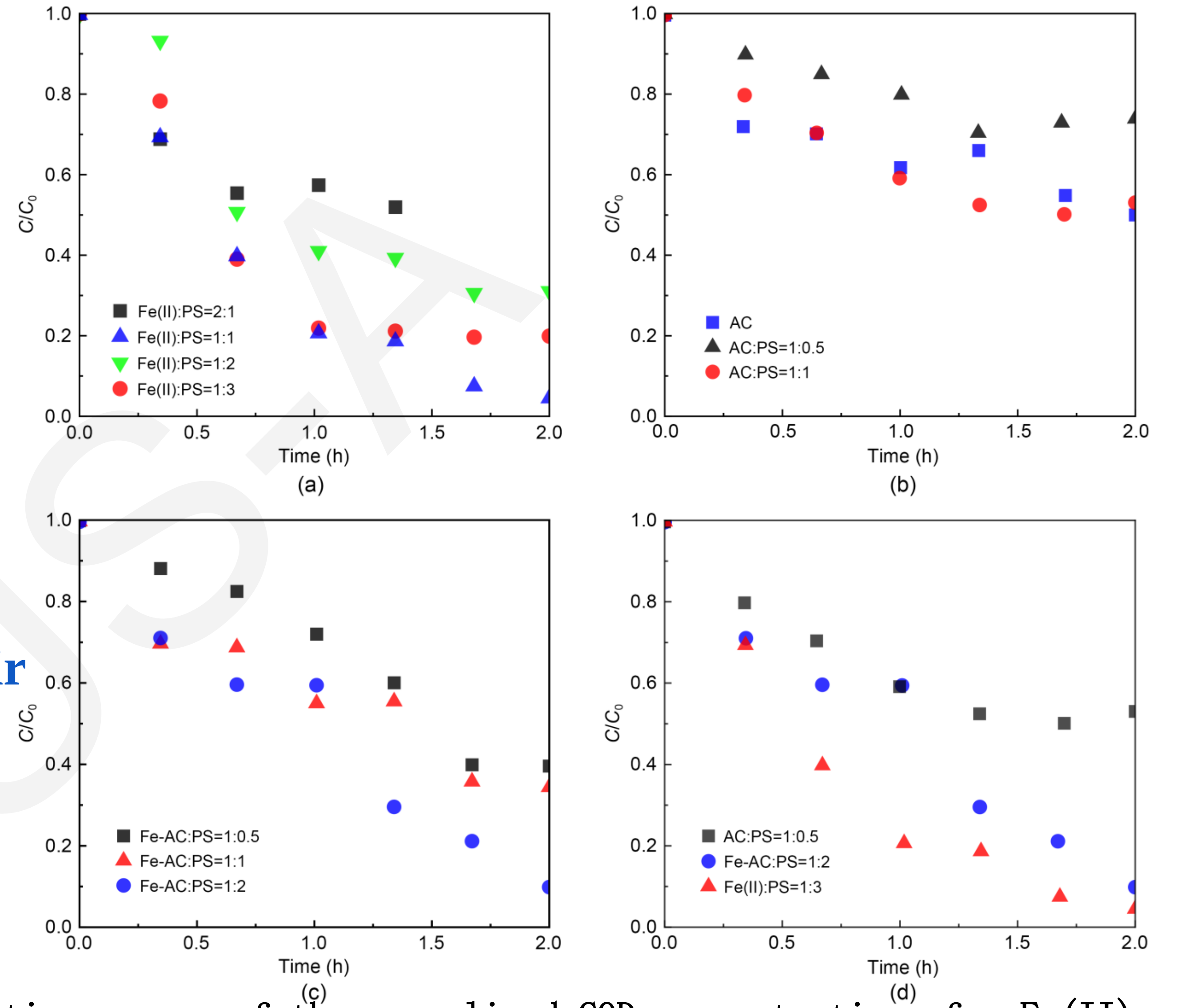
- $Cr_2O_7^{2-} + 3S_2O_8^{2-} + 2H^+ \rightarrow 2Cr^{3+} + 6SO_4^{2-} + H_2O + 3O_2.$
- COD removal by Fe-AC-catalyzed PS
- **First-order** kinetic reaction assumption
  - ***K* is 0.83 h^{-1}**
  - **$t_{0.5}$ is 0.83 h**
- COD removal by Fe-AC-catalyzed 4 pebbles of sustained-release PS balls
- **Pseudo-first-order** kinetic reaction assumption
  - ***K* is 0.15h^{-1}**
  - **$t_{0.5}$ is 4.62 h**





