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Evaluation of reactive-mat containing low-grade charcoal to control leaching of organic pollutants

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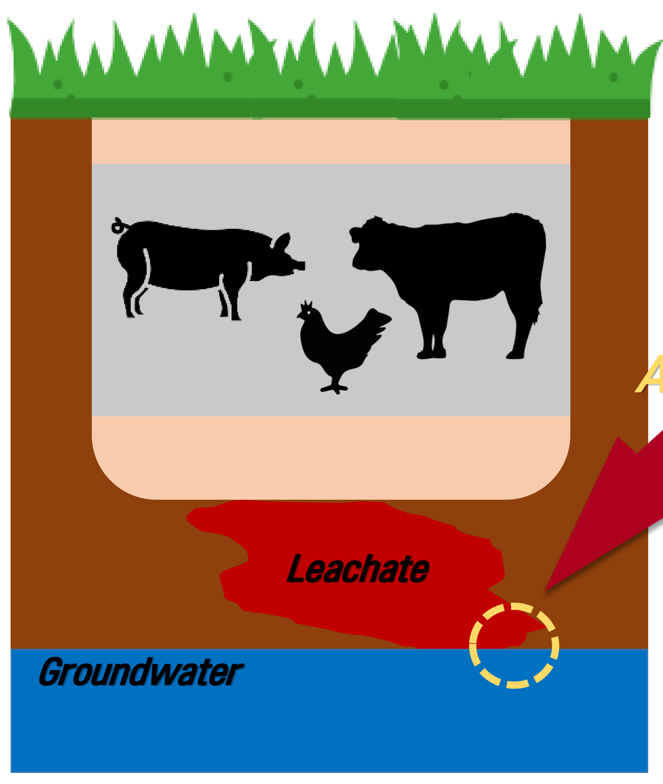
Introduction

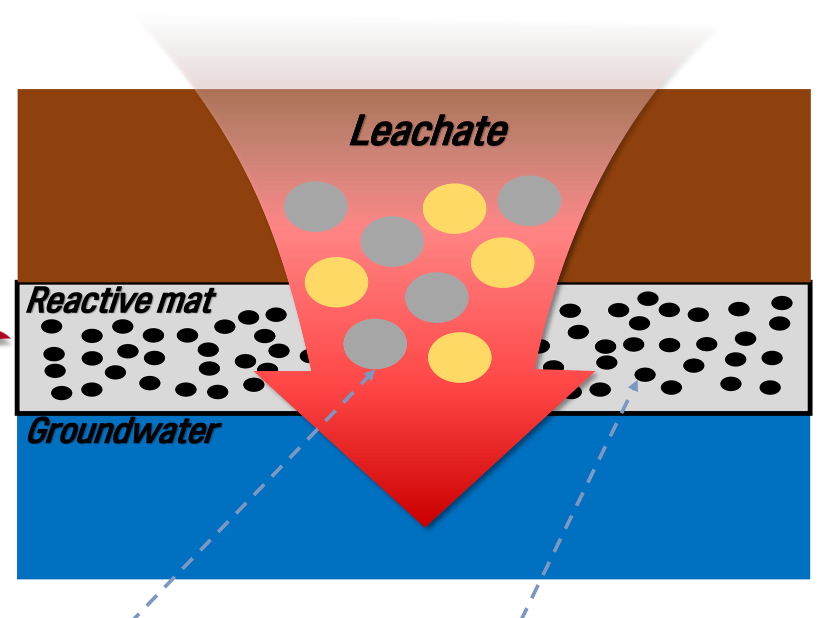
Leachate of livestock burial site

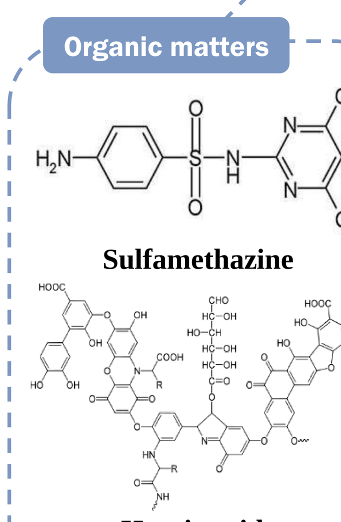


There are lots of organic matters in the leachate, and antibiotics are tiny amounts compared to total organic matters. (Kim and Pramanik, 2016)

