The Adsorption Analysis of Hazardous Substances by Biochar Derived from Agricultural-based
Material Wastes

# 農業廃棄物由来の生物炭による有害物質吸着現象の解析

Graduate school of Engineering, Nagasaki University 長崎大学大学院 工学研究科

Obey Gotore オベイ ゴトレ

# Background and objetives

In the environment, chromium generally exists as Cr (III) and Cr(VI) chrome forms and due to its mutable oxidational conditions it also becomes an injurious public health pollutant. The Cr (VI) is three hundred times more toxic than Cr(III) and has cancer-causing, mutagenic, teratogenic and deadly properties on the living world. The presence of pharmaceuticals such as antibiotics, Fluoroquinolone (FQ) group, in natural waters may increase antimicrobial resistance, demanding the development of new powerful antibiotics. Moreover, the continuous antibiotic compounds discharge may lead to resistance among native bacterial populations. Since they are soluble in water, some water analysis results have shown that ciprofloxacin and tetracycline concentrations in surface and effluent-dominated water are ng L<sup>-1</sup> to µg L-1. Conventional processes in wastewater treatment plants (WWTPs) are difficult to eliminate antibiotics], so alternative treatment research is highlighted to be therefore necessary. In this study, different pyrolysis conditions and residence times were examined for carbonization of a corn cob on adsorption properties of Cr(VI), Iodine, Ciprofloxacin (CFX) and Delafloxacin (DFX), and Bayesian nonlinear regression was applied in the data analysis to evaluate the results. In addition, the physicochemical character of biochar was analyzed by FTIR and FESEM to deeply investigate the effect of different pyrolysis temperatures and retention times on the adsorption of different adsorbates examined in this research.

## Analysis of antibiotics fluoroquinolone adsorption on corn cob charcoal

Estimated adsorption capacity  $Q_{max}$  for CFX and DFX was highest at 900°C for 2h pyrolysis, similar to Iodine adsorption. Judging from the estimated  $Q_{max}$  values in Table 2 and probability values of dQmax >0 (or <0) (see Table 3), the order of  $Q_{max}$  for CFX is as follows: 900 °C/2h >900 °C/1h > 700 °C /1h ~ 600 °C /2h ~600 °C /2h ~600 °C /2h, where ">" means 90% or more reliability (that is, the probability of dQmax >0 is greater than 0.9), and "~" means less than 90% reliability in bigger and smaller judgment. For instance, the  $Q_{\text{max}}$  of CFX is 27 times higher that of DFX at 600°C and 1h. Furthermore, at 900°C and 2h, it exhibits that CFX was 2.6 times higher than DFX, and the differences between CFX and DFX decreased at 900°C pyrolysis temperature. This difference is consequently articulated to the adsorption character between CFX and DFX which could be induced by different molecular sizes considering the hydration radius. In fact, the dimensions of CFX (1.00 nm<sup>2</sup>) is slightly smaller than the dimensions of DFX (1.21 nm<sup>2</sup>) under the molecular weight ratio assumption. It was reported that  $\pi$ - $\pi$  electron donoracceptor ( $\pi$ – $\pi$  EDA interaction) can give a major binding force between FQs and biochar. It is thought that the halogen atom bonded to the heteroaromatic ring in FQs can provide a stronger  $\pi$ - $\pi$  EDA interaction, because halogen atom has the intense electron negativity. the FTIR spectram (Fig. 2), CCBC of 900 °C clearly exhibits the larger peak by carboxyl group (-COO<sup>-</sup>) around 1350–1450 cm<sup>-1</sup>, and it was smaller peak for 600°C then it was very weak for CCBC of 700°C. Then the peak of C=O stretching of the carboxyl group at 1760–1610 cm<sup>-1</sup> and was also very clear for 900°C (with aromatic rings overlap which are related primarily to the vibrational movements of C=C bonds in these aromatic rings, with several weak and strong distinguishing peaks. The results of these IR spectra can explain the question if the temperature condition of 900°C has a very high adsorption capacity of FQs in terms of the hydrogen bond capacity of CCBC. The order of  $K_L$  in pyrolysis temperature is also consistent with the peak height of the IR spectra, but substantiating the peak height differences seem to be difficult to explain these differences by the residence time This study exhibited that 900°C pyrolysis temperature and 2h residence time exhibited better adsorption mechanisms of CFX and DFX antibiotics from the aqueous solution.