COD removal efficiency

- Fe(II):PS = 1:2, COD removal rate was 95%
- Catalysis of PS by Fe-AC impressive COD removal rate of up to **90%**
  - **$S_2O_8^{2-}$:12COD ratio was 1.02**
  - **Fe^{2+} easily oxidizing in the presence of air**



Time-evolution curves of the normalized COD concentrations for Fe(II) (ferrous sulfate) and PS at different ratios (a), AC and PS at different ratios (b), Fe-AC and PS at different ratios (c), and AC and PS, Fe-AC and PS, as well as Fe(II) and PS at a certain ratio (d)

COD removal efficiency

- Linear relationship between the ball diameter *D* (mm) and half-life period
  - $t_{0.5}$=0.060*D*+0.215
- The ball diameter and kinetic rate constant of PS release (*k*)
  - *k*=544.6/*D*

Release rates of the sustained-release PS balls

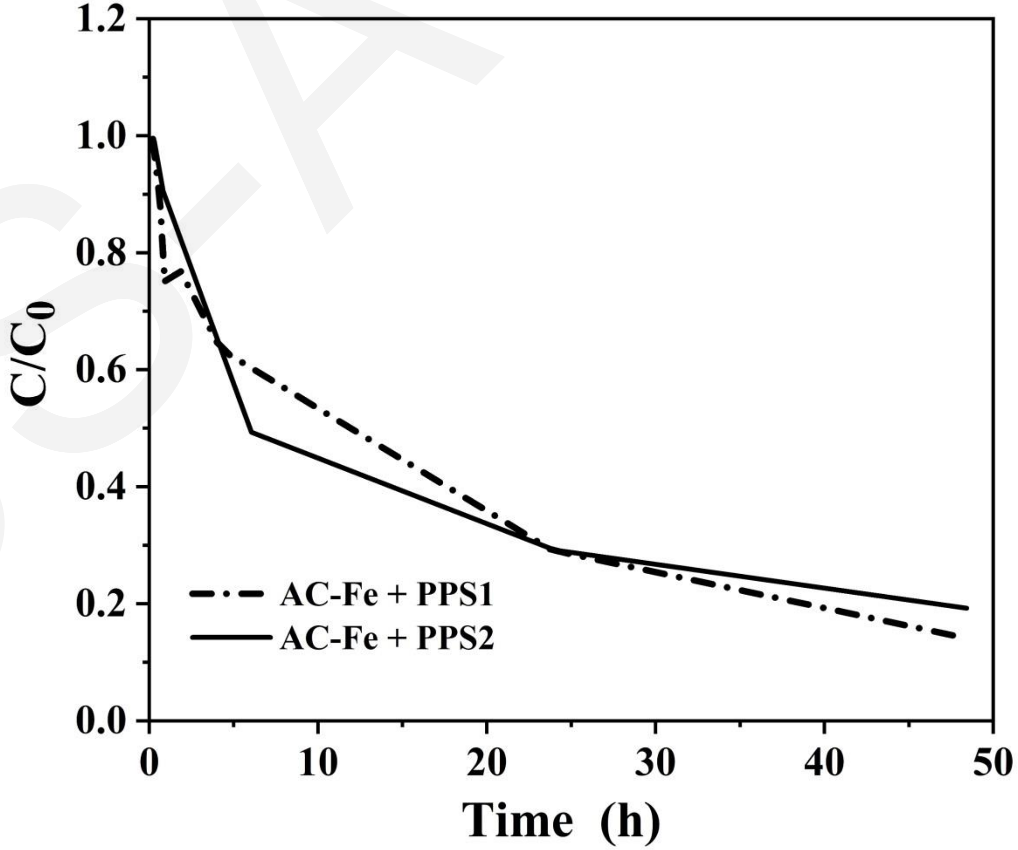
Particle size (mm)	Fitting curve	Release rate (mg/(g·d))	$t_{0.5}$ (d)
5	$q_1 = 7098t/(63.14 + 112.27t)$	112.27	0.56
10	$q_2 = 4370t/(55.23 + 79.14t)$	79.14	0.70
15	$q_3 = 1064t/(35.92 + 29.60t)$	29.60	1.21
20	$q_4 = 778t/(32.91 + 23.63t)$	23.63	1.39

Sustained-release ball parameters for different sizes

Ball diameter (mm)	q_{max} (mg/g)	K (mg/(g•d))	SSE	R^2
5	63.14	112.27	14.61	0.9879
10	55.23	79.14	16.77	0.9873
15	35.92	29.60	15.82	0.9779
20	32.91	23.63	8.05	0.9872

