Biochar supported magnetite and zerovalent iron nanoparticles for selenium removal

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Inland wetland:

- The source and sink of heavy metals and recalcitrant organic compounds;
- Great impact on water environment and ecological safety.

Increasing severe pollution of Dongting Wetland by recalcitrant organics and heavy metals

- ➔ Serious pollution on rice, sedge and reed
- ➔ Ecological deteriorating

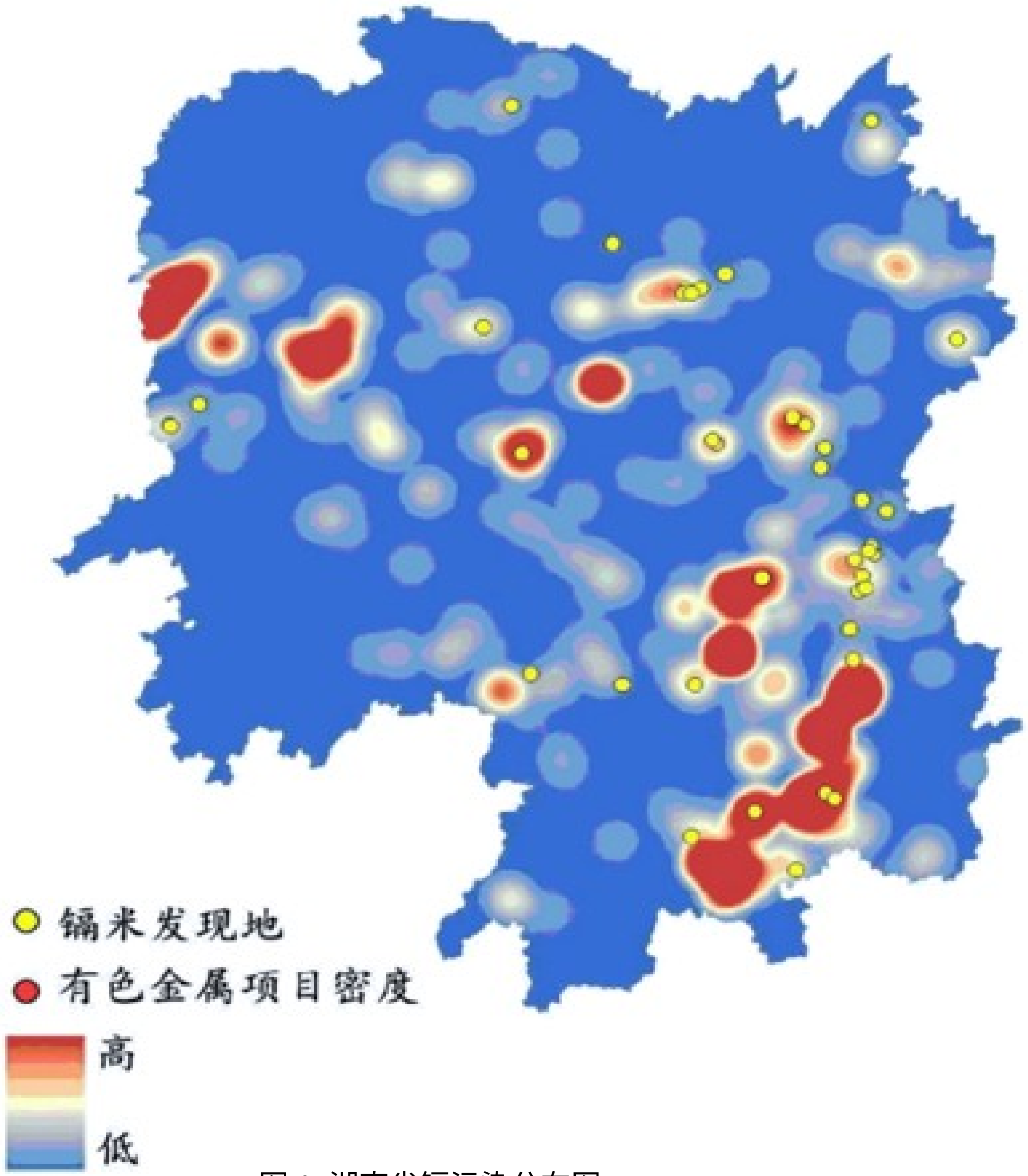


图 1 湖南省镉污染分布图

Black is the new green

Nature 442, 624–626 (2006)

Chemical Engineering Journal 373 (2019) 902–922

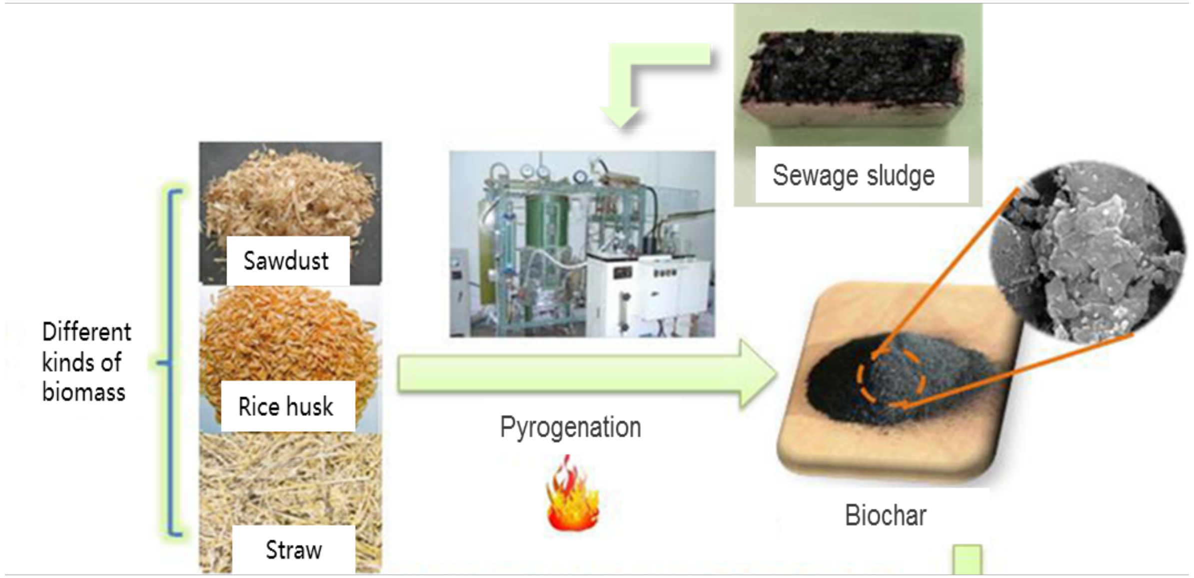
Remediation of wetland polluted by heavy metals and recalcitrant organics

A high-profile subject!

- to build functional materials that can adsorb and degrade heavy metals and recalcitrant organics with high efficiency;
- to find remediation technologies with high efficiency, energy conservation and free secondary pollution.

- Good biocompatibility and low environmental risk;
- Developed pore structure, abundant oxygen-containing functional groups and large specific surface area;
- Ability to remove pollutants by adsorption, redox and catalytic degradation;
- Great application potential in in-situ remediation wetland polluted by heavy metals and recalcitrant organics;
- Low cost of materials preparation for large-scale application.

