Sorption model identification for chromium transport in unconsolidated sediments

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Introduction

The transport of reactive solute like Cr(VI) in groundwater environment can be largely influenced by adsorption/desorption process. In this process, the influence of the porous media with different properties, which causes heterogeneity to some extent, cannot be ignored. In this study, six different kinds of sediments were collected to investigate the adsorption and mobility of Cr(VI) in varied sediments using batch and column experiments. The results of batch experiments were described by three kinetic models and two equilibrium isotherms. Four model identification criteria were used to rank these alternative models and identify the sorption mechanism. The adsorption parameters derived from column experiments were compared with batch experiments. The results from this study provide important insight for us to understand the transport behaviors of Cr(VI) in porous media.

Materials and methods

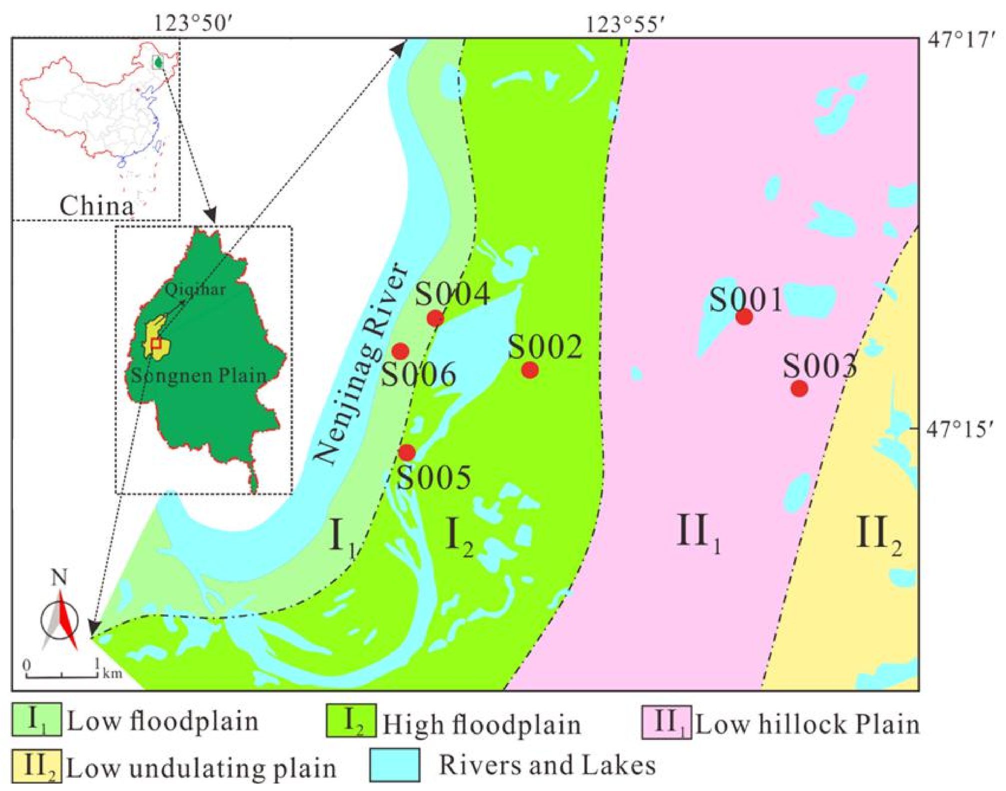

Figure 1. Geological localization of sediments used in this work.

A study site under threats, which is a typical alluvial valley plain in the north east of China, was chosen for the sample collection. The study site has been in a fluvial and lacustrine sedimentary environment and deposited thick Pleistocene unconsolidated sediments since the Quaternary.

We collected the six sediment samples along the transverse direction.

Table 1
Particle size and sediment type characterization

	Clay (%)	Silt (%)	Sand (%)	SSA	type
	< 0.002 mm	0.002-0.02 mm	0.02-0.2 mm		
S001	2.69	6.33	90.98	0.086	Loamy sand
S002	5.83	22.12	72.05	0.185	Sandy loam
S003	2.08	6.06	91.86	0.066	Loamy sand
S004	16.35	58.75	24.90	0.481	Silty loam clay
S005	10.41	44.30	45.29	0.332	Loam
S006	7.74	29.81	62.45	0.246	Sandy loam

Table 2
Main chemical and mineral components (%)

Samples	Quartz	Plagioclase	Clay minerals	Al_2O_3	Fe_2O_3	FeO	LOI
S001	33	20	24	13.94	3.08	0.54	2.01
S002	40	8	43	14.22	3.17	0.52	2.84
S003	32	14	36	13.94	2.88	0.59	2.1
S004	34	17	42	16.09	3.21	0.63	5.99
S005	27	11	57	14.6	3.45	0.63	4.28
S006	35	13	47	13.96	3.06	0.52	3.42

All the batch experiments were performed at room temperature (25±1 °C) in the SHA-C oscillator at a rate of 200 rpm. Each sample in a conical flask contains 2 g soil and 50ml solution. In kinetic experiments, theconcentration of Cr(VI) was 5 mg/L in initial solution. Then the Cr(VI) was analyzed at different time intervals. In equilibrium experiments, concentrations of Cr(VI) in graded levels were contained in the samples, i.e., 2, 5, 10, 20, 30, 40 and 50 mg/L. The transport experiments were carried out in the plexiglass columns. The diameter of the column used for the S001, S002 and S003 was 6cm and the filling height was 10cm. Smaller column with 2cm diameter was used for S004, S005 and S006 and filling height was 1 cm.

