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Comparison of Different Methods for Linear Regression of Pseudo Second Order Adsorption Kinetics of Cadmium

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ABSTRACT: The present paper would discuss the four linear regression of kinetic model of pseudo second order to describe the adsorption phenomenon. The adsorption parameters have been estimated by means of nonlinear method of pseudo second order as well as four linear regression methods are assessed. The results showed that, the nonlinear method of pseudo second order is a suitable method in estimating of adsorption parameters. A type 1 pseudo second order linear kinetic model has the highest coefficient of determination. It was also found that, among the regression methods, all of them except the regression type 2 would be useful recommendation for estimation of adsorption parameters.

ORIGINAL ARTICLE

Keywords: Adsorption, Adsorption potential, Adsorption kinetics, linear regression.

INTRODUCTION

Chemical waste effluents into waterways, is a common practice in present days which its hazardous impacts are very intense and longstanding environmental problem. From environmental engineering and hydrodynamics view points, it is necessary the flow, transport and metamorphosis of such materials to be carefully studied in waterways. Displacement of chemical materials in flow reach is influenced by physical, chemical, and biological processes. The relative impact of each process is dependent on the ambient conditions and chemical characteristics of different solutions.

In common, the polluting agents may affect the water quality of rivers either as point or scattered sources. Point sources include municipal and industrial effluents which offload into the rivers. Whereas, the scatter sources may encounter the outflow from agricultural drainage systems and/or seeping streams from petroleum conveyance networks and mining enterprises.

For any river quality model, selection of an appropriate model to predict chemical and biological reactions, knowledge of pollution sources and properties, advection, diffusion, dispersion, interchanges from one phase to another, and their interaction (soil-water, water-air,…) would be required. Therefore, it is the first obligation in any research to study each of these processes and their impacts.

Among the physical processes, advection and dispersion are two key factors in transporting the soluble materials. The central displacement of soluble materials along the water reach is governed by convection while, the dispersion is responsible for their cross displacement.

The process by which the soluble material is moved and attached to solid particles known as adsorption. This phenomenon includes the accumulation of materials on solid surface as well mixing the material with solid particles. The reverse of this process is known as desorption. Sediment particles because of their tendency to absorb the heavy metals as well as mineral and organic materials would play a distinguished role in movement and transformation of polluting agents resulted from agricultural activities. Therefore, adsorption process is one of the important processes which need a careful attention. Fig.1, demonstrates a collection of chemical and biological reactions which should be considered in any models dealing with pollutions.

The role of adsorption and desorption was widely studied by various investigators. Windom *et al.* (1991) showed that the suspended loads in the rivers of Eastern US were transporting 62, 40, 90, and 80 percents of Cd, Cu, Pb, and Zn respectively. Therefore, the rivers could act as a self refining system which may become effective in decreasing the pollution sources. On the other hand, Huang (2003) reported that the re-suspension of sediments through dredging, tides, floods and cleaning of silting basins causes the polluting materials re-enter in the rivers. This indicates that detachment of polluting materials from sediments particles may play a long living role in water pollution. It is noted that the changes in chemical properties of water such as; pH, salinity, and etc can be effective in liberating the polluting materials.

Taqvy et *al.* (2006) studied the adsorption of cadmium by delta sediments. Later, Sharma *et al.* (2007a) conducted a similar research using river bed materials. According to various experimental and field observations, it is found that, the adsorption of soluble materials with granular particles is performed by kinetics. Smith and Comans (1996) studied cesium adsorption with natural sediments and reported that, the advection in both short and long intervals. The sorptive removal of chromium (VI) from aqueous solutions by calcined Mg–Al–CO3 hydrotalcite was investigated in a batch mode by Lazaridis and Asouhidou (2003). The influence of agitation speed, solution pH, initial chromium concentration, sorbent concentration and temperature has been tested in kinetic runs. Three kinetic models have been evaluated to fit the experimental data: the pseudo-first order, the modified-second order and the Elovich equation. It was shown that the first-order model could best describe the sorption kinetics. Donghui Wen *et al.* (2006) assessed the adsorption of ammonium by zeolite where the pseudo-first order adsorption and pseudo-second order adsorption were compared. Sharma *et al.* (2007b) considered both equilibrium and kinetics processes to study the adsorption of chromium (VI) by river bed sediments. Svilovic *et al.* (2009) investigated adsorption kinetics of cupper by zeolite in which the effect of several parameters such as size of absorbing particles, concentration and temperature of solution were considered.