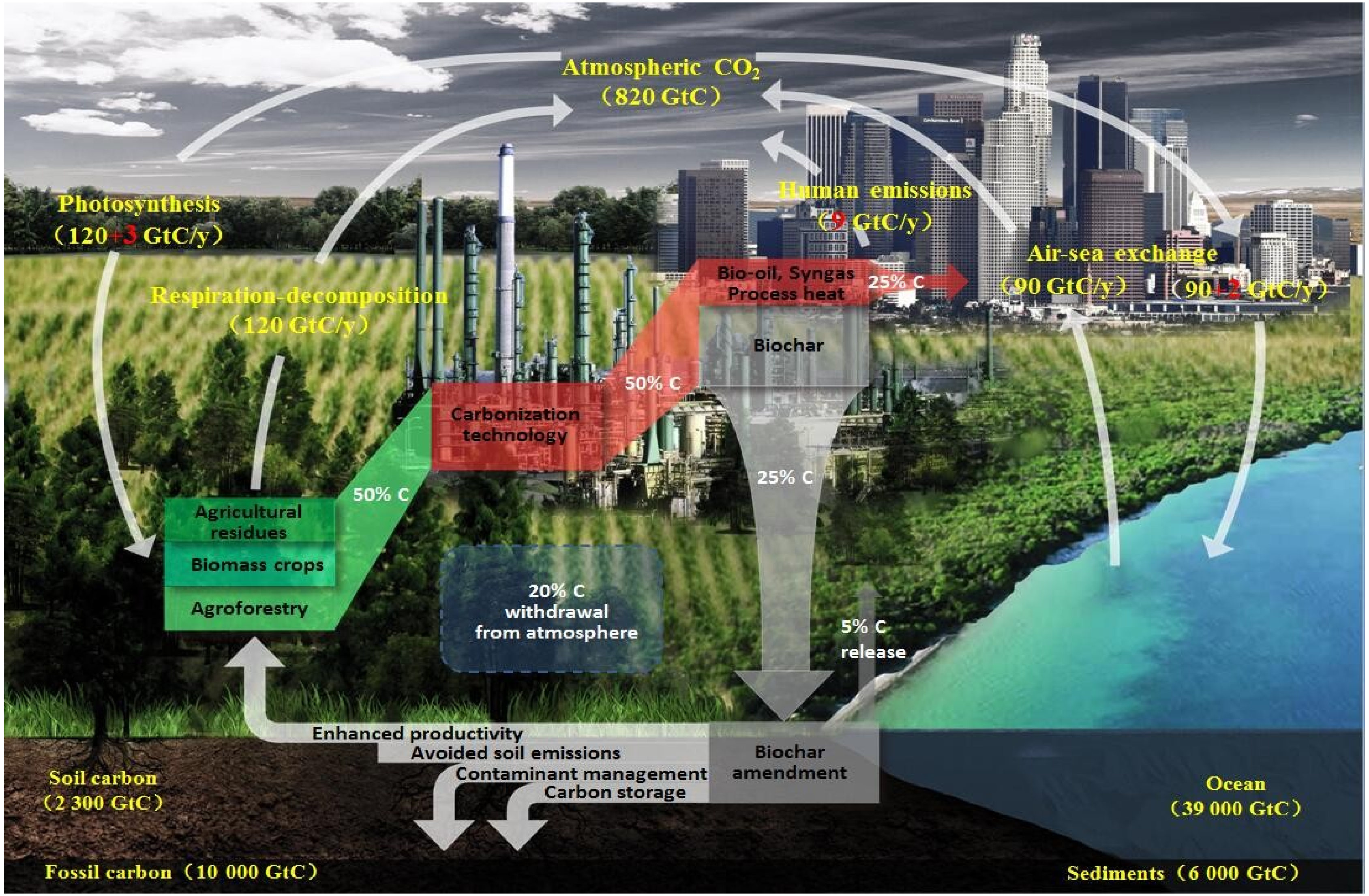
Biochar



- Prepared via pyrolysis and carbonization of bio-feeds in anaerobic or anoxic condition;
- Main composition elements: C, H, O, N, S and a small quantity of microelement;
- Existing in the form of amorphous carbon and graphite structure.

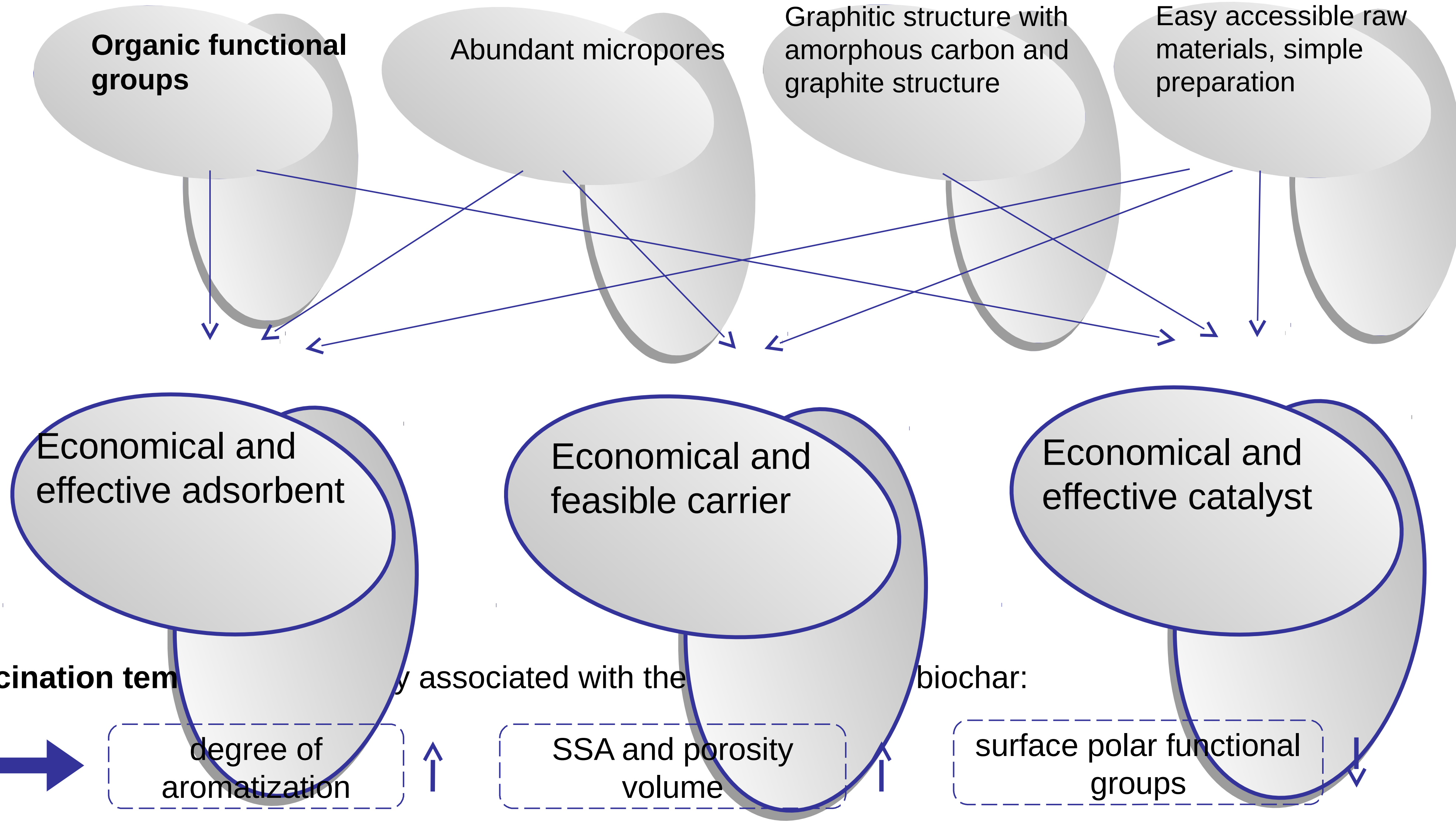
Farming and forestry supply **Livestock manure** **Household refuse** **Activated sludge**

Sustainable biochar applications and the global carbon cycle and biomass carbonization technology



Chemical Engineering Journal 373 (2019) 902–922

Biochar



Characteristics

Organic functional groups

Abundant micropores

Graphitic structure with amorphous carbon and graphite structure

Easy accessible raw materials, simple preparation

Application

Economical and effective adsorbent

Economical and feasible carrier

Economical and effective catalyst

Raw materials and **calcination tem** y associated with the biochar:

Calcination temperature ↑ → degree of aromatization ↑

SSA and porosity volume ↑

surface polar functional groups ↓

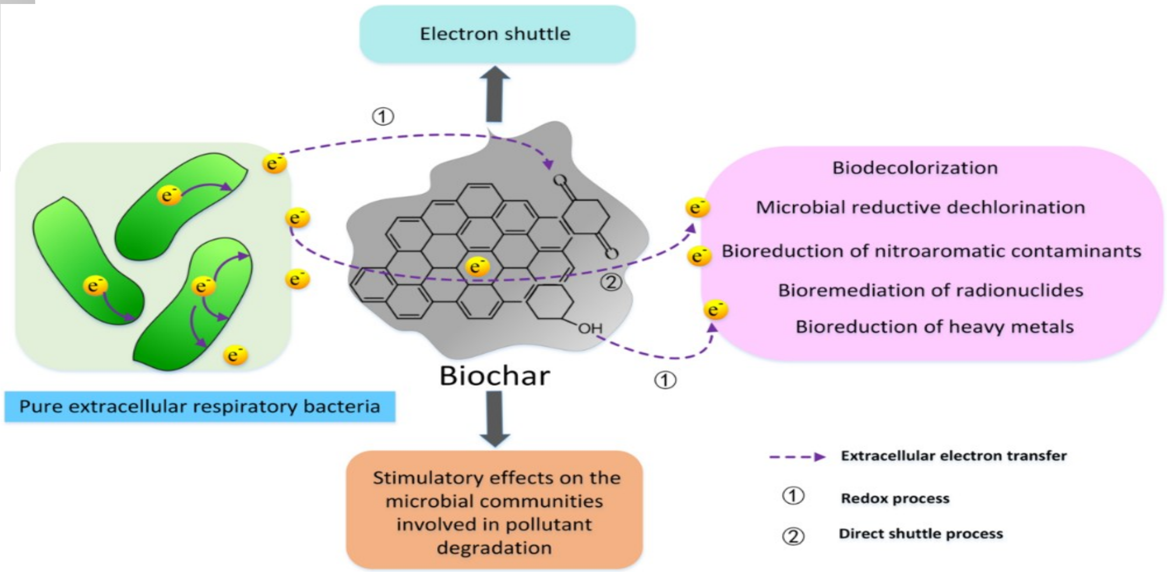
Biochar

Characteristics

Organic functional groups

Redox-active group

condensed aromatics



Application

Cooperating with the electron transfer process of microorganisms to realize the redox degradation of environmental pollutants.

The necessity of biochar modification

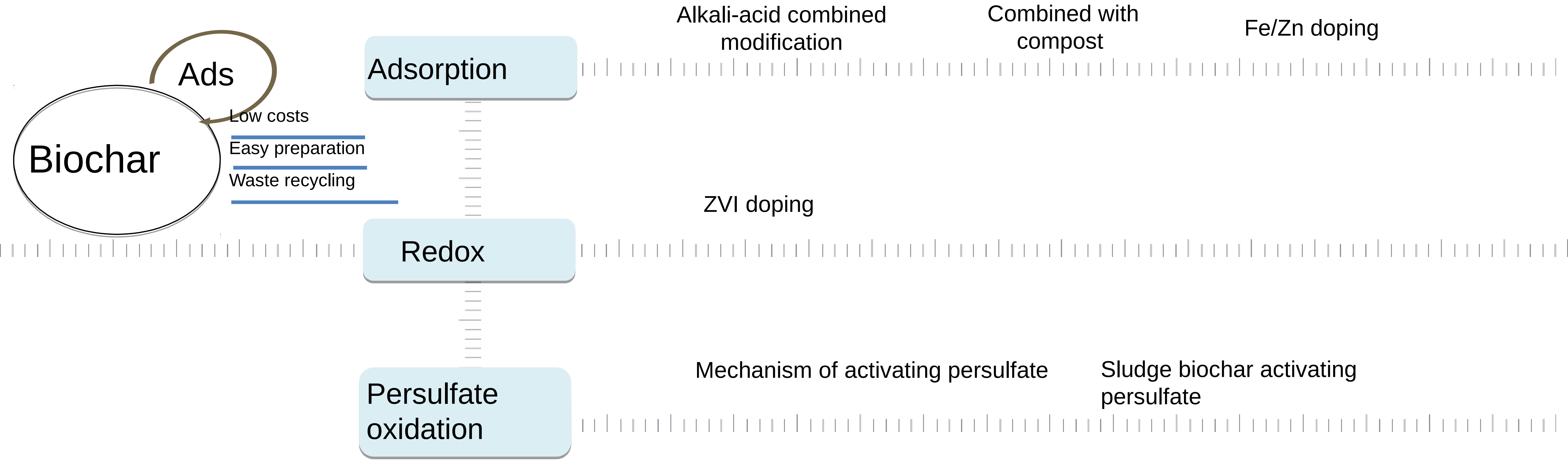
Biochar application has bright prospects, based on the combination of solid waste recycling and environmental pollution prevention.

Unmodified Biochar

- Abundant micropores lack of mesoporous structure;
- Limited types and quantities of surface organic functional group;
- Few adsorption sites and weak adsorption capacity;
- Few effective catalytic sites and weak catalytic capacity;
- Not conducive to the load of larger particulate matter.

It is needed to modify biochar appropriately for its performance improvement.