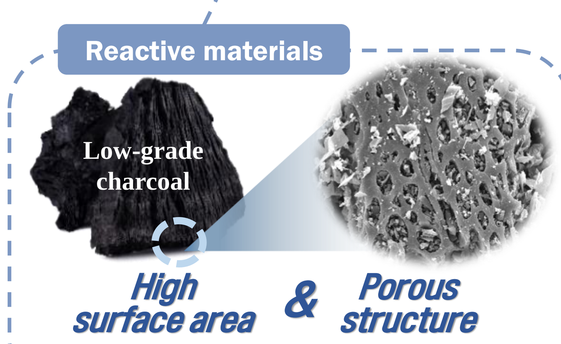
Mechanism of reactive-mat

Application of reactive-mat to leachate of livestock burial site





▲ Fig.1 Structural formula of Sulfamethazine and Humic acid.



▲ Fig.2 Low-grade charcoal SEM image.

Effective adsorbent to remove organic matters in leachate.

- Reactive-mat is a diffusion control system of various contaminants from one compartment to others, and it can be applied to contaminated sediment, landfill, and carcass burial site.
- The mat can adsorb target pollutants leaching from contaminated media onto the reactive materials. Thus, adsorption is the basic working mechanism of the reactive-mat in the environmental application.
- Because the adsorption is a non-selective process, the target pollutants should be evaluated in the presence of other competing materials.
- In this study, the performance of the reactive-mat was evaluated through lab-scale tests to apply the system to the environment.
- Additionally, we proposed low-grade charcoal, one of the industrial by-products, as a reactive material inside the mat. It has a large surface area and porous structure that can adsorb organic matters.
- The leachate from livestock burial sites contains lots of organic matters, and the antibiotics are tiny amounts compared to total organic matters. And they need to purified because they cause toxicity and allergies in small amounts.
- Accordingly, *Sulfamethazine*(SMZ), which can remain in leachate, was selected as the target pollutants, and a high concentration of *humic acid*(HA) was selected as competing materials in present study.

Research objectives

✓ To evaluate the performance of reactive-mat in the presence of a high concentration of organic matter.
✓ To investigate the adsorption characteristics of SMZ onto low-grade charcoal as adsorbent.

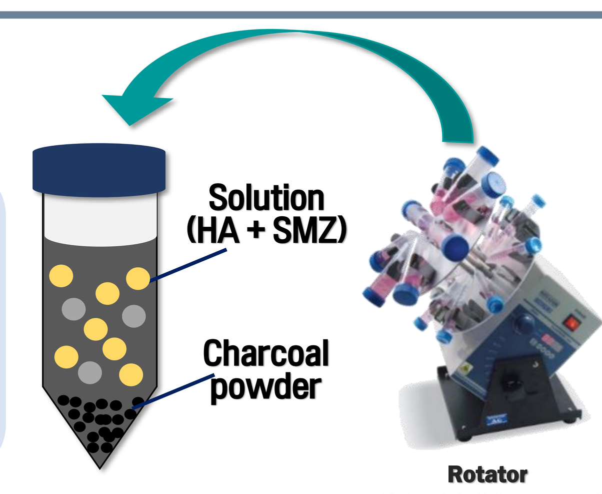
Materials & Methods

◎ Adsorbent preparation

▲ Fig.3 Adsorbent (low-grade charcoal) preparation process

◎ Solution preparation

- **Sulfamethazine(SMZ) : DW + SMZ → 100 mg/L, dilute and use**
- **Humic acid(HA) : 0.05M NaOH + HA → 2,000 mg/L**
- **Final solution : SMZ + HA**
- **After the final solution was prepared, it was titrated to pH 7 corresponding to leachate using NaOH and HCl** (Kang et al, 2012).



Analysis equipments

◎ Experimental conditions

Batch test	
HA Conc. (mg/L)	100, 2,000
SMZ Conc. (mg/L)	10
S/L ratio (g/L)	0.5, 1, 5, 15, 30, 50
Reaction time (h)	4
Temperature	Room temperature

	Kinetic test	Isotherm test
HA Conc. (mg/L)	2,000	
SMZ Conc. (mg/L)	10	0.5, 1, 5, 15, 30, 50, 100, 150, 200
S/L ratio (g/L)	1	
Reaction time (min)	10, 30, 60, 120, 240, 480, 720, 960	720
Temperature	Room temperature	

▲ Table 1. Experimental conditions of batch, kinetic, isotherm test.