In this study, sorption pseudo-second-order kinetic model was studied. A comparison was made of the linear least-squares method and a trial-and-error non-linear method of the widely used pseudo-second-order kinetic model for the sorption of cadmium onto fine sediment particles.

Related equations

Numerous models could be used to analyze the kinetics of adsorption process. Azizian (2004) reported that, the pseudo-second order equation for determining the adsorption rate of soluble materials could be expressed as:

$$\frac{dq}{dt} = k\,(q_e - q)^2 \qquad 1$$

With a similar integration to Eq. (3) and some rearrangements we would have:

$$q_t = \frac{k\,q_e^{\,2}\,t}{1 + k\,q_e t} \qquad 2$$

Where, k is the constant of pseudo-second order adsorption rate, q_t and q_e are the mass of chemical material to unit mass of sediment at certain time (t) and equilibrium state, respectively.

The coefficient k in equations 1 and 2, is function of the initial concentration of soluble, size of particles, organic content of particles, and ambient conditions such as pH and salinity.

As would be recognized from Eq.2, the kinetic model of second order adsorption contains two parameters q_e and k which should be determined by iteration *i.e.;* by nonlinear method. These parameters could be also obtained by linearization of Eq.2 which can be attempted by using several methods. Four typical methods of this kind have been considered in this research.

First, Eq.2 would be arranged in form of:

$$q_t = \frac{t}{1/k\,q_e^{\,2} + t/q_e} \qquad 3$$

With some mathematical work, this equation can be altered to linear regression equation of type (1) as:

$$\frac{t}{q_t} = \frac{1}{kq_e^{\,2}} + \frac{1}{q_e}t \qquad 4$$

To use linear regression equation of type (1), one has to plot $\frac{t}{q_t}$ with t, which would ease determine the adsorbed mass of chemical material to unit mass of sediment at equilibrium state q_e, and also the magnitude of k. There are some more types of linear regression of the kinetic model of second order adsorption which are summarized in Table.1 that can be used to for different types of regression and obtain their required parameters.

MATERIALS AND METHODS

To assess and compare the strength of different methods of adsorption kinetics 10 series of experimental data from cadmium adsorption by fine sediments were used. A sediment size of 0.115 mm was selected by using standard sieving apparatus (particles remained between sieves 120 and 140) and then was carefully washed with distilled water. Cadmium was the heavy metal which used in whole experiments, because of its toxicity and hazardous impact on human life. Cadmium measurement was conducted by using an ICP-OES Varian VISTA-MPX device.

During the experiments, first a solution of cadmium was prepared and its temperature, pH, and EC were adjusted to certain desired level. Depending on the concentration of selected solution, a certain amount of sediment with 50 ml of solution was poured in each flask. Each flask was then rotated by 200 r/m speed where the temperature was kept constant. Each experiment was repeated to avoid any likelihood errors and then the sample was taken to proceed with required measurements.

The relevant curves in Table.1, designated for each linear methods, were depicted and the parameters of q_e and k were determined. Also the “solver tool” in excel software was used to determine the required parameters for pseudo-second order method where it was attempted to minimize the Sum of Square Error (SSE).

$$SSE = \sum_{i=1}^{n} (p_i - o_i)^2 \qquad 5$$

Where p_i and o_i are estimated and observed values, respectively.

RESULTS AND DISCUSSION

As the first step, the estimated values of q_e were assessed by different methods and results are shown in Fig.2. It is evident from the plots in Fig.2 that, all method demonstrate an acceptable estimate of q_e.To assess the level of accuracy in different estimations; SSE values were calculated for each method which are tabulated in Table 2. Careful study of Table 2 shows that pseudo-second order gives a better estimation for q_e. Among the linear models, type one is most desirable to estimate q_e whereas; type two would be the worst. Using the estimated values of q_e, the magnitudes of q_t were computed at various times using the second order kinetic model of adsorption. Approximately, 145 values of q_t were determined by using Eq.4 and then compared with measured values in Figure 3.