Biochar modification for wetland remediation



Biochar

Ads

Low costs

Easy preparation

Waste recycling

Adsorption

Alkali-acid combined modification

Combined with compost

Fe/Zn doping

Redox

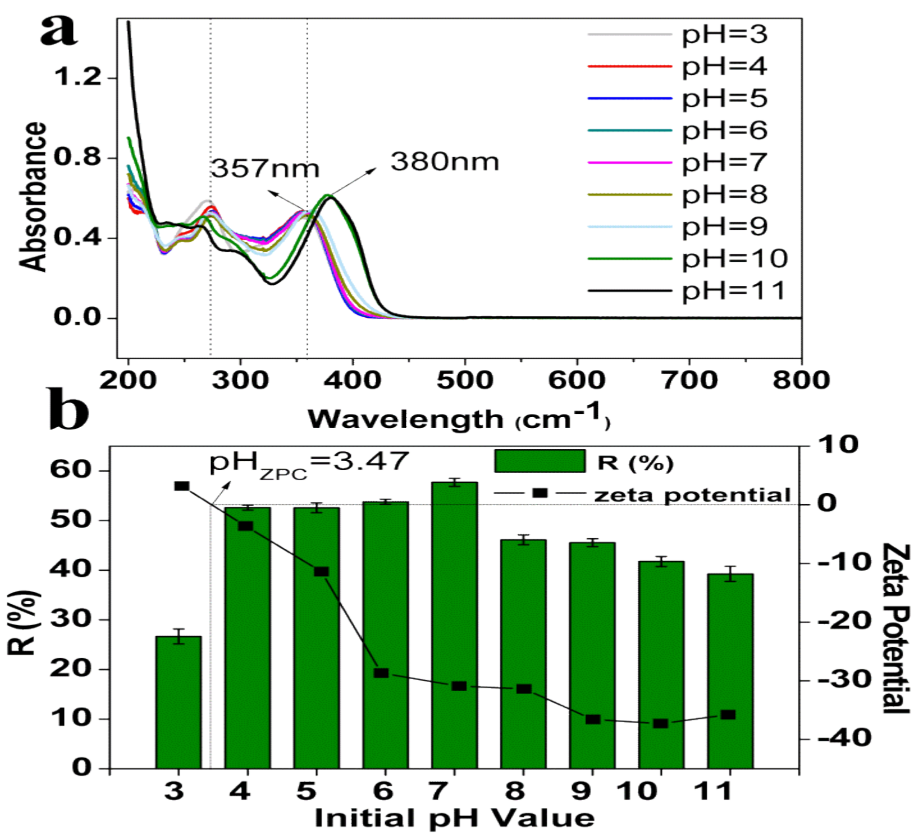
ZVI doping

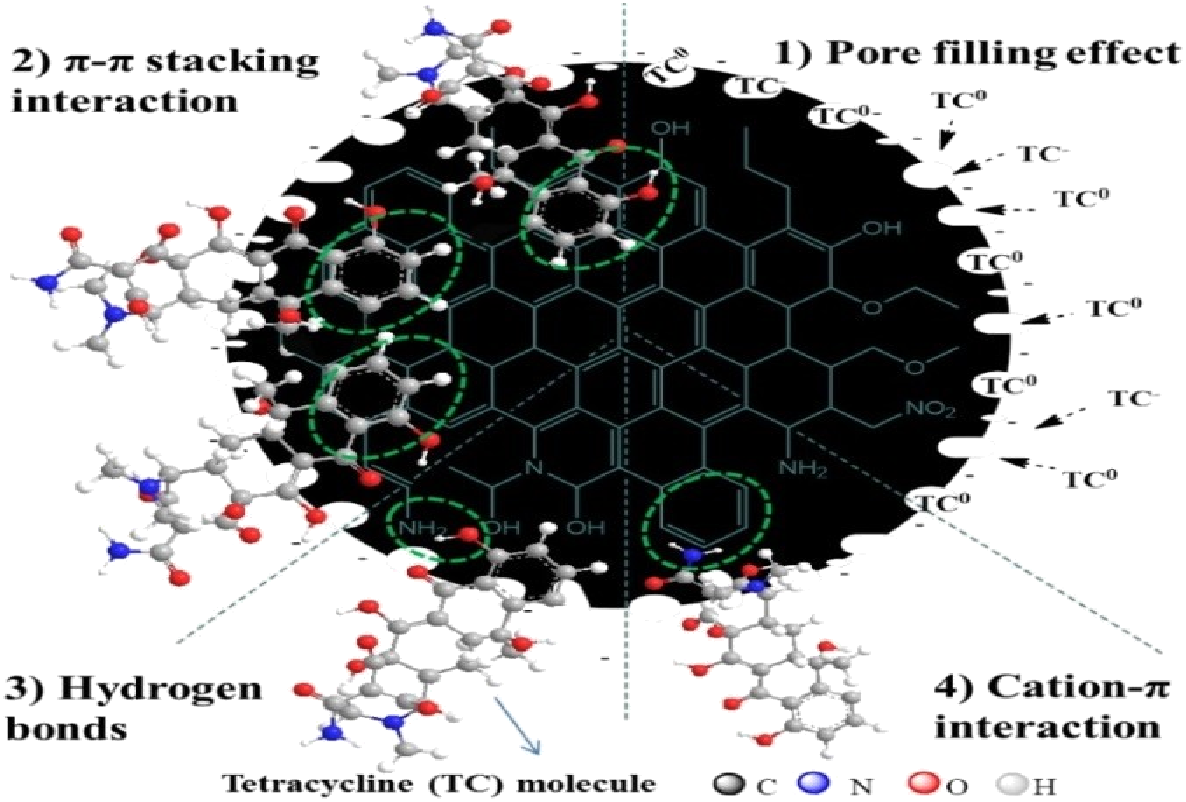
Persulfate oxidation

Mechanism of activating persulfate

Sludge biochar activating persulfate

Alkali-acid modified biochar derived from sludge for tetracycline (TC) removal





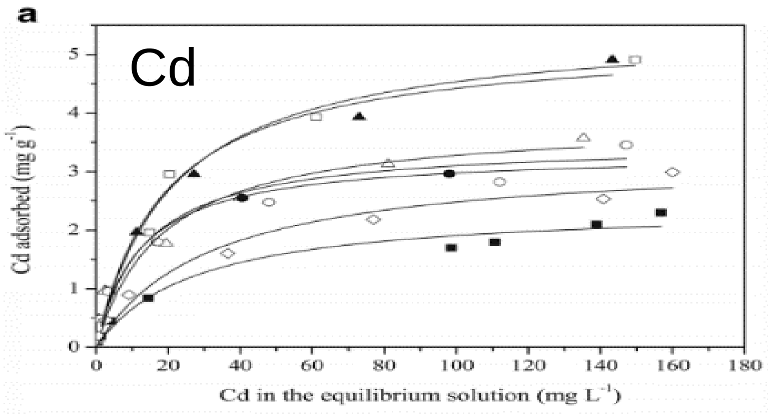
- When pH<4 or >8, there existed strong electrostatic repulsion, not conducive to adsorption;
- In neutral condition, electrostatic repulsion was the minimum and adsorption effect was the best.

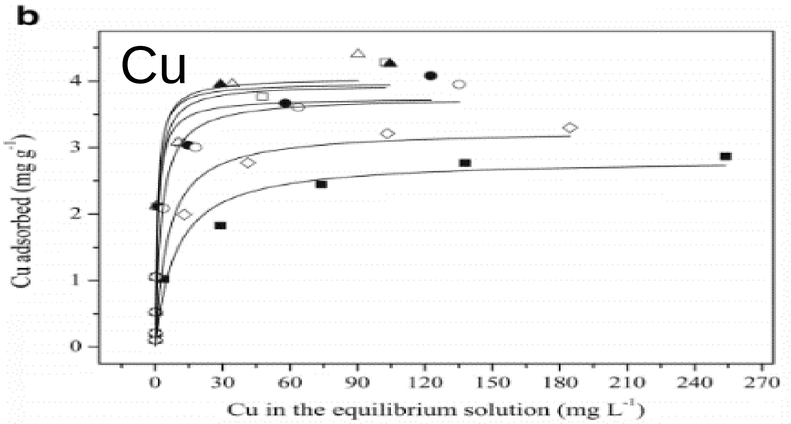
- Adsorption process of TC included **external effusion, surface diffusion, microporous diffusion and final adsorption process**, of which the high removal efficiency was realized through pore filling effect, π-π stacking, hydrogen bonds and cation-π interaction respectively.

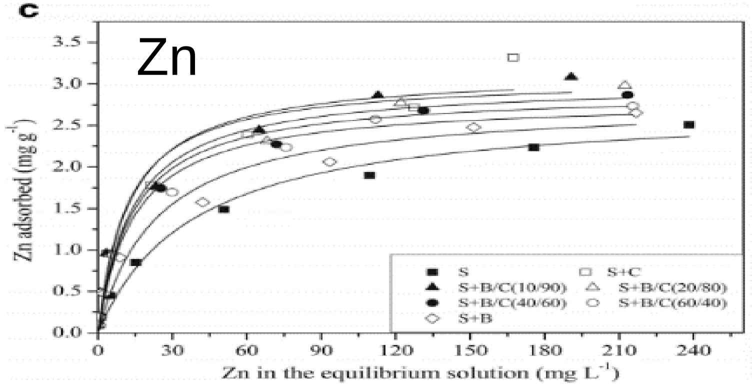
Chemical Engineering Journal, 2018, 336:160-169

Application of Biochar combined with compost restorer (B/C) in adsorption and desorption of heavy metals