◎ Analysis method

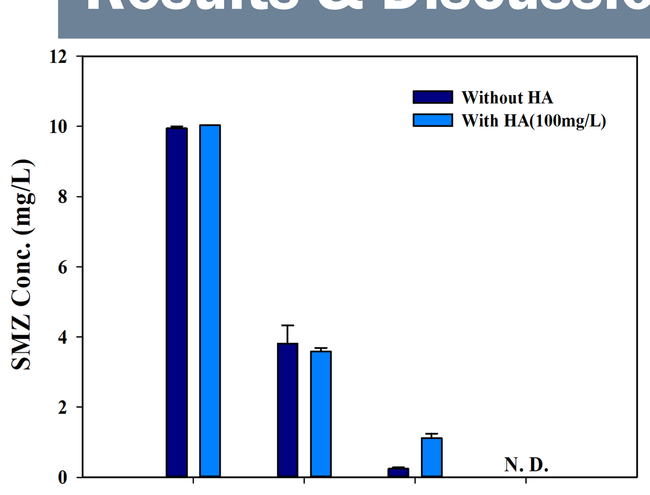
HPLC	
Column	C_{18}
UV wavelength	268 nm
Flow rate	1 ml/min
Oven temperature	40 ℃
Eluent	De-ionized water 55% + Acetonitrile 45%

▲ Table 2. Analysis method of HPLC.

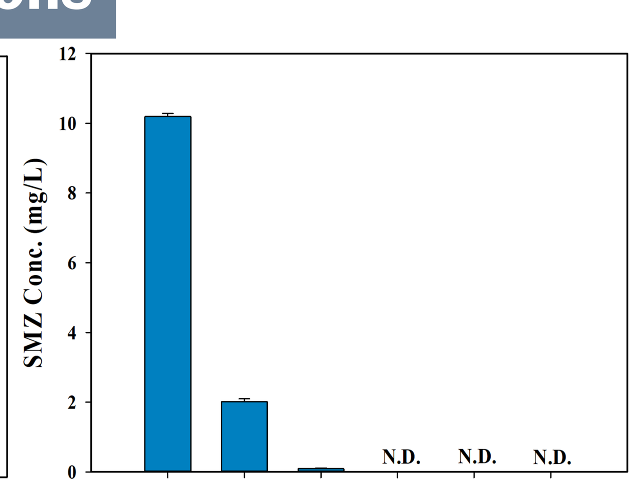
Pre-treatment

*** The pH of solution was to 1 to eliminate the interference of HA in the analysis of SMZ. (HA precipitates at pH 1)**

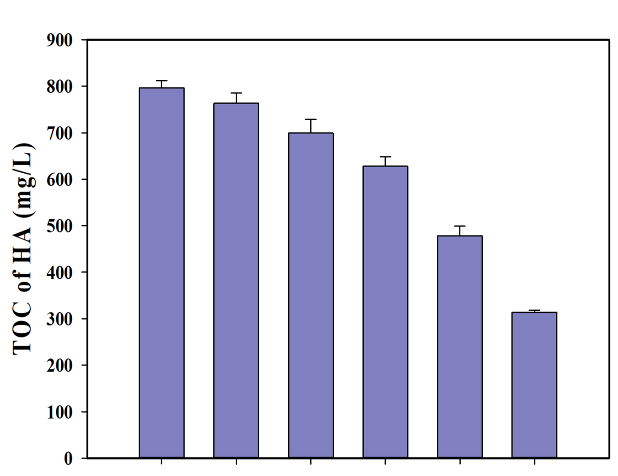
Results & Discussions



▲ Fig.4 Dosage of low-grade charcoal. (Initial concentration of SMZ: 10 mg/L, HA : 100 mg/L)