To study the precision of estimated values of q_t and their conformity with experimental observations, SSE were again calculated and results are demonstrated in Table 3. Comparing the results in Tables 2 and 3, shows that the method of pseudo-second order is the best model to estimate both q_e and q_t.

Table 1. Types of second order kinetic linear regression for adsorption

Type of regression	Equation	Plotting parameters
Type 1	$\frac{t}{q_t}=\frac{1}{kq_e^2}+\frac{1}{q_e}t$	$\frac{t}{q_t}$ against t
Type 2	$\frac{1}{q_t}=\left(\frac{1}{kq_e^2}\right)\frac{1}{t}+\frac{1}{q_e}$	$\frac{1}{q_t}$ against $\frac{1}{t}$
Type 3	$q_t=q_e-\left(\frac{1}{kq_e}\right)\frac{q_t}{t}$	q_t against $\frac{q_t}{t}$
Type 4	$\frac{q_t}{t}=kq_e^2-kq_eq_t$	$\frac{q_t}{t}$ against t

Table 2. SSE values of estimated q_e with different methods

Method	Linear type one	Linear type two	Linear type three	Linear type four	pseudo-second order
SSE	0.00085	0.0027	0.0015	0.001	0.0008

Table 3. SSE of estimated q_t values from different methods compared with measured values

Method	Linea r type one	Linear type two	Linear type three	Linear type four	pseudo-second order
SSE	0.014 2	0.036	0.013	0.0111	0.0094