Adsorption



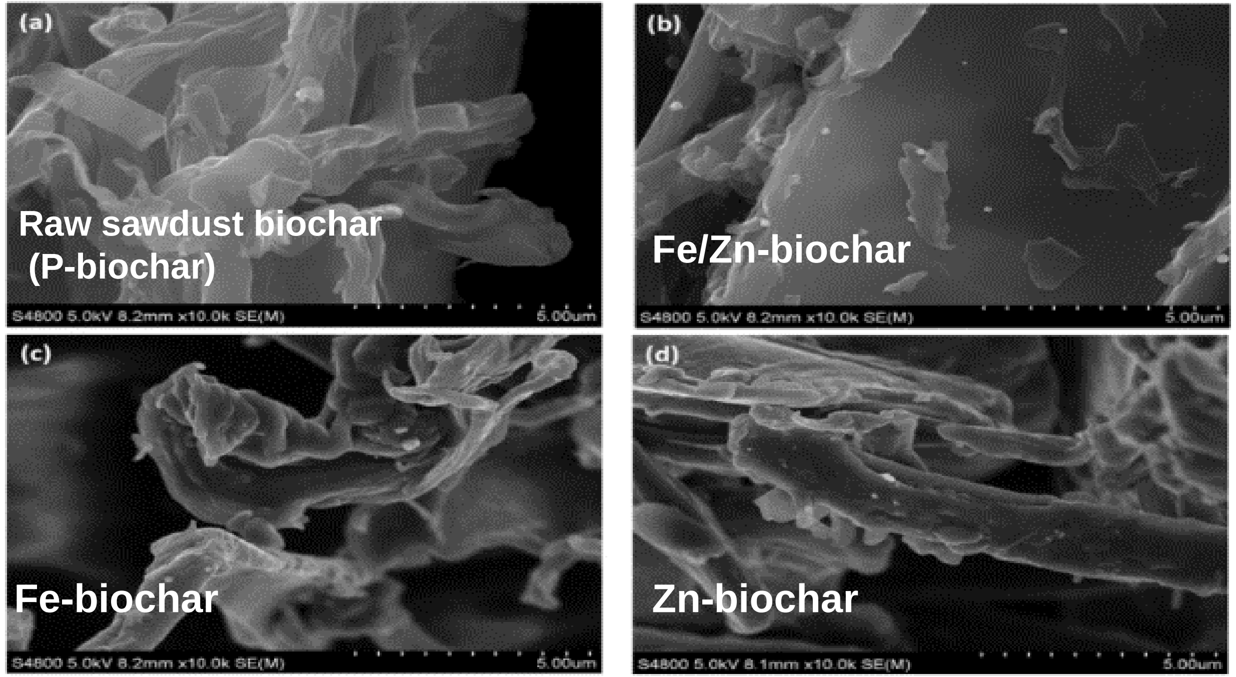


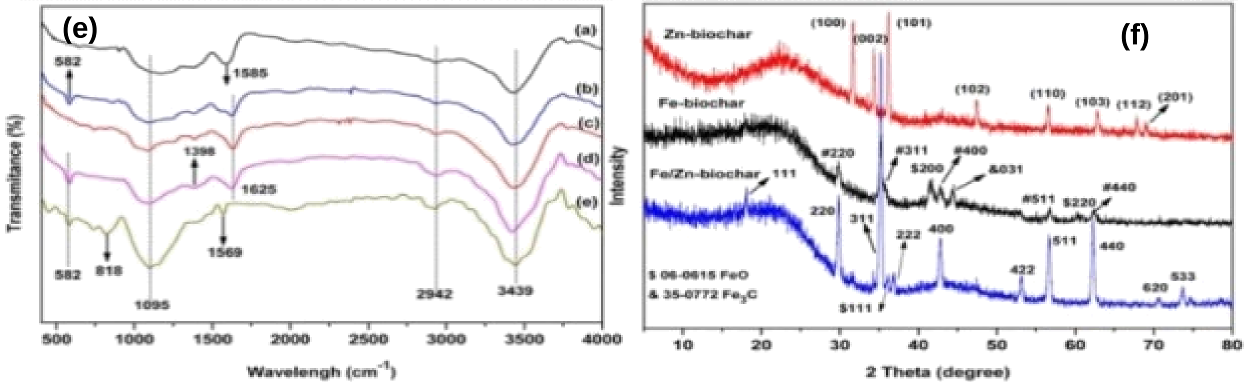


- The mixture ratio of B/C influenced the adsorption capacity of restorer for heavy metals;
- With higher ratio of compost, restorer could achieve the maximum adsorption capacity for Cd and Zn and stronger buffering capacity.

Journal of Soils and Sediments, 2017,2:1-10

Fe/Zn-biochar for p-nitrophenol (PNP) and lead adsorption and removal

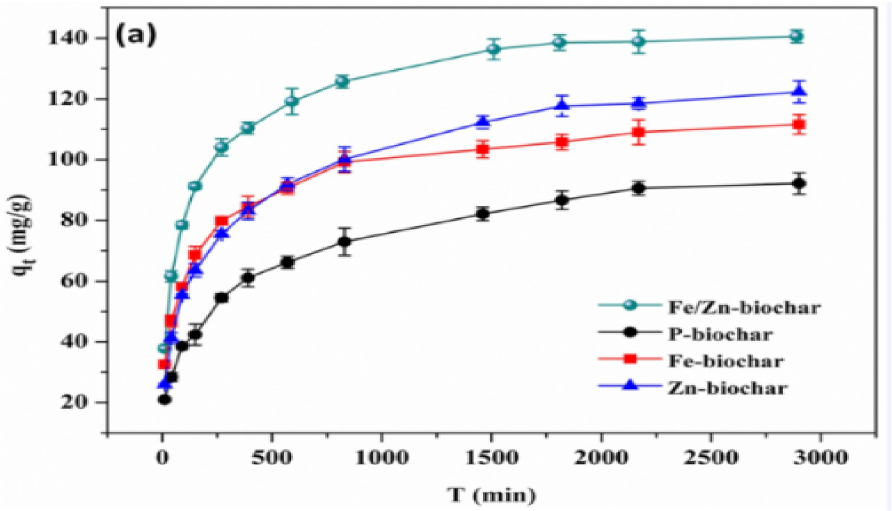




- ➢Zn doping contributed to hydroxyl generation on the surface of biochar, and its precursor solution ($ZnCl_2$) increased porosity of biochar;
- ➢The doped Fe existed in the form of Fe_3O_4, which empowered the biochar Good magnetic separation ability.

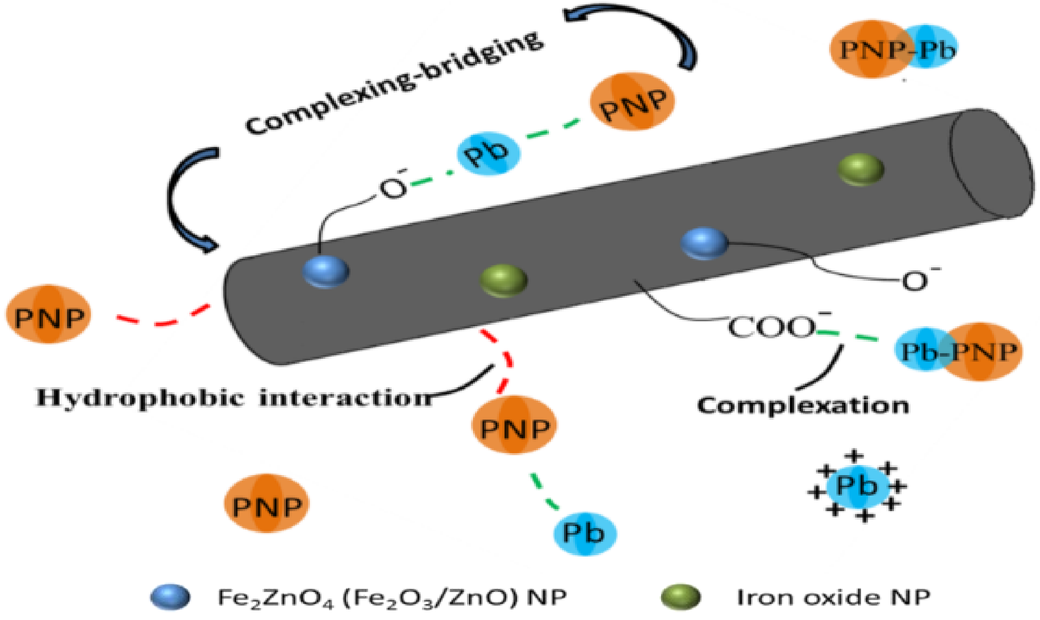
Applied Surface Science, 2017,392:391-401

Fe/Zn-biochar for p-nitrophenol (PNP) and lead adsorption and removal



- Fe/Zn co-doping achieved better PNP adsorption efficiency than monometal doping.

- Pb(II) was adsorbed on adsorbents mainly through chelation;
- Competitive adsorption existed between PNP and Pb(II).



Applied Surface Science, 2017,392:391-401

Biochar Supported Magnetite and Zero-valent Iron Nanoparticles for Selenate Removal

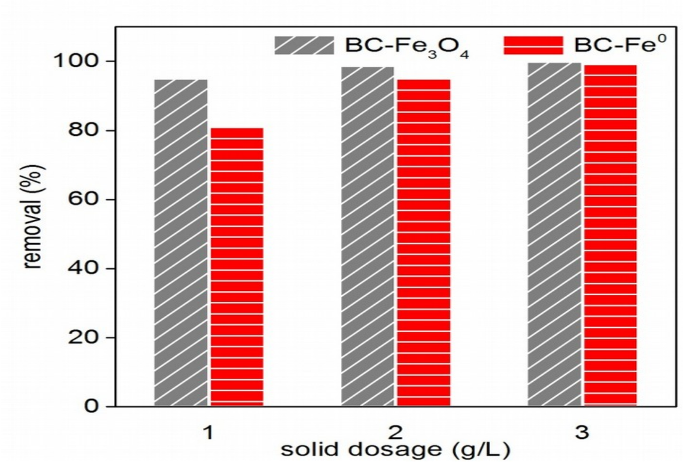


Fig. 3. Selenate removal efficiency of BC-nFe$_3$O$_4$ and BC-nFe^0.