### Analysis of heavy metal Cr(VI) adsorption on corn cob charcoal

The AIC results reveals that Elovich model best described the data from lower pyrolysis (600°C, 700°C and 800°C-1hr) and the PSO model fits the data from higher pyrolysis (800°C for 2hr only and 900°C). This is a surface phenomenon, and it informs that as pyrolysis increases, the rate of adsorption is determined by the chemisorption processes or the rate limiting factor is chemical sorption, and some locations develops more affinity for Cr(VI) than others. This adsorption mechanism at 900°C is strongly associated with the corn cob biochar surface characteristics, the immobilization of Cr(VI) is well described by the PSO model at high pyrolysis than lower pyrolysis. The  $k_i$  and qe values of PFO were lower than that of the PSO model which were in excellent consistency with the experimental data. It can be noted that sorption phase of Cr(VI) was rapid on 800°C-2hr and 900°C-2hr pyrolyzed BC than lower temperatures. For higher pyrolysis, initial Cr (VI) sorption took place within 150 mins and 60 mins for 800°C-2hr and 900°C-2hr pyrolysis respectively. Later, the rate of adsorption increased gently over time until the equilibrium stage is reached after 24 hours. this indicates an element of chemisorption from different pyrolysis conditions and specific BC structural makeup. It can be observed that the experimental qe and calculated qe values are in better agreement with PSO kinetic model than PFO kinetic model. However, rate constants in the pseudo first order model indicated that  $k_1$  values were higher than  $k_2$ values, which translates to rapid adsorption of Cr(VI) onto the biochar for all pyrolysis conditions. The values of  $\alpha$  were higher than the values of  $\beta$  at higher pyrolysis and sometimes vice-versa at lower pyrolysis. So, the affinity for adsorption tend to increase with an increase in pyrolysis temperature because between 600°C and 700°C, the affinity seems to be generally low though alternating. This alternation at 600°C and 700°C carbonization temperatures could be induced by the reversible characteristics of the corn cob produced at these conditions. On the other hand, the rate and adsorption mechanism are governed by three basic steps, boundary layer diffusion, pore diffusion with adsorption on active sites and saturation stage with core adsorption sites. Therefore, the findings suggested that the adsorption mechanisms of the corn cob biochar under varying pyrolysis conditions was in rapport with the PSO model. The assumption of the PSO model articulates chemisorption as the rate limiting step of adsorption which presupposes valency forces exchange of electrons between the Cr(VI) ions and the corn cob biochar. Langmuir model fits the isotherm data with AICc values of -10.415 and 47.384 which are lower than 9.1 and 56.7 for Freundlich model respectively. It can be concluded that his model is the most suitable for heavy metal adsorption on the edge surface of layer silicate minerals because many experiments on heavy metal adsorption using the constant ionic strength and constant pH solutions.

### Characterization of Matamba fruit shell, Mushuma and Mupane Tree bark biochar

The pseudo-second-order model well described the kinetics of Iodine adsorption onto MSHBC and MPNBC, accompanied by the Elovich model. The Intra particle diffusion model did not pass through the origin, so it was clear that other mechanisms could have been contributed to the adsorption of Iodine onto the bark biochar. This confirms a heterogeneous surface characteristic with significant chemisorption mechanisms developed during pyrolysis of the agro-biobased biochar. The qt estimations of 40.712 and 41.639 mmol/g than conventional statistics with 40.01 and 40.29 mmol/g for Mushuma and Mupane biochar were obtained. Field Emission Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy exhibited C (81.93 mol% and 86.91 mol %) and O (16.12 mol% and 11.49 mol%) for Mushuma and Mupane respectively. However, EDX revealed high content of Carbon (72.68 wt.%), N (14.14 wt.%) and O (10.35 wt.%) on the biochar surface. The available O composition provides enough polarization ability for high iodine adsorption (43.65 mmol/g) from the experimental data significantly induced by weak van der Waals forces and  $\pi$ - $\pi$  and  $\pi$ -stacking interaction on the biochar surface and its micropores. Elovich and Intra particle diffusion better described well the kinetic adsorption through Iodine adsorption on Matamba Biochar. The maximum capacity of adsorption of the Matamba Fruit shell was 2.122 mmol L<sup>-1</sup> and 2.12 mmol L<sup>-1</sup> and SSA of 267.0 m<sup>2</sup> g<sup>-1</sup> with Langmuir model fitting the data. The Fruit shell has different functional groups including the hydroxyl (-OH) and the carbonyl groups (C=O), C=C stretches of aromatic rings, and the carboxylate (C-O-O-) groups.