

Biosorption of heavy metals and rare earth elements by using various carbonized materials

(炭化材料を用いた重金属と希土類元素のバイオ吸着)

ポヌ ジョジアヌ

The need for more effective, economic and environmental friendly methods for the removal of heavy from aqueous systems led to the development of emerging technologies for metal concentration and separation. Conventional physicochemical methods such as reverse osmosis, electrodialysis, ultrafiltration, ion-exchange resins, chemical precipitation, phytoremediation etc for metal removal from aqueous solutions involve high cost, or sludge. Moreover, they are less efficient for certain ions, or lead to the formation of hydroxide compounds, and or required long processing time. As historical method, adsorption has been recognized as an alternative for concentrating heavy metals and rare earth elements from wastewaters or low-grade ores aqueous solution. The use biomass as sorbent, improve the process and make it more efficient in many ways for metal removal and recovery. Then the use of biomass as sorbent change the name “adsorption” to “biosorption”. The technology developed in work is quite adequate to the famous phrase of the so called “Father of modern chemistry”, the French scientist Antoine Lavoisier: “nothing is lost, nothing is created, everything is transformed” since the biomass wastes have transformed and reused as sorbent for further purpose.

Biosorption deals with the removal of ions from aqueous solution based on interactions between ions and active sites of biomass. The uptake of ions starts with the ion diffusion to the surface of the biosorbents. Once the diffused to the biomass surface, it may bind to the sorbent sites that show some affinity for ions species. The major advantages of biosorption development over conventional methods include low-cost of biosorbents, low operative cost, high efficiency for metal removal and recovery, possibility of biosorbent regeneration, rapid processing time, limited generation of sludge and environmental positive impact.

Furthermore, the improvement of the sorption capacity of biosorbents led to the modification of the biomass using chemical reagents, in order to obtain a desire functional group able to react with the target ion, or thermal conversion process of biomass especially carbonization or slow pyrolysis process leads to the formation of biochar. The main advantages of using carbonization process over the use of chemical reagents for biomass pre-treatment is the production of highly porous carbon characterizing by large adsorption surface area, used as biosorbent in water purification system without reverse effect on human beings. The combination of biosorption and carbonization processes is called “carbo-biosorption” in the present thesis. Carbo-biosorption process deals with carbonization of biomass at an appropriate (optimum) temperature in order to activate some functional groups governing the macromolecules composing any biomass. This method has more advantages than biosorption since it contributes to improve the adsorption capacity of the biomass, reduces the processing time, and reduces the probability to clog filters pores during the filtration process.

As results, the study concerning banana peels, details a novel approach of production of porous material using banana peels. The carbons produced are then used as biosorbents for the removal of cadmium ions from aqueous solution. Then, highly ordered low-cost micro and mesoporous carbon have been prepared from banana peels at five pyrolysis temperatures (350°C, 450°C, 550°C, 650°C or 800°C). Except the macromolecules (cellulose, hemicelluloses and lignin) that are the main component of biomass, banana peels contain also potassium chloride as mineral salt. X-rays patterns showed that potassium chloride becomes more visible with increasing temperature and the stage of decomposition of macromolecules may be quite related to the way the peaks of potassium chloride appeared.

In addition, the effects of carbonization temperature and activation time on the porosity of the carbon have been investigated experimentally. An increase in the porosity was observed with increasing temperature until 550 °C which was found to be the optimum temperature at which banana peels macromolecules finished decomposing. The destruction of created pores was observed at temperatures higher than above. The highly porous material produced from banana-peels has been used as biosorbents for cadmium removal process from wastewater. Carbonization enhances the quality of organic by-product used as biosorbent, reduces the equilibrium time and improves the quality of the final product (water). Evaluation of the effects of pH, contact time and solution temperature showed that the uptake of cadmium ions was highly dependent on these factors which increased with pH and solution temperature. Furthermore, the presence of carbo-acid groups on the surface of banana peels by-product enhanced the uptake of cadmium on the biosorbents surface. The maximum biosorption capacity was obtained with 350°C carbonized banana peels (BP350) (119.84 mg/g). In addition, desorption process was carried out with various concentration of hydrochloric acid and its values increase with decreasing acid concentration. The maximum desorption percentage of 89.65% was obtained for BP350.

Biosorption studies of chromium(VI) were conducted on 350°C or 450°C carbonized pineapple leaves as well as the dried one. The investigation of the functional groups governing the selected biosorbents on the Fourier transform infrared spectrometer (FT/IR) reveals that dried pineapple leaves are mainly composed on cellulose, ligno-cellulose and amorphous silicate and the carbonization shifts these structures to humic acid and fumarodinitrile. Thermo gravimetric/differential thermal analysis (TG-DTA) of raw pineapple leaves reveals two main peaks indicating the change in structure of the material with increasing temperature. Some important parameters such as pH, contact time and solution temperature were evaluated and the results showed a high dependence on those factors with chromium(VI) anions uptake. The optimum pH was found at pH = 2 (pH=1 for dried pineapple leaves) with the biosorption percentage of 90.1 % and the maximum biosorption capacity of 18.77 mg/g was registered for 450°C carbonized pineapple leaves. Consistent with an endothermic reaction, the mechanism was found to be chemisorption and the system was well described by the pseudo-second order kinetic model. The intraparticle diffusion model, on the other hand, indicated that the system is governed by both film diffusion and intraparticle diffusion. Biosorption isotherm data were described by both Langmuir and Freundlich models. Gibbs free energy investigation shows the spontaneity of each system. Moreover, FT/IR studies point out the carboxylate ions, aliphatic group and unsaturated group like alkene as responsible for chromium binding process. These results notice that the selected materials are appropriate for removing chromium(VI) anions from wastewater. Carbo-biosorption of rare earth elements (REEs) have been investigated using by-product of

mandarin-orange peels, ginkgo leaves and parachlorella.