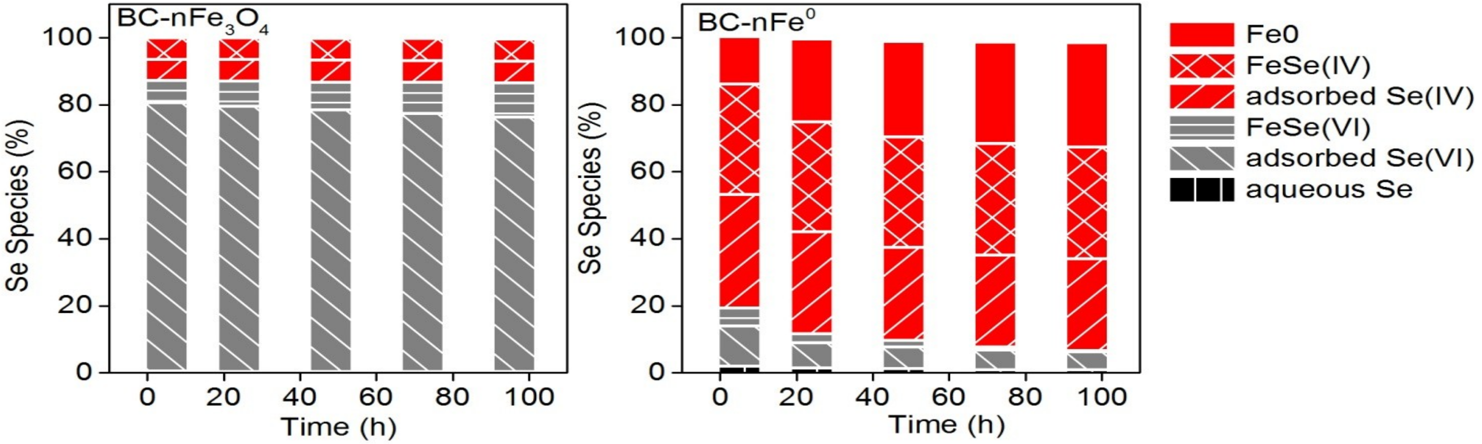


Fig. 4. Results of sequential extraction of the materials reacted for 5, 24, 48, 72, 96 h.

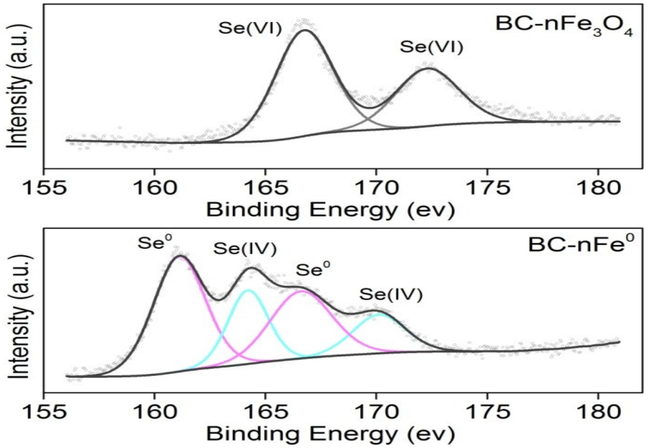


Fig.5. Curve fitting of the Se 2p3/2 XPS peaks.

- Although BC-nFe$_3$O$_4$ and BC-nFe^0 achieved similar selenate removal efficiency from water, selenate was the main Se species on BC-nFe$_3$O$_4$, while selenite and elemental Se were the main Se species on the BC-nFe^0.

BC-nFe$_3$O$_4$ **Adsorption**

BC-nFe^0 **Reduction** + **Adsorption**

Unpublished

Biochar Supported Magnetite and Zero-valent Iron Nanoparticles for Selenate Removal

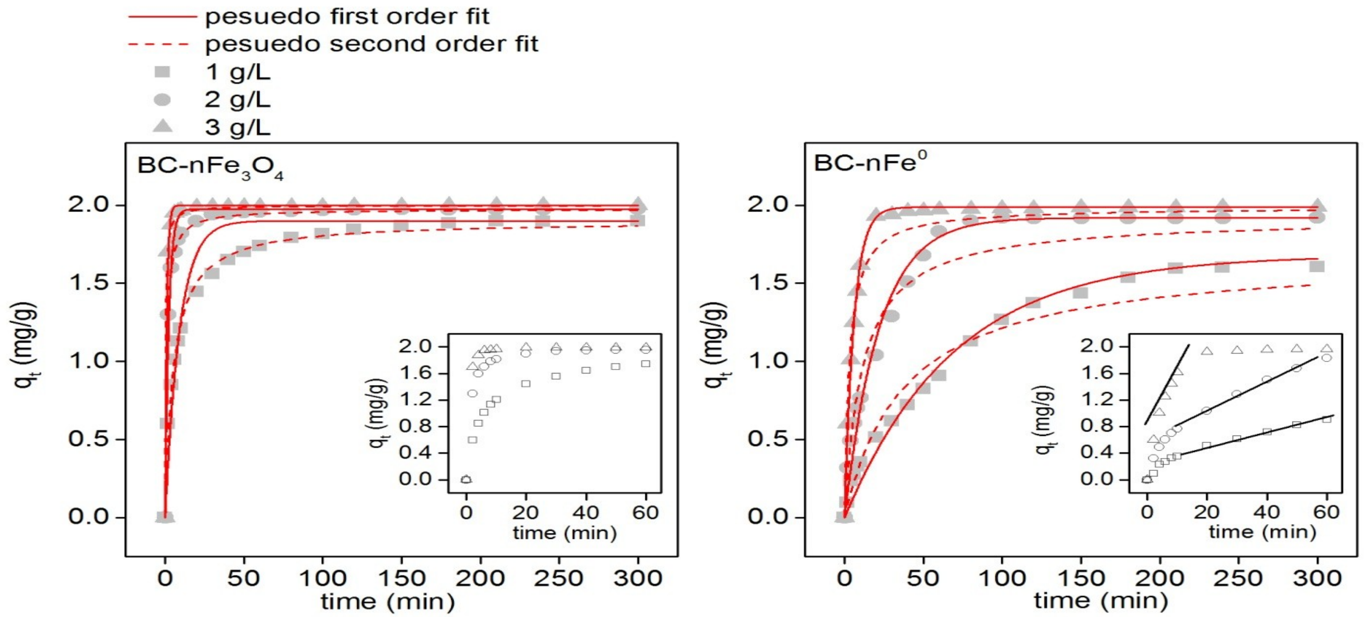


Fig. 6. Psuedo-first kinetics and pseudo-second kinetics fitting for removal kinetics.

Table 1. Fitting parameters obtained from the nonlinear fit of pseudo-first-order and pseudo-second-order kinetics model

	dosage (g/L)	pseudo-first-order		pseudo-seconde-order	
		R^2	k_1	R^2	k_2
BC-nFe$_3$O$_4$	1	0.9291	0.1095	0.9954	0.0992
	2	0.9781	0.4353	0.9989	0.5251
	3	0.9972	0.9059	0.9984	1.7081
BC-nFe^0	1	0.9825	0.0144	0.9670	0.0155
	2	0.9827	0.0455	0.9623	0.0469
	3	0.9989	0.1693	0.9724	0.1613

- The better fit of pseudo-second-order kinetics to the selenate-BC-nFe$_3$O$_4$ system indicates the limited adsorption sites on the surface. And lager dosage led to the increased fitting of pseudo-first-order kinetics；
- For BC-nFe^0, the better fitting with pseudo-first order kinetics might be caused by the continuously generated reducing agents.
- The removal rate of BC-nFe$_3$O$_4$ was faster than that of BC-nFe^0, owing to the limited adsorption sites of BC-nFe^0 and the relatively slow reduction of selenate on the surface.