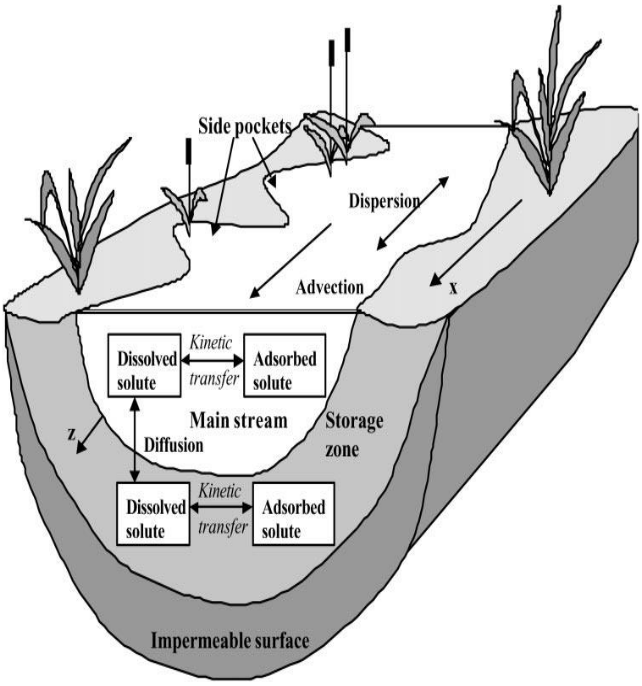

Figure 1. Typical scheme of processes in rivers

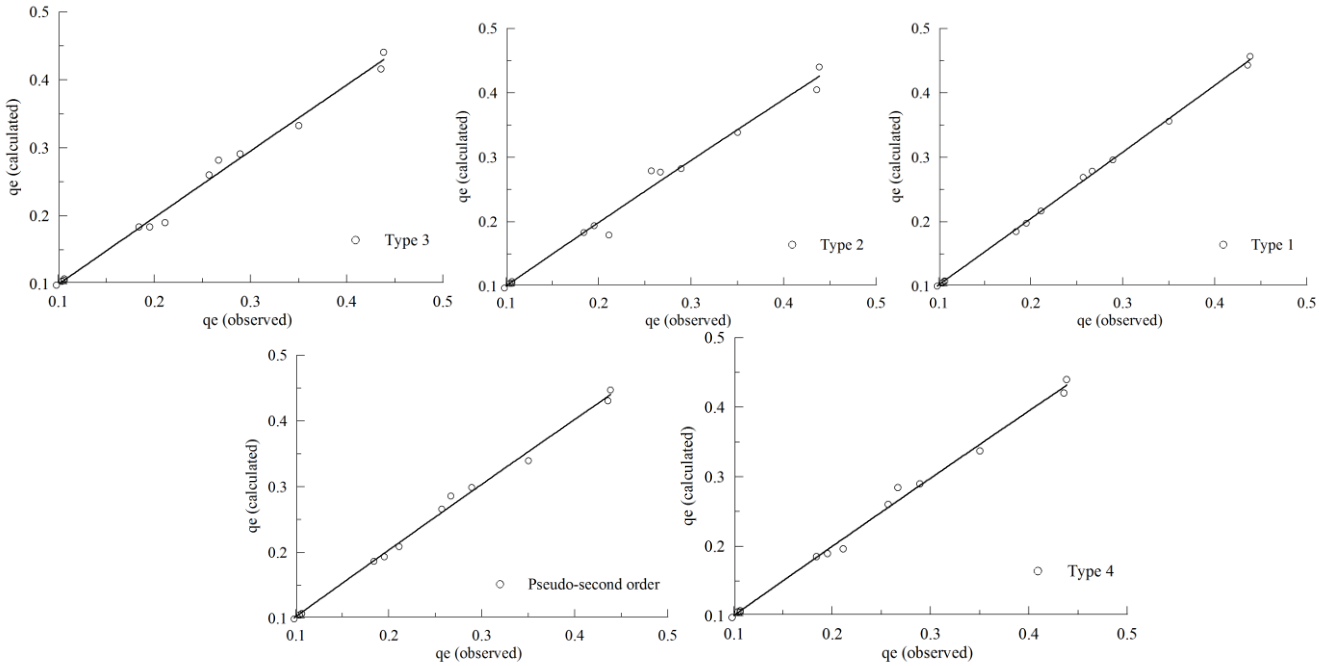

Figure 2. Estimated values of q_e by different methods (ppm)

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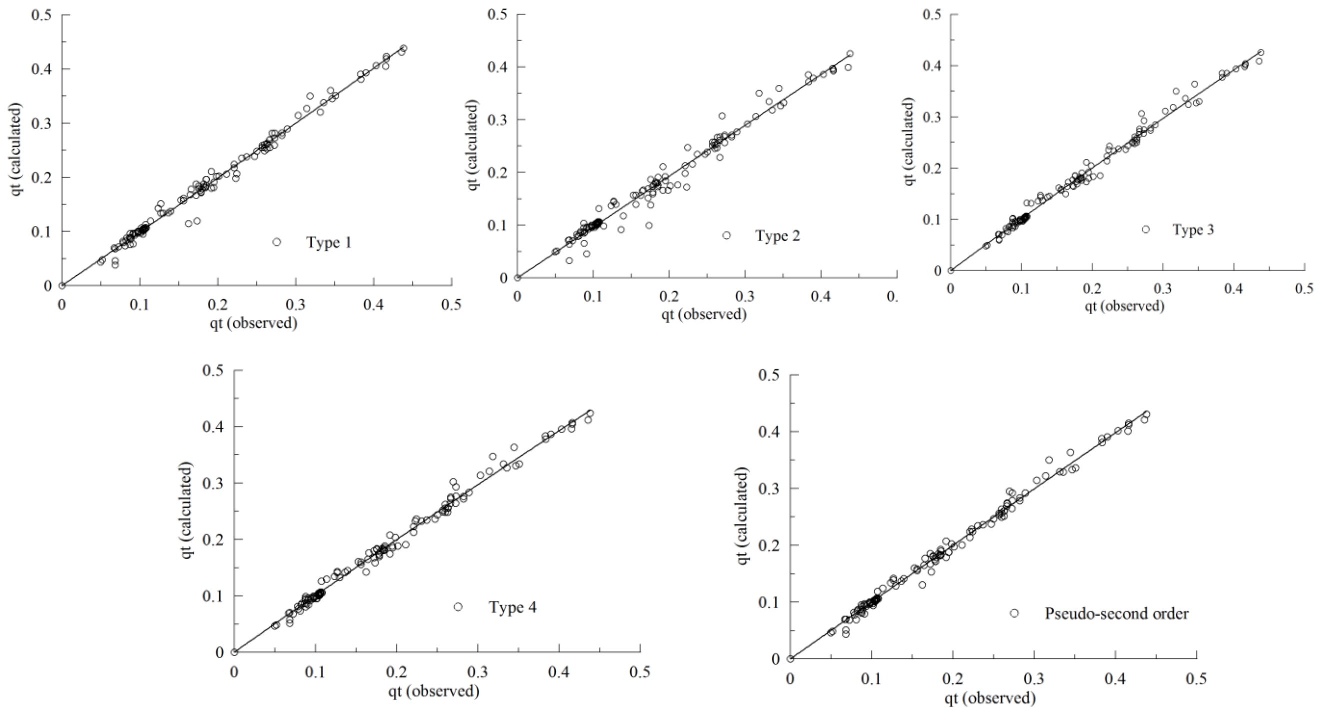