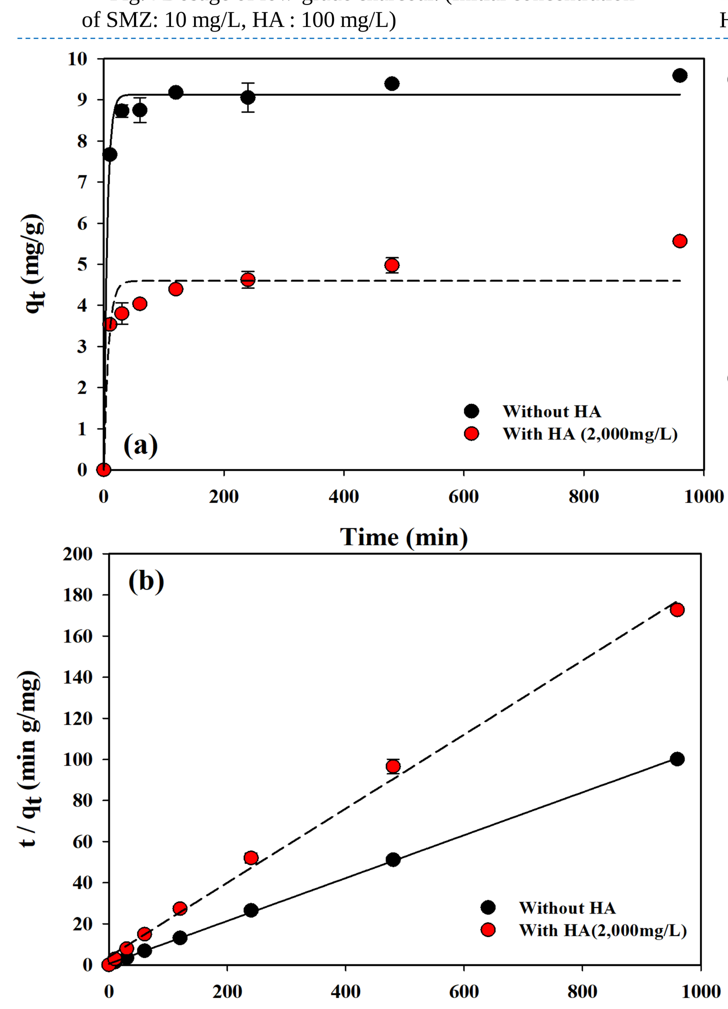


▲ Fig.5 Dosage of low-grade charcoal in the 2,000 mg HA/L. (Initial concentration of SMZ: 10 mg/L)



▲ Fig.6 Removal of HA(2,000mg/L) in different dosage of charcoal

- Above a dosage of 5 g/L, SMZ was completely removed regardless of HA presence (Fig. 4). The presence of HA lowered the adsorption capacity of low-grade charcoal for SMZ showing that HA affects the adsorption of SMZ. A high concentration of HA (2,000 mg/L) decreased the adsorption of SMZ onto the charcoal more than a low concentrations of HA (100 mg/L) (Fig.5).
- Figure 6 shows that low-grade charcoal can remove HA, which indicates that the adsorption of HA onto charcoal lowered the adsorption of SMZ. Probably, the two materials are adsorbed on the same sites, and the competitive adsorption decreased the removal of SMZ in the presence of HA. In other point, however, HA and SMZ can be removed simultaneously by the low-grade charcoal.