The ongoing development of new advanced technologies, created increasing demands for REEs in the international market, which emphasis on identifying new resources to ensure adequate supply. Carbo-biosorption of scandium ions was conducted using 450°C carbonized mandarin-orange peels (MP450) and ginkgo leaves (GL450) as well as the dried ones (MP, GL). Evaluating the effect of pH with respect to contact time, results indicated a rapid biosorption of scandium ions onto the surfaces of the biosorbents. Equilibrium was reached within 5 min (15min for GL) of contact, with the best biosorption capacity of 104.51 mg/g obtained with carbonized ginkgo leaves. In addition, the recovery process of adsorbed scandium was studied using hydrochloric acid, nitric acid, sulfuric acid and hot water. Maximum desorption percentage of 99.63% and 77.69% were obtained for dried ginkgo leaves and mandarin-orange peels using HNO₃, respectively, whereas 94.12% and 91.88% were obtained using HCl for 450 °C carbonized ginkgo leaves and mandarin-orange peels, respectively.

Furthermore, the possibility of biosorption-desorption of dysprosium ions using dried and carbonized mandarin-orange peels and ginkgo leaves was also evaluated. A rapid biosorption of dysprosium ions onto the surfaces of the biosorbents characterized the biosorption process of dysprosium with the selected biosorbents. The equilibrium of the system biosorbent-biosorbate was reached within 5 min of contact and the best biosorption capacity of 25.64 mg/g was registered for carbonized ginkgo leaves. The desorption of dysprosium ions was studied using hydrochloric acid, nitric acid, sulfuric acid and hot water. As for scandium, high desorption percentage were obtained with acids but not with hot water. Maximum desorption percentage of 86.06% and 100% were obtained for dried ginkgo leaves and mandarin-orange peels, respectively, whereas 86.40% and 96.88% were obtained for 450 °C carbonized ginkgo leaves and mandarin-orange peels, respectively. This suggests that carbonization treatment significantly improves the biosorption performance of ginkgo leaves and mandarin-orange peels using both scandium and dysprosium ions. In addition, the use of dried as well as carbonized parachlorella (alga) in biosorption-desorption of multi-component solution containing Y(III), La(III), Sm(III), Dy(III), Pr(III), Nd(III), Gd(III) were investigated using dried or 250°C and 350°C carbonized parachlorella. The thermal decomposition of dried parachlorella helps the choice of 250°C and 350°C as optimum temperatures to proceed to carbonization. The optimum pH for dried and 250°C carbonized parachlorella was 7 whereas 350°C reaches it maximum uptake at pH 4. Rapid adsorption within the first 5 min of contact followed by a slight variation the following 20 min characterized the sorption processes onto parachlorella by-products. However the ions as Mg, K, Ca, Si containing in the ores solutions, were not adsorbed by parachlorella species indicated selectivity in the biosorption processes. The mechanism of the biosorption is explained by a combination of complex reactions occurring simultaneously in the biosorption process.

In addition, desorption process has been investigated using various concentrations of HCl, HNO₃, and H₂SO₄ at different temperatures. It was found that the reversible process is rapid, less temperature and pH dependent with high desorption percentage. Moreover, only light REEs were desorbed regardless of the kind of acid and the solution temperature. Parachlorella is found to be good and low-cost biosorbent for the recovery of above cited REEs from aqueous solutions and good biosorbents to separate light rare earth from heavy rare earth elements.

The generalization of the carbo-biosorption technology used in the present thesis help to understand that in multi-component solution, pore distribution of the biosorbents, the functional groups governing the surface of the biosorbents as well as the ratio of ionic radius and atomic weight of the reacting ion are some important parameters explaining the mechanism of the process. We also understand that banana peels carbonized at 350 ° C shows affinity to many cations than others tested in the present work. Those carbo-biosorbents as MP450 and PL450 can be used in selective removal or recovery of some metals as Pb and Cd.

The five biomasses composed on leaves, peels and algae studied in the present work prove the affinity of biomasses, independently on the type of the biosorbent, (whether they are leaves or peels or algae) to the biosorption of heavy metals and REEs. Each biosorbent has its own particularity and affinity to adsorb an ion than other. Therefore, tested many biosorbents for specific ions become essential. The proposed methods are believed to be useful for many practical applications regarding water purification system whether in small or large scale.

This thesis work is based on the following articles published in peer-reviewed journals.

- 1- Ponou J., Kim J., Wang L. P., Dodbiba G., Fujita T., (2011), **Sorption of Cr(VI) anions in aqueous solution using carbonized or dried pineapple leaves**, Chemical Engineering 172, 906-913.
- 2- Ponou J., Wang L. P., Dodbiba G., Fujita T.,(2012), **Effect of carbonization on banana peels for removal of cadmium ions from aqueous solution**, Environmental Engineering and Management Journal (In press).
- 3- Ponou J., Wang L. P., Dodbiba G., Fujita T.,(2014), **Evaluation of the flocculation and de-flocculation performance and mechanism of polymer flocculants**, Water Science and Technology doi:10.2166/wst.2014.004.
- 4- Ponou J., Wang L. P., Dodbiba G., Fujita T., (2014), **Recovery of dysprosium ions by biosorption-desorption onto organic plants wastes**,International Journal of the Society of Materials Engineering for Resources,20, In press.
- 5- Ponou J., Wang L. P., Dodbiba G., Fujita T., (2014), **Recovery of rare earth elements from aqueous solution obtained from Vietnamese clay minerals using dried and carbonized parachlorella**, Environmental Chemical Engineering, 2, 1070-1081.