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Biosorption of Heavy Metals from Aqueous Solutions Using Water Hyacinth as a Low Cost Biosorbent

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Abstract

In this study, biosorption of Cu(II) and Zn(II) ions from aqueous solutions by water hyacinth fiber was investigated as a function of initial solution concentration, initial biomass concentration and temperature. Solutions containing copper and zinc ions were prepared synthetically in single component and the time required for attaining adsorption equilibrium was studied. The optimum sorption conditions were studied for each metal separately. The adsorption equilibrium data were adequately characterized by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equations. The equilibrium biosorption isotherms showed that water hyacinth possess high affinity and sorption capacity for Cu(II) and Zn(II) ions, with sorption capacities of 99.42 mg Cu^{2+} and 83.01 mg Zn^{2+} per 1 g biomass, respectively. All results showed that water hyacinth fiber is an alternative low cost biosorbent for removal of heavy metal ions from aqueous media.

Keywords: biosorption, low cost biosorbent, wastewater treatment, heavy metal

1. Introduction

Many industrial processes, such as mining, metal pigment, refining ores, fertilizer industries, tanneries, batteries manufacturing, paper industries and pesticides, result in the release of heavy metals to aquatic ecosystems. Heavy metals are toxic pollutants, which can accumulate in living tissues causing various diseases and disorders. The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn etc. Removal of toxic contaminants from wastewaters is one of the most important environmental issues. Since all heavy metals are non-biodegradable, they must be removed from the polluted streams for the environmental quality standards to be met (Witek-Krowiak *et al*. 2011). Several methods have been employed to remove heavy metal ions from wastewater, which include chemical precipitation, chemical oxidation/reduction, flotation, reverse osmosis, ion exchange, membrane-related process, ultra filtration, electrochemical technique and biological process (Dursun 2006; Satapathy & Natarajan 2006; Vijayaraghavan *et al*. 2007; Wang *et al*. 2006; Deng *et al*. 2007; Hanif *et al*. 2007; Preetha & Viruthagiri 2007). Adsorption is the most attractive method due to its simplicity, convenience and high removal efficiency. In common sorption processes, activated carbon and synthetic resins are usually used to gain high removal efficiency. However, due to their high production cost, water decontamination by using these two sorbents is rather expensive (Southichak *et al*. 2006; Choi & Jang 2008; Francesca *et al*. 2008; Zheng *et al*. 2009).

Since 1990's the adsorption of heavy metal ions by low cost renewable organic materials has gained momentum (Vieira & Volesky, 2000; Rao & Parwate 2002). The utilization of seaweeds, moulds, yeasts, and other dead microbial biomass and agricultural waste materials for removal of heavy metals has been explored (Sudha & Abraham 2003). Agricultural materials particularly those containing cellulose shows potential metal biosorption capacity. The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals (Hashem *et al*. 2005; Hashem *et al*. 2007). Agricultural waste materials being economic and ecofriendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation (Sud *et al*. 2008).

Water hyacinth (*Eichhornia crassipes*) is a noxious weed that has attracted worldwide attention due to its fast spread and congested growth, which lead to serious problems in navigation, irrigation, and power generation. On the other hand, when looked from a resource angle, it appears to be a valuable resource with several unique properties. As a result, research activity concerning control (especially biological control) and utilization (especially wastewater treatment or phytoremediation) of water hyacinth has boomed up in the last few decades (Malik 2007). The objective of this study was to investigate the potential of water hyacinth for absorbing copper (II) and zinc (II) from aqueous solution. Also the influence of various parameters such as initial solution concentration, initial biomass concentration and temperature on biosorption potential of agricultural waste material was studied in detail.