Compatibility between the PRB flow rate and the PS release rate

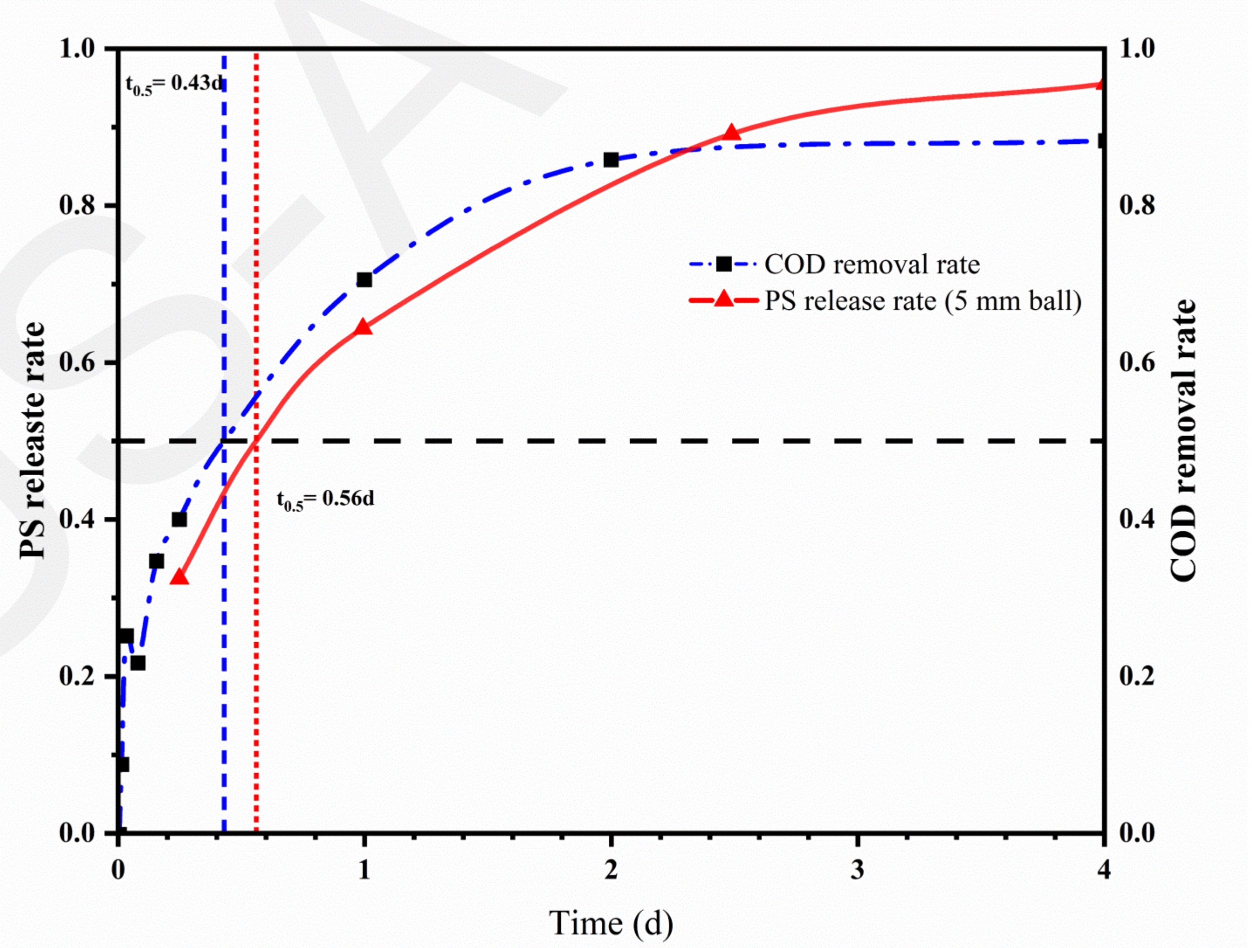
- $aAV_0C_0 \leq \frac{A}{D^2Mk} \times 10^6$
- **Column test**
- **COD concentration = 200 mg/L**
- **maximum flow rate in the PRB =0.21 m/d**



Removal effect of COD with an oxidizing filler by using Fe-AC with two pebbles (PPS1) and four pebbles (PPS2) of sustained-release PS balls