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Biochar Supported Magnetite and Zero-valent Iron Nanoparticles for Selenate Removal

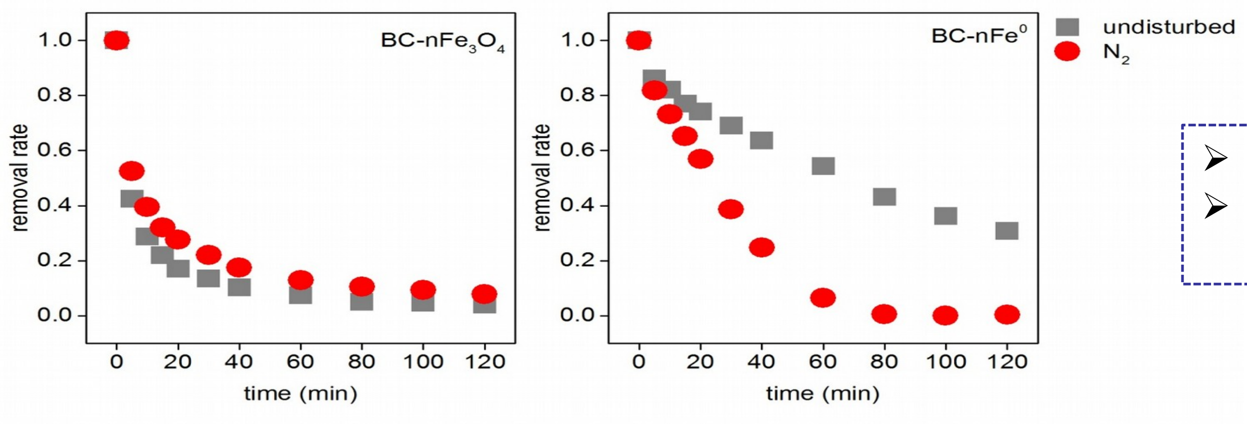

Fig. 8. Effect of DO on selenate removal process by BC-nFe$_3$O$_4$ and BC-nFe^0.

- For BC-nFe^0, the introduction of N_2 promoted the removal process.
- DO could compete with selenate for the reducing agents and promote surface passivation.

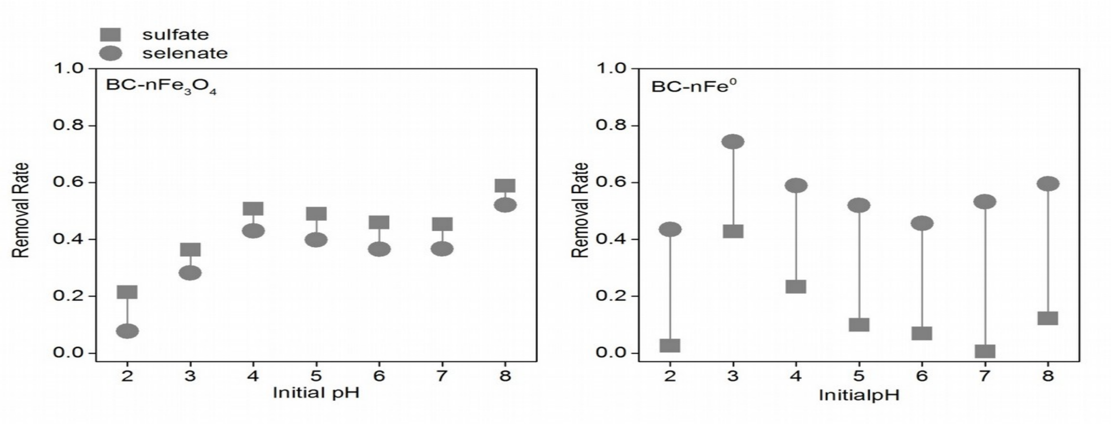

Fig. 9. The removal efficiency of selenate and sulfate under different initial pH in the binary system.

- For BC-nFe$_3$O$_4$, the similarity of the macroscopic adsorption efficiency of sulfate and selenate was observed, due to a large similarity in surface complexes of them;
- For BC-nFe^0, the redox potential of sulfate is much lower than selenate;
- Sulfate could not serve as a competitive electron acceptor for selenate reduction.

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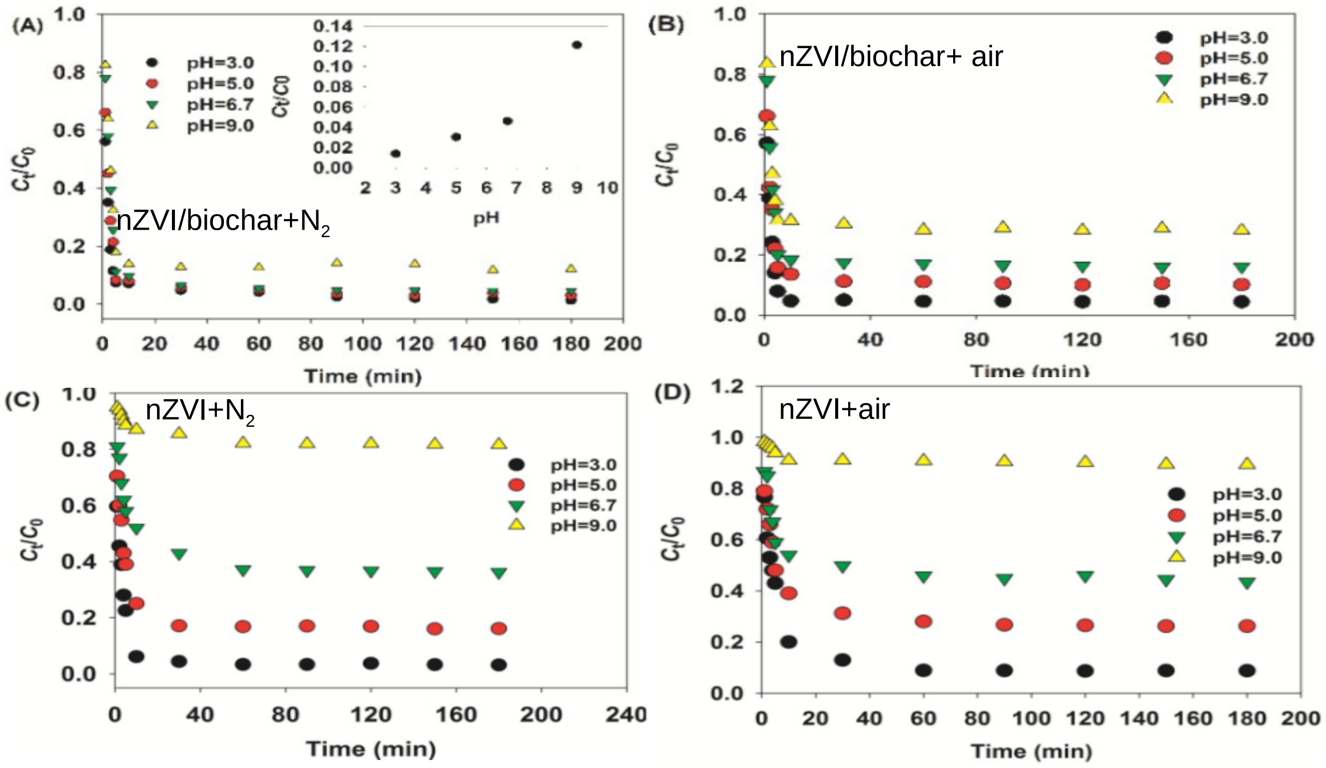
Biochar Supported Magnetite and Zero-valent Iron Nanoparticles for Selenate Removal

BC-nFe$_3$O$_4$	**BC-nFe^0**
Adsorption	**Reduction + Adsorption** (a prerequisite)
Faster	**Slower**
A better choice for fast selenate removal under near neutral pH and aerobic conditions	**A better choice under acidic and oxygen-limited conditions to transform selenate to more immobile selenite and elemental Se possessed higher selectivity toward selenate when coexisting with sulfate**

Unpublished

Biochar supported nZVI composite and nZVI removing p-nitrophenol (PNP) under anaerobic or aerobic conditions