2. Experimental

2.1 Biosorbent Preparation

Reaction of cellulose with phosphoric acid was performed according to the method described in the previous research (Suflet *et al*. 2006). In a 500 mL, three-necked flask equipped with a nitrogen inlet, a condenser, a thermometer, and a stirrer, 224 g urea was added, heated at 140 ^oC and flushed with nitrogen. 30 g water hyacinth and 168 mL phosphorous acid were added alternatively portionwise to the molten urea in order to reduce the foaming. The reaction was allowed to proceed at 150 ^oC for 2 h. The fiber was washed with distilled water and acetone. A sample of fiber was treated with 0.5 M hydrochloric acid for 24 h under slow stirring. The modified cellulose was washed several times with deionized water to remove excess acid from biosorbent. It was dried for 24 h at 60 ^oC in an oven before starting the experiments.

2.2 Metal Solution Preparation

All chemicals used were analytical grade reagents (Merck, >99 %purity). Stock solutions of metals were prepared in a concentration of 2,000 ppm using nitrate salts dissolved in deionized water with a resistivity value of 17 MΩ. The chemicals used in the batch experiments were nitrate solutions of $Cu(NO_3)_2$ and $Zn(NO_3)_2$.

2.3 Isotherm Experiments

Batch mode adsorption isotherm was carried out at 30-70 ^oC. Amount of 1.0-5.0 g modified cellulose were introduced into conical flasks with 100 mL of heavy metal solution. The flasks were placed in a thermostatic shaker and agitated for 150 min at a fixed agitation speed of 700 rpm. Samples were taken periodically for measurement of aqueous phase of heavy metal concentrations. Adsorption isotherms were performed for initial heavy metal concentrations of 250-1,250 ppm. The Cu (II) and Zn (II) concentration of the samples were determined by using a Varian Liberty 220 inductive coupled plasma emission spectrometer (ICP-ES).

The amount of adsorbed Cu^{2+} and Zn^{2+} ions (mg metal ions/g biomass) were calculated from the decrease in the concentration of metal ions in the medium by considering the adsorption volume and used amount of the biosorbent:

$$q_e = \frac{(C_i - C_e)\,V}{m} \tag{1}$$

where q_e is the amount of metal ions adsorbed into unit mass of the biosorbent (mg/g) at equilibrium, C_i and C_e are the initial and final (equilibrium) concentrations of the metal ions in the solution (ppm), V is the volume of metal solution (L) and m is the amount of biosorbent used (g).

2.4 Adsorption Isotherm Models

Batch Adsorption isotherms for copper and zinc ions removal by water hyacinth in terms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models were expressed mathematically. The obtained experimental data here are expectedly well fitted with the linearized form of four two-parameter isotherm models.

The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneous adsorption energy. This model (Langmuir 1916; Langmuir 1918) is expressed as follows:

$$q_e = \frac{K_L a_L C_e}{1 + a_L C_e} \tag{2}$$

where K_L and a_L are the Langmuir constants related to the adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. The theoretical maximum monolayer adsorption capacity, q_m (mg/g), is given by K_L/a_L.

The Freundlich isotherm is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent. The Freundlich model (Freundlich 1906) is expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F and n are indicative isotherm parameters of adsorption capacity (mg/g) and intensity, respectively.

Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm (Temkin & Pyzhev 1940) is expressed by the following equation:

$$q_e = \frac{RT}{b} \ln \left(K_{Te} C_e \right) \tag{4}$$

where K_{Te} is equilibrium binding constant (L/g), b is related to heat of adsorption (J/mol), R is the gas constant (8.314×10^{-3} kJ/K mol) and T is the absolute temperature (K).

Dubinin-Radushkevich isotherm is applied to find out the adsorption mechanism based on the potential theory assuming heterogeneous surface (Dabrowski 2001). Dubinin-Radushkevich isotherm (Dubinin & Radushkevich 1947; Dubinin 1960; Kalavathy & Miranda 2010) is expressed as follows:

$$q_e = q_m \exp \left(-K\varepsilon^2 \right) \tag{5}$$

where q_m is the maximum adsorption capacity (mg/g), K is a constant related to the mean free energy of adsorption and ε is the Polanyi potential.

3. Results and Discussion

Biosorption of heavy metal ions onto the surface of a biological material is affected by several factors, such as initial solution concentration, initial biomass concentration and temperature.