Compatibility of the PS release rate and COD oxidation rate

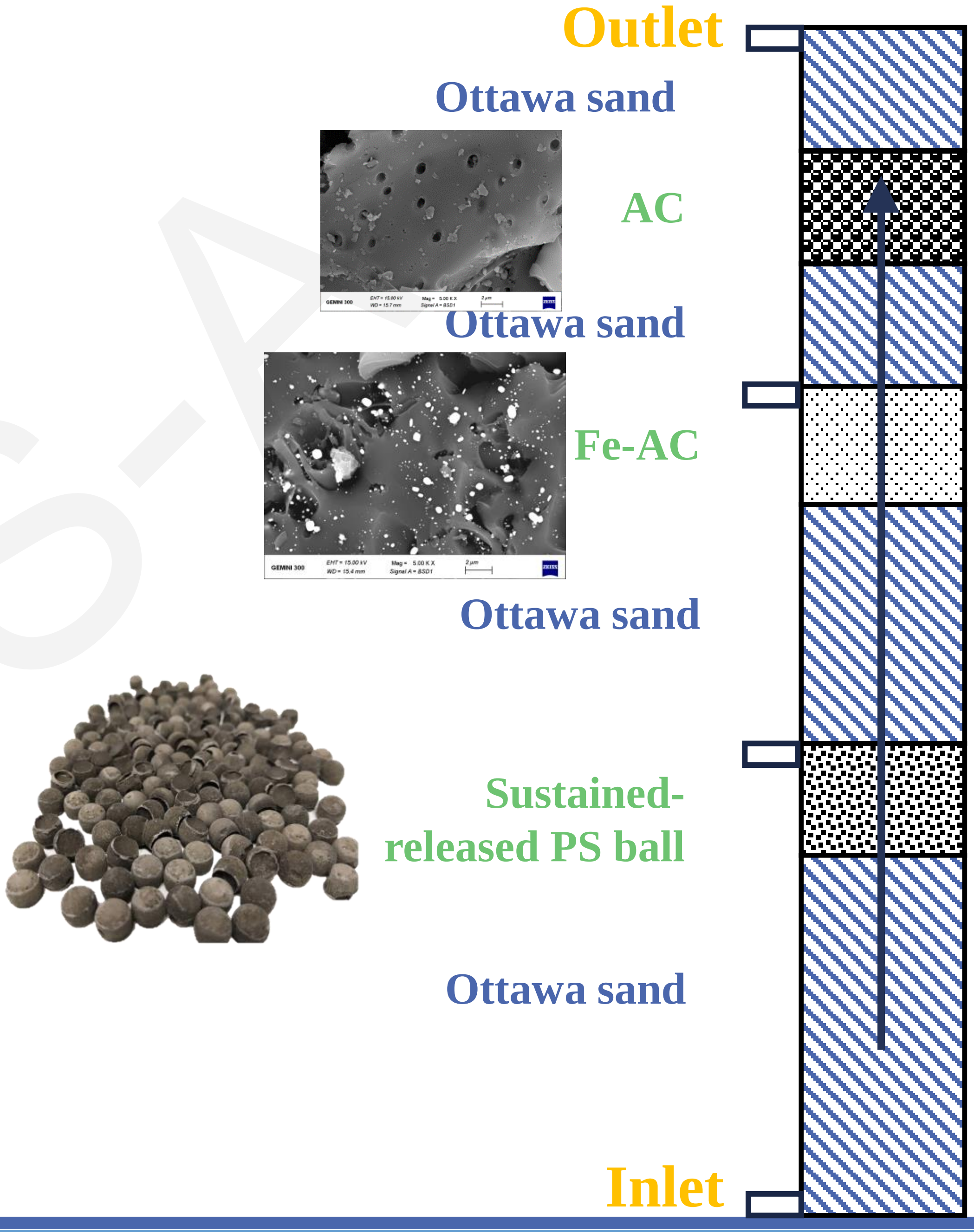
- $R_{\text{COD}} = k \cdot \frac{\partial c_{COD}}{\partial t}$
- **Oxidation reaction half-life (0.43 d) close to PS release half-life (0.56 d) of a 5 mm ball**



Kinetic chemical reaction results of Fe-AC-catalyzed sustained-release PS balls that oxidize COD

Simulation of PRB serviceability

- $\frac{C_f}{C_0} = \frac{1}{2}\,\mathrm{erfc}\left(\frac{R_d L - V_s t_b}{2\sqrt{D_h R_d t_b}}\right)\frac{1}{2}\exp\left(\frac{V_s L}{D_h}\right)\mathrm{erfc}\left(\frac{R_d L + V_s t_b}{2\sqrt{D_h R_d t_b}}\right)$
- V_0=0.21 m/d
- R_d=1.27
- L=3 m (thickness of the PRB)
- Service life of this PRB with a breakthrough threshold of 10% is two years



Conclusions

- An investigation of the COD oxidation by persulfate sustained-release balls in a PRB setup carried out
- the highest COD removal rate of 95% obtained at optimum dosage ratios of Fe-AC:PS balls and initial PS:COD ratio (12:1 and 12.24:1)
- Sustained-release PS ball diameter of 5mm is compatible with COD oxidation rate
- COD oxidation rate ($t_{0.5}$=0.43 d) compatible with the 5 mm PS balls release rate ($t_{0.5}$=0.56 d)