Figure 3. Comparison of estimated q_t from different methods with measured values (ppm)

CONCLUSION

From the measured and estimated data of cadmium adsorption with fine sediments in this research, the following remarks would be concluded.

1. Pseudo-second order gives a better estimation for q_e. Among the linear models, type one is the most desirable to estimate q_e whereas; type two would be the worst.
2. Nonlinear method of second order and linear method of type four would attain first and second position in estimating q_t values, respectively. Although the nonlinear method of second order is in the first rank to estimate q_t values but, it needs a lot of iteration which makes its application somehow difficult. Therefore, it indicates that the linear method of type four would end up with an easier procedure and better approximation in second order of adsorption kinetic equation.
3. It was also recognized that, nonlinear method would gives a better estimation of q_e than all linear regression methods.

Notation

SSE Sum of Square Error

k constant for pseudo-second order of adsorption rate

q_e amount of Cd absorbed with unit mass of sediment at equilibrium state *(µg/g)*

q_t amount of Cd absorbed with unit mass of sediment at time *t (µg/g)*

REFERENCES

Azizian S. (2004). Kinetic models of sorption: a theoretical analysis, J. Colloid Interf. Sci., Vol. 276; 47–52.

Donghui Wen, Yuh-Shan Ho, Xiaoyan Tang. (2006). Comparative sorption kinetic studies of ammonium onto zeolite, J. Hazard. Mater, Vol.133; 252–256.

Huang SL. (2003). Investigation of cadmium desorption from different-sized sediments, J. of Env. Eng. ASCE, 129(3): 241-247.

Lazaridis NK, Asouhidou DD. (2003). Kinetics of sorptive removal of chromium (VI) from aqueous solutions by calcined Mg–Al–CO3 hydrotalcite, Water Res, 37:2875–2882.

Sharma YC, Kaul SN, Weng CH. (2007). Adsorptive separation of cadmium from aqueous solutions and wastewaters by river bed sand, Environmental pollution, Vol.150; 251-257.

Sharma YC, Weng CH. (2007). Removal of chromium (VI) from water and wastewater by using riverbed sand: kinetic and equilibrium studies, J. Hazard. Mater, Vol.142; 449–454.

Smith JT, Comans RNJ. (1996). Modeling the diffusive transport and remobilization of 137Cs in sediments: the effects of sorption kinetics and reversibility, Geochim. Cosmochim, Acta 60; 995–1004.

Svilovic S, Rusic D, Stipisic R. (2009). Modeling batch kinetics of copper ions sorption using synthetic zeolite NaX, J. Hazard. Mater, Vol.170: 941–947.

Taqvy SIH, Hasany SM, Bhanger MI. (2006). Sorption profiles of Cd (II) ions onto beach sand from aqueous solutions, J. of Hazardous Materials, Vol.10, No.3; 69–81.

Windom HL, Byrd T, Smith RG, Huan F. (1991). Inadequacy of NASQUAN data for assessing metal trends in the nation's rivers, Environ SciTechnol, 25: 1137-1142.