3.1 Effect of Initial Solution Concentration

Figure 1 illustrates the adsorption of Cu(II) and Zn(II) ions by water hyacinth as a function of initial metal ion concentration. This increase continues up to 1,000 for Cu^{2+} and 750 ppm for zn^{2+} and beyond this value, there is not a significant change at the amount of adsorbed metal ions. This plateau represents saturation of the active sites available on the biosorbent samples for interaction with metal ions. It can be concluded that the amount of metal ions adsorbed into unit mass of the water hyacinth at equilibrium (the adsorption capacity) rapidly increases at the low initial metal ions concentration and then it begins to a slight increase with increasing metal concentration in aqueous solutions in the length between 1,000 and 1,250 ppm for copper, but 750 and 1,250 ppm for zinc. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution. The metal uptake can be attributed to different mechanisms of ion exchange and adsorption processes as it was concerned in much previous work (Bektas & Kara 2004; Buasri *et al*. 2007).

3.2 Effect of Initial Biomass Concentration

Experiments conducted with different initial biomass concentrations show that the metal ions uptakes increase with the biosorbent concentration (Figure 2). The number of sites available for biosorption depends upon the amount of the biosorbent. The metal ions uptake was found to increase linearly with the increasing concentration of the biosorbent up to the biomass concentration of 2 and 3 g/100 mL for Cu(II) and Zn(II), respectively. Beyond this dosage, the increase in removal efficiency was lower. Increasing the biosorbent dosage caused a wise in the biomass surface area and in the number of potential binding sites (Witek-Krowiak *et al*. 2011).

3.3 Effect of Temperature

From Figure 3, the amounts of adsorbed copper and zinc ions onto the water hyacinth increase with an increase in the temperature of heavy metal solution. The maximum adsorption capacities was calculated as 87.69 mg Cu^{2+} and 75.53 mg Zn^{2+} per 1 g biomass for initial concentration of 500 ppm at 70 ^{o}C, showed that this biosorbent was suitable for heavy metals removal from aqueous media. Concerning the effect of temperature on the adsorption process, the metals uptake is favored at higher temperatures, since a higher temperature activates the metal ions for enhancing adsorption at the coordinating sites of the minerals. Also, it is mentioned that cations move faster with increasing temperature. Likely explanation for this is that retarding specific or electrostatic, interactions become weaker and the ions become smaller, because solvation is reduced (Babel & Kurniawan 2003; Inglezakis *et al*. 2004).

3.4 Effect of Initial Biomass Concentration

In addition to the experimental data, the linearized forms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms using Eqs. (2), (3), (4) and (5), are compared. The relationship between the adsorbed and the aqueous concentrations at equilibrium has been described by four two-parameter isotherm models. The isotherm constants and corresponding correlation coefficients for the adsorption of Cu(II) and Zn (II) are presented in Table 1. The correlation coefficients demonstrate that Langmuir, Freundlich and Temkin models adequately fitted the data for Cu adsorption. However, the coefficient of determination (R^2) values are higher in the Langmuir model for copper and Freundlich model for zinc adsorption when compared to other models. The Temkin isotherm shows a higher correlation coefficient for both metal ($R^2 = 0.9886$ for Cu^{2+} and $R^2 = 0.9870$ for Zn^{2+}, which may be due to the linear dependence of heat of adsorption at low or medium coverages. This linearity may be due to repulsion between adsorbate species or to intrinsic surface heterogeneity (Kalavathy & Miranda 2010; Caliskan *et al*. 2011). The experimental data for both heavy metal ions fit well with the linearized Langmuir, Freundlich, Temkin and

Dubinin-Radushkevich isotherms. R^2 values ranged from 0.8397 to 0.9933 and 0.8041 to 0.9948 for adsorption of Cu^{2+} and Zn^{2+}, respectively. These results indicated that the equilibrium adsorption data of copper and zinc conformed reasonably well to the four two-parameter isotherm models equations.

