

ADSORPTION OF HEAVY METALS ON ROAD-DEPOSITED SEDIMENT: KINETIC AND ISOTHERM INVESTIGATIONS

Jin Zhang, Zhuqing Yu, Gongduan Fan, Pei Hua, Peter Krebs

Institute of Urban Water Management, Technische Universität Dresden, 01062 Dresden, Germany

College of Civil Engineering, Fuzhou University, 350108 Fujian, China

jin.zhang@tu-dresden.de

Keywords: Adsorption isotherm; adsorption kinetic; heavy metal; stormwater management

Introduction

Road-deposited sediment (RDS) often contains elevated heavy metals which are commonly at least an order of magnitude higher than those in neighboring solid (Zhang *et al.* 2015). In terms of stormwater best management practices, RDS and its adsorbed heavy metals have been regarded as a leading contributor to the stormwater non-point pollution. It has been reported that during the wet weather period, rainfall leaches and flushes the RDS on urban watershed. Certain content of the RDS adsorbed metals dissolved in runoff as free or complexed species (Zhang *et al.* 2016). Therefore, to better understand the potential desorption behaviors of metals, it is essential to study the adsorption kinetic and isotherm of metals on RDS.

Consequently, this study intends to provide an in-depth understanding on the adsorption properties of heavy metals on RDS for a stormwater pollution aspect. The adsorption kinetic and isotherm of Cu, Zn, Ni, and Cd on RDS were systematically investigated.

Materials and methods

Sample collection

The RDS samples were collected from an asphalt traffic road (St. Petersburger Str., average daily traffic: 12600 vehicle/day, % of heavy traffic: 3–4) in the city centre of Dresden (51°02'55" N, 13°44'29" E), located in the state of Saxony, Germany. The sampling site was selected due to the elevated RDS adsorbed pollutants levels according to the previous study (Zhang *et al.* 2015).

Adsorption experiment

Kinetic studies were carried out to determine the adsorption dynamics of heavy metals onto RDS by a batch method. 20 mL solution was collected after the stirring time of 1 min, 3 min, 10 min, 30 min, 1 h, 5.5 h, 8 h, 24 h, and 30 h. The adsorption isotherm experiments were conducted at the Cu, Zn, Ni, and Cd initial concentration of 1, 5, 10, 20, 30, 50, 100, and 200 mg·L⁻¹. 0.5 g (dry mass) of RDS with 25 mL 0.01M NaNO₃ solutions were stirred with an Orbital Shaker at 125 rpm for 8 h, and then kept still for 22 h at a constant room temperature. The collected solutions were filtered through a 0.2 μm cellulose nitrate membrane filter. The filtrates were analysed for the dissolved heavy metal concentration. Cu, Zn, Ni, and Cd dissolved in the filtrates were determined following the German Norm DIN 38406-7 (E7) and DIN 38406-8 (E8) by an atomic absorption spectrophotometer (Varian, SpectrAA 220 Fast Sequential AAS-220 Z).

Adsorption kinetic and isotherm

Pseudo-first-order and Pseudo-second-order equations as shown in Eq. 1 and 2 in *Full Paper* were applied for the kinetic analysis of adsorption. Langmuir, Freundlich and Temkin isotherms were adopted to describe the experimental data, which can be expressed respectively as Eq. 3, 4 and 5 in *Full Paper*.

Results and discussion

Adsorption kinetics

Results of kinetic experiments are shown in Fig. 1 in *Full Paper*, the adsorption amounts increased remarkably in the first 30 min for all the metals, which accounted for about 95% Cu, 85% Zn, 75% Ni, and 90% Cd of the total amounts adsorbed after 30 h. The adsorption rate decreased gradually until adsorption equilibrium was obtained. The initial sorption rate has an order of $Cd > Cu > Zn > Ni$. The calculated R^2 indicates that the pseudo-second-order equations are more successful to fit the adsorption process of Cu, Zn, Ni, and Cd. This suggests that the chemisorption of these four metals was a rate-controlling step. The pH value decreased observably within the first 3 mins, then decreased slowly and increased extremely slowly later until the equilibrium. It could be due to the protons dissociated from $-OH_2$ and $-OH$ groups by exchanging with metal cations in the solution or result from the forming complexes on the surface.

Adsorption isotherms

In terms of the adsorption isotherm, the adsorption amounts of Cu, Zn, Ni, and Cd increased almost linearly at a low equilibrium concentration range and tend to flat at a high equilibrium concentration range. Both of the Langmuir and Freundlich isotherms described well for Zn, Ni, and Cd. The good fitness with Langmuir model indicated that monolayer chemisorption was the main mechanism in the adsorption procedure. However, the good fitness with Freundlich isotherm showed that the binding energy for each site is not identical. Therefore, other adsorption mechanism such like electrostatic adsorption and/or Van der Waals force concurrence besides chemisorption. The Langmuir isotherm was superior to Freundlich isotherm for matching the adsorption process of Cu. Furthermore, the values of $1/n$ for four heavy metals in Freundlich isotherm were fell in the range of 0.1 - 0.5 which indicates that the adsorbate was easily adsorbed by adsorbent.

Conclusion

Bath adsorption experiments were applied to study the adsorption characteristics of Cu, Zn, Ni, and Cd onto road-deposited sediment (RDS). Results show that RDS has a great efficiency to absorb heavy metal within a short time. The adsorption data were fitted well by the pseudo-second-order model for four metals, indicating chemisorption was predominant in the adsorption process. Cu has a greater affinity with RDS than other three metals, and Cd has the highest initial sorption rate.

References

- Zhang J., Hua P. and Krebs P. (2015). The build-up dynamic and chemical fractionation of Cu, Zn and Cd in road-deposited sediment. *Science of The Total Environment* **532**, 723-32.
- Zhang J., Hua P. and Krebs P. (2016). The influences of dissolved organic matter and surfactant on the desorption of Cu and Zn from road-deposited sediment. *Chemosphere* **150**, 63-70.