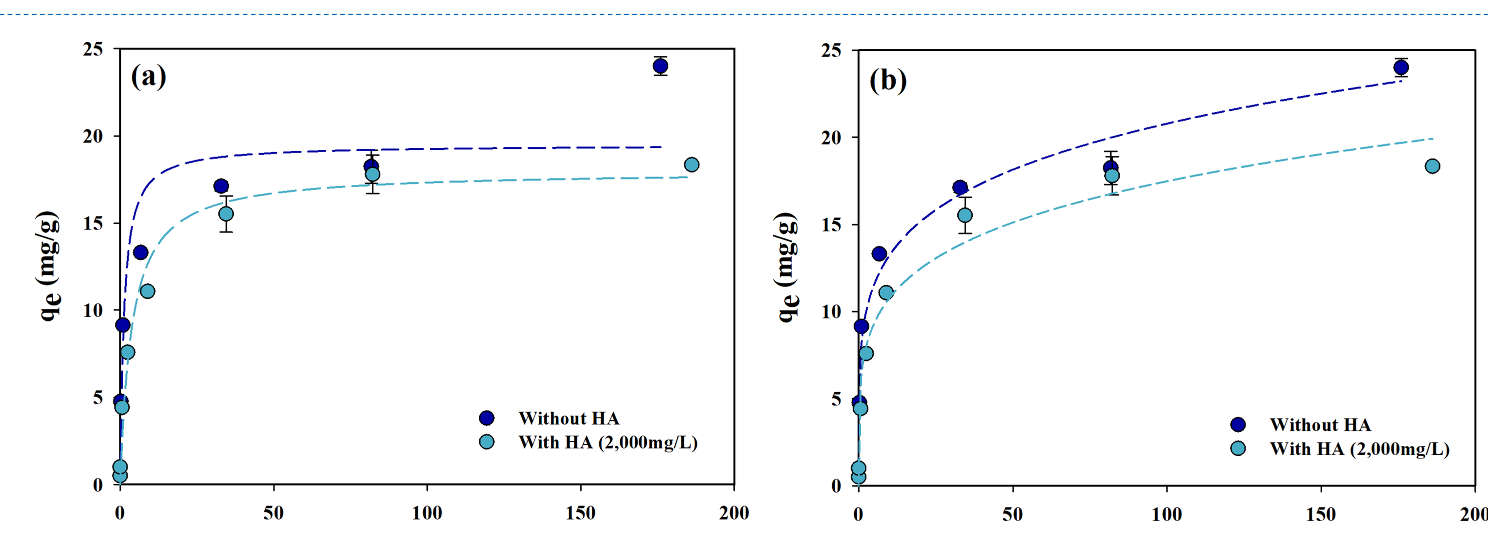


- Adsorption kinetics showed that adsorption took place spontaneously (Fig. 7a). In without HA, the adsorption equilibrium was achieved within 120 minutes, and the equilibrium was achieved within 240 minutes in the presence of HA. This result shows that, SMZ adsorption onto low-grade charcoal takes a long time to reach an equilibrium as well as lowers the adsorption capacity in the presence of HA.
- To describe characteristics of adsorption, pseudo-first order and pseudo-second order model were applied (Fig.7). The pseudo-second order model fitted the data well based on high correlation coefficient (Table 3) suggesting chemisorption. This indicates that the surface of low-grade charcoal is strongly negatively charged and adsorbed by the combination of π-π EDA (Electron Donor-Acceptor) due to the amino functional group and the N-Heteroaromatic ring of SMZ.

	Pseudo-first-order model			Pseudo-second-order model		
Sample	q_e(mg/g)	k_1(min^{-1})	R^2	q_e(mg/g)	k_2(g/mg · min)	R^2
Without HA	9.126	0.182	0.990	9.597	0.020	0.999
With HA	4.600	0.132	0.899	5.546	0.008	0.995

▲ Table.3. Adsorption kinetic parameters. A concentration of 10 mg/L SMZ was used. (Pseudo-first-order, Pseudo-second-order model)

◀ Fig.7 Adsorption kinetics of SMZ onto low grade charcoal fitted by (a) pseudo-first order, (b) pseudo-second order kinetic model. (Initial concentration of SMZ:10 mg/L, HA concentration was 2,000 mg/L, and S/L ratio was 1 g/L.)



▲ Fig.8 Adsorption isotherm of SMZ onto low-grade charcoal (a) Langmuir isotherm, (b) Freundlich isotherm model in the co-presence of 2000 mg HA/L. (S/L ratio was 1 g/L and reaction time was 720 min.)

	Langmuir isotherm			Freundlich isotherm		
Sample	q_{max} (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
Without HA	19.485	0.827	0.921	8.431	2.046	0.980
With HA	17.979	0.266	0.986	6.647	4.760	0.970

◀ Table 4. Adsorption isotherm parameters of SMZ onto low-grade charcoal (Langmuir, Freundlich).

- In Fig.8, the presence of HA decreases slightly the adsorption capacity of low-grade charcoal for SMZ.
- Given the high correlation coefficient (R^2) of the Langmuir adsorption isotherm and the high n value of the Freundlich adsorption isotherm (Table 4), the Langmuir adsorption model describes the adsorption characteristics well.
- The adsorption could be expressed well as mono-layer adsorption, which indicates chemisorption.

Conclusions

➢ The low-grade charcoal showed a good performance that adsorbed both SMZ and HA. And the adsorption of SMZ onto low-grade charcoal is a chemisorption.
➢ A high concentration of competing organic matters (HA in this study) lowered slightly the adsorption capacity of low-grade charcoal for SMZ, which indicates that the charcoal can remove SMZ effectively in the presence of HA.
➢ In the reactive-mat to treat leachate from carcass burial site, the charcoal can be used as a reactive material to control the antibiotics.

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