4. Conclusion

Water hyacinth is an environmentally friendly potential biosorbent for heavy metals. This work examined the efficiency of this sorbent in removal of Cu(II) and Zn(II) ions from aqueous environment. The results indicated that several factors such as initial solution concentration, initial biomass concentration and temperature affect the biosorption process. The physico-chemical characteristics of wastewaters from varying sources can be much more complex compared to the aqueous metal solution used in this study. Because of this, the effects of other components of wastewaters on commercial metal adsorption process should be determined. However, this work can be considered a preliminary study to conclude that water hyacinth is suitable and efficient material for the adsorption of Cu^{2+} and Zn^{2+} from aqueous solution. The experimental results were a good fit with the adsorption isotherm models.

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References

Babel, S. & Kurniawan, T.A. (2003), "Low-cost adsorbents for heavy metals uptake from contaminated water", *Journal of Hazardous Materials* **97**, 219-243.

Bektas, N. & Kara, S. (2004), "Removal of lead from aqueous solutions by natural clinoptilolite: Equilibrium and kinetics studies", *Separation and Purification Technology* **39**, 189-200.

Buasri, A., Chaiyut, N., Ponpatcharasakul, N., Artsalee, P. & Potisook, S. (2007), "Factors affecting the removal of copper(II) and zinc(II) from aqueous solutions with clinoptilolite", *Journal of Research in Engineering and Technology* **4**, 1-17.

Caliskan, N., Kul, A.R., Alkan, S., Sogut, E.G. & Alacabey, I. (2011), "Adsorption of Zinc(II) on diatomite and manganese-oxide-modified diatomite: A kinetic and equilibrium study", *Journal of Hazardous Materials* **193**, 27-36.

Choi, M. & Jang, J. (2008), "Heavy metal ion adsorption onto polypyrrole-impregnated porous carbon", *Journal of Colloid and Interface Science* **325**, 287-289.

Dabrowski, A. (2001), "Adsorption-from theory to practice", *Advances in Colloid and Interface Science* **93**, 135-224.

Deng, L., Zhu, X., Wang, X., Su, Y. & Su, H. (2007), "Biosorption of copper (II) from aqueous solutions by green alga *Cladophora fascicularis*", *Biodegradation* **18**, 393-402.

Dubinin, M.M. & Radushkevich, L.V. (1947), "Equation of the characteristic curve of activated charcoal", *Chemisches Zentralblatt* **1**, 875-890.

Dubinin, M.M. (1960), "The potential theory of adsorption of gases and vapours for adsorbents with energetically non-uniform surfaces", *Chemical Reviews* **60**, 235-241.

Dursun, A.Y. (2006), "A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*", *Biochemical Engineering Journal* **28**, 187-195.

Francesca, P., Sara, M. & Luigi, T. (2008), "New biosorbent materials for heavy metal removal: Product development guided by active site characterization", *Water Research* **42**, 2953-2962.

Freundlich, H.M.F. (1906), "Over the adsorption in solution", *Journal of Physical Chemistry* **57**, 385-470.

Hanif, M.A., Nadeem, R., Bhatti, H.N., Ahmad, N.R. & Ansari, T.M. (2007), "Ni(II) biosorption by *Cassia fistula* (golden Shower) biomass", *Journal of Hazardous Materials* **139**, 345-355.

Hashem, A., Abdel-Halim, E.S., El-Tahlawy, K.F. & Hebeish, A. (2005), "Enhancement of the adsorption of Co(II) and Ni(II) ions onto peanut hulls through esterification using citric acid", *Adsorption Science & Technology* **23**, 367-380.

Hashem, A., Akasha, R.A., Ghith, A. & Hussein, D.A. (2007), "Adsorbent based on agricultural wastes for heavy metal and dye removal: A review", *Energy Education Science and Technology* **19**, 69-86.

Inglezakis, V.J., Loizidou, M.D. & Grigoropoulou, H.P. (2004), "Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility", *Journal of Colloid and Interface Science* **275**, 570-576.