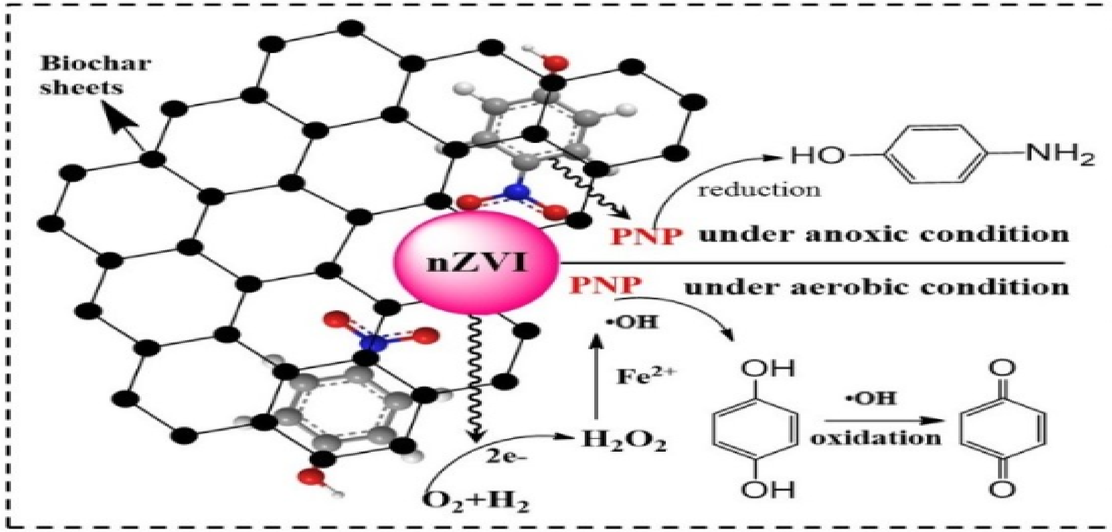


- Compared to aerobic condition, the PNP removal rate was faster:

   1) N_2 could remove the dissolved oxygen to improve the reduction activation of nZVI;

   2) N_2 could keep sufficient agitation to promote the efficiency of the reaction system.

- nZVI/biochar could achieve better PNP removal efficiency than nZVI.



- **The mechanism of PNP removal by nZVI/biochar:**

  1) Under aerobic condition, oxidation is combined with reduction;

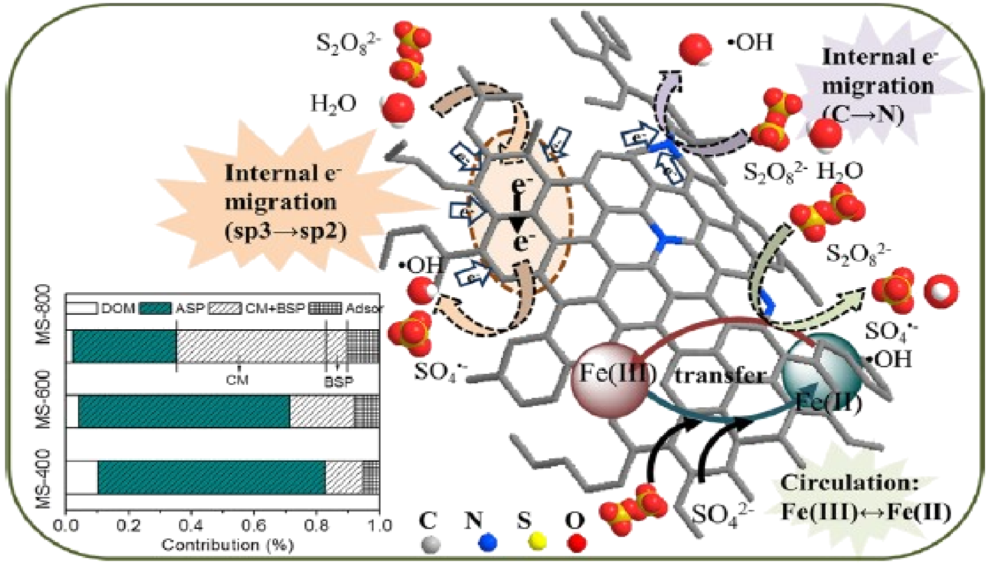
  2) Under anoxic condition, reduction played a leading role to produce aminophenol;

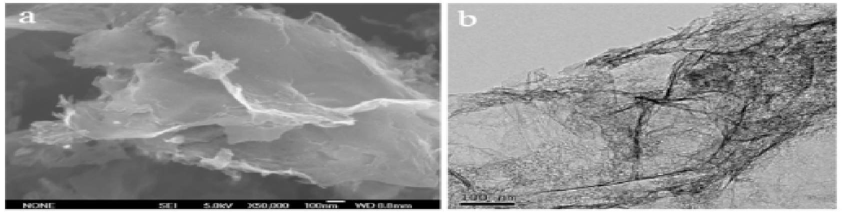
- Biochar could not only improve the effective utilization rate of nZVI as its excellent carrier, but also reducing the leaching rate of nZVI to lower the risk of secondary pollution.

RSC Advances, 2017, 7: 8755-8761.

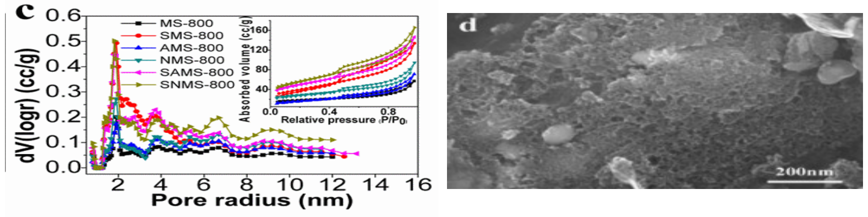
Persulfate activation for recalcitrant organics degradation

- Modified biochar from municipal sewage sludge for degradation of recalcitrant organics in sediment by activated persulfate;
- Achieving complete degradation and even mineralization of recalcitrant organics like 2, 4-dichlorophenol, norfloxacin within 120 min;
- Obtaining almost 100% decomposition of soluble organic pollutants within 2 h.





Graphene-like nanosheet structure biochar



Mesoporous biochar

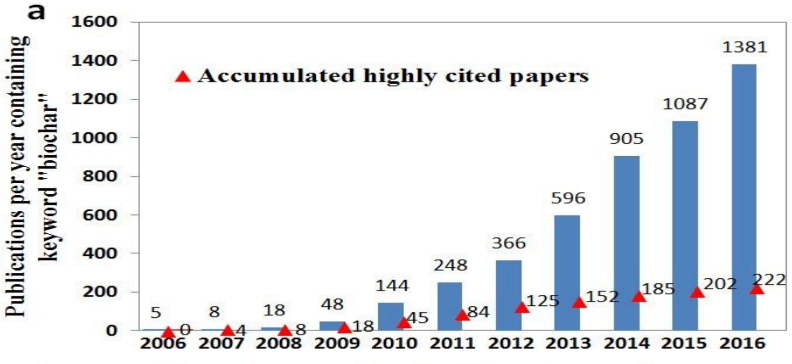
Modified mesoporous biochar can directly adsorb or activate persulfate in recalcitrant organics degradation.

Applied Catalysis B: Environmental 231 (2018) 1–10.

Chemical Engineering Journal, 2019, 364, 146-159.

Researches on wetland remediation by biochar

- **Widespread application in practical engineering of Xiang River sediment and Dongting wetland remediation.**




Zhuzhou Xiawan Harbor Sediment and wetland ecological restoration and demonstration project

These researches were accord with the requirement of reduction, detoxification and resource recovery of municipal sludge disposal, creating new ways for sludge recycle, greatly reducing the remediation cost of refractory polluted wetland, and developing a new technology with superior performance, low cost and no secondary pollution for restoration of contaminated sediment.

Appl Catal B: Environ (SCI 2016 IF=9.446), 2018, 231: 1-10； **Chemosphere (SCI 2016 IF=4.208),** 2017, 189: 224-238
Biores Tech (SCI 2016 IF=5.651), 2017, 245: 266-273； **Chem Eng J (SCI 2016 IF=6.216),**, 2017, 316: 410-418； **Chemosphere(SCI 2016 IF=4.208)**, 2015. 125 : 70-85;
Critical Rev Biotech (SCI 2016 IF=6.542), 2017, 37(6): 754–764

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