Kalavathy, M.H. & Miranda, L.R. (2010), "Moringa oleifera-A solid phase extractant for the removal of copper, nickel and zinc from aqueous solutions", *Chemical Engineering Journal* **158**, 188-199.

Langmuir, I. (1916), "The constitution and fundamental properties of solids and liquids: Part I. Solids", *Journal of the American Chemical Society* **38**, 2221-2295.

Langmuir, I. (1918), "The adsorption of gases on plane surfaces of glass, mica and platinum", *Journal of the American Chemical Society* **40**, 1361-1403.

Malik, A. (2007), "Environmental challenge vis a vis opportunity: The case of water hyacinth", *Environment International* **33**, 122-138.

Preetha, B. & Viruthagiri, T. (2007), "Batch and continuous biosorption of chromium(VI) by Rhizopus arrhizus", *Separation and Purification Technology* **57**, 126-133.

Rao, M. & Parwate, A.V. (2002), Utilization of low-cost adsorbents for the removal of heavy metals from wastewater - A review", *Journal* of *Environmental Pollution Control* **5**, 12-23.

Satapathy, D. & Natarajan, G.S. (2006), "Potassium bromate modification of the granular activated carbon and its effect on nickel adsorption", *Adsorption* **12**, 147-154.

Southichak, B., Nakano, K., Nomura, M., Chiba, N. & Nishimura, O. (2006), "Phragmites australis: A novel biosorbent for the removal of heavy metals from aqueous solution", *Water Research* **40**, 2295-2302.

Sud, D., Mahajan, G. & Kaur, M.P. (2008), "Agricultural waste materials potential absorbent for sequestering heavy metal ions from aqueous solutions", *Bioresource Technology* **99**, 6017-6027.

Sudha, B.R. & Abraham, E. (2003), "Studies on Cr (VI) adsorption-desorption using immobilized fungal biomass", *Bioresource Technology* **87**, 17-26.

Suflet, D.M., Chitanu, G.C. & Pora, V.I. (2006), "Phosphorylation of polysaccharides: New results on synthesis and characterization of phosphorylated cellulose", *Reactive and Functional Polymers* **66**, 1240-1249.

Temkin, M.I. & Pyzhev, V. (1940), "Kinetics of ammonia synthesis on promoted iron catalysts", *Acta Physiochem* **12**, 327-356.

Vieira, R.H. & Volesky, B. (2000), "Biosorption: a solution to pollution?", *International Microbiology* **3**, 17-24.

Vijayaraghavan, K., Palanivelu, K. & Velan, M. (2007), "Biosorption of copper (II) and cobalt (II) from aqueous solutions by crab shell particles", *Bioresource Technology* **97**, 1411-1419.

Wang, X., Xia, S., Chen, L., Zhao, J., Chovelon, J. & Nicole, J. (2006), "Biosorption of cadmium(II) and lead(II) ions from aqueous solutions onto dried activated sludge", *Journal of Environmental Sciences* **18**, 840-844.

Witek-Krowiak, A., Szafran, R.G. & Modelski, S. (2011), "Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent", *Desalination* **265**, 126-134.

Zheng, J.C., Feng, H.M., Lam, M.H., Lam, P.K., Ding, Y.W. & Yu, H.Q. (2009), "Removal of Cu(II) in aqueous media by biosorption using water hyacinth roots as a biosorbent material", *Journal of Hazardous Materials* **171**, 780-785.

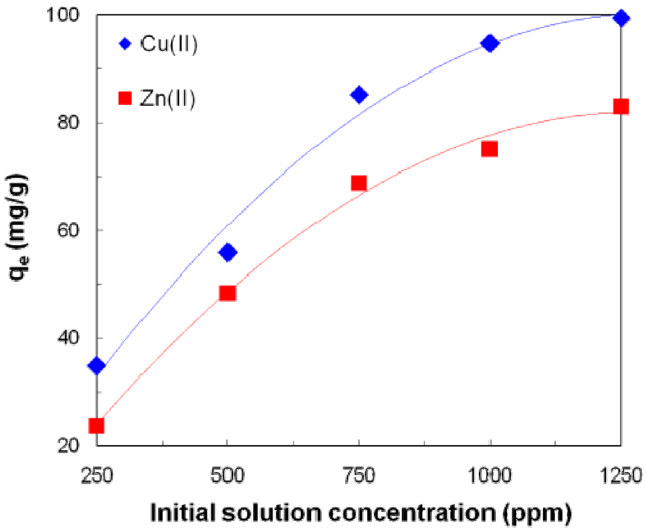

Figure 1. Effect of initial solution concentration on the removal of Cu(II) and Zn(II) by water hyacinth (amount of biosorbent = 2.0 g, temperature = 30 °C and contact time = 150 min)

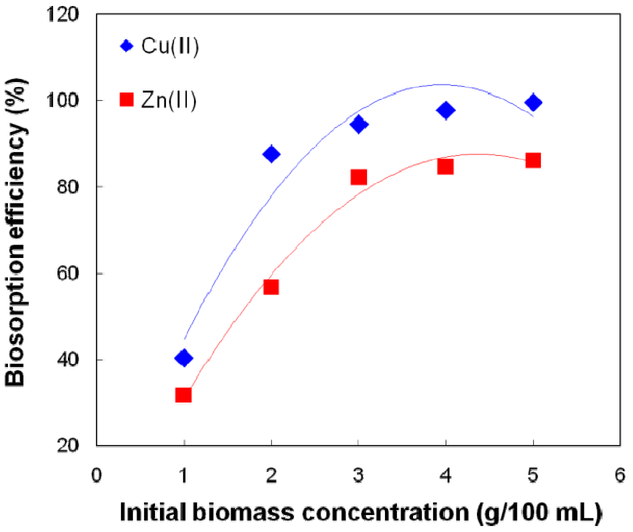

Figure 2. Effect of initial biomass concentration on the removal of Cu(II) and Zn(II) by water hyacinth (initial solution concentration = 500 ppm, temperature = 30 °C and contact time = 150 min)

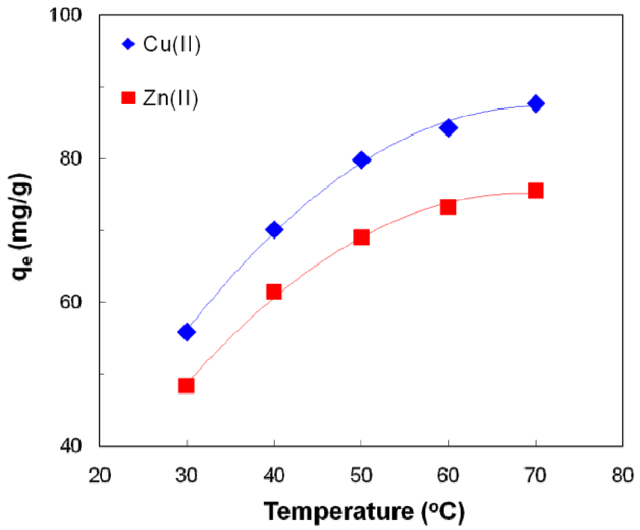

Figure 3. Effect of temperature on the removal of Cu(II) and Zn(II) by water hyacinth (initial solution concentration = 500 ppm, amount of biosorbent = 2.0 g and contact time = 150 min)

Table 1. Isotherm constants for the biosorption of Cu(II) and Zn(II) on water hyacinth

Isotherm constants	Copper	Zinc
Langmuir model		
K_L (mg/g)	11.5372	17.6710
a_L (L/mg)	0.2168	0.1432
R^2	0.9933	0.9559
Freundlich model		
K_F (mg/g)	2.9154	3.7740
n	2.7198	2.2530
R^2	0.9801	0.9948
Temkin model		
K_{Te} (L/g)	2.8016	6.3063
b	1.1200	0.7220
R^2	0.9886	0.9870
Dubinin-Radushkevich model		
q_m (mg/g)	8.5975	11.4866
K	0.9429	0.4602
R^2	0.8397	0.8041

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