Kinetic and equilibrium models

Kinetic models

pseudo-first-order model: $\ln\left(1-\frac{q_t}{q_e}\right) = A + k_1 t$

pseudo-second-order model: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$

Elovich model: $\frac{q_t}{q_e} = R_e \ln\left(\frac{t}{t_e}\right) + 1$

Equilibrium models

Henry model: $q_e = K_H C_e$

Langmuir model: $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$

Freundlich model: $q_e = K_F C_e^{\frac{1}{n}}$

Model selection criteria

Promoted by the development of maximum likelihood theory, model selection criteria for evaluating model simplifications and process-conceptual models have been established successively, such as (Dai et al.,2012; Ye et al., 2008) . The Akaile Information Criterion (AIC) proposed by Akaile is the most popular criterion (Akaike, 1974),

$$AIC_k = N_Z \ln \hat{\sigma}_{ML}^2 + 2P_k$$

where N_z is the number of data; P_k is the number of estimated parameters; k indicates the kth alternative process-conceptual model, $k = \overline{1,K}$. $N_Z \ln \hat{\sigma}_{ML}^2$ is a term obtained from unbiased least square estimator,

$$\hat{\sigma}_{ML}^2 = \frac{\phi}{N_Z}$$

where ϕ is the generalized sum of squares residuals. In AIC, a deviation affecting the accuracy occurs when $N_Z / P_k < 40$. In order to correct this deviation, (Hurvich and Tsai, 1989) considered the calibration data set size and proposed a more reliable modified Akaile information criterion (AICc),

$$AIC_{C_k} = N_Z \ln \hat{\sigma}_{ML}^2 + 2P_k + \frac{2P_k(P_k+1)}{N_Z - P_k - 1}.$$

Based on the background of Bayesian information, (Schwarz, 1978) deduced the Bayesian information criterion (BIC),

$$BIC_k = N_Z \ln \hat{\sigma}_{ML}^2 + P_k \ln N_Z$$

Another consistent criteria, Hannan information criterion (HIC), have been introduced by (Hannan and Quinn, 1979).

$$HIC = N_Z \ln \hat{\sigma}_{ML}^2 + 2N_Z \ln(\ln P_k)$$

Our data analysis applies least squares approach. Therefore, ϕ can be obtained and values of AIC, AICc, BIC, and HIC are calculated in this study. The best model has the lowest values of AIC, AICc, BIC, and HIC.

Results

According to the model selection criteria, the results are not exactly the same with correlation coefficients. As for sorption kinetics, it is found that Elovich equation is superior to the other two models to describe the kinetic data of S006. And S001, S004 has the best fitness to pseudo first order equation. As for sorption equilibrium, Langmuir model is more favorable than Freundlich model for S001, S002 and S003. Model selection criteria are more sensitive to the performances of different model fittings and can make the differences more intuitive.

Table 3
Parameters evaluated from three kinetic models

	Elovich			Pseudo first order				Pseudo second order			
	t_e	Re	R^2	A	k_1	q_e	R^2	k_2	q_e	R^2	Expected q_e
S001	45	0.3035	0.9608	0.32	0.1344	4.86	0.9889	0.0342	5.23	0.9964	5
S002	72	0.1305	0.9926	-0.65	0.0586	11.49	0.9897	0.0222	12.02	0.9987	11.7
S003	91	0.1401	0.9895	-0.41	0.0970	8.61	0.9516	0.0299	9.07	0.9989	8.9
S004	3090	0.1554	0.9607	-0.32	0.0019	40.91	0.9811	0.0001	44.50	0.9853	43
S005	3958	0.0930	0.9852	-0.66	0.0024	66.61	0.9251	0.0002	68.43	0.9937	69.15
S006	1447	0.1516	0.9956	-0.43	0.0036	21.17	0.9784	0.0006	24.24	0.9975	21.45

Table 4
Model parameters calculated from Langmuir and Freundlich adsorption models

	Henry's		Freundlich			Langmuir		
	K_H	R^2	K_F	n	R^2	K_L	q_m	R^2
S001	0.8974	0.9954	1.5987	1.1921	0.9982	0.0080	145.4441	0.9992
S002	1.9049	0.9703	6.9369	1.5737	0.9908	0.0301	131.2814	0.9980
S003	0.9787	0.9565	4.5454	1.7666	0.9881	0.0445	56.4204	0.9980
S004	3.8232	0.9392	24.1317	2.1448	0.9790	0.0764	172.0555	0.9191
S005	6.4300	0.8881	59.8972	2.9213	0.9918	0.1968	222.3172	0.9331
S006	2.6827	0.9839	7.7114	1.4321	0.9948	0.0176	244.9329	0.9826

Table 5
Values of AIC, AICc, BIC, HIC from three kinetic models

		Elovich	Pseudo first order	Pseudo second order
S001	AIC	-12.07	-23.13	-16.03
	AICC	-9.67	-17.13	-12.03
	BIC	-11.91	-22.89	-16.44
	HIC	-13.14	-24.73	-17.69
S002	AIC	-22.37	-30.90	-40.43
	AICC	-20.65	-27.90	-38.72
	BIC	-21.76	-29.45	-39.83
	HIC	-23.03	-31.44	-41.10
S003	AIC	-15.76	-8.41	-22.51
	AICC	-13.36	-3.61	-19.51
	BIC	-15.60	-7.82	-22.61
	HIC	-16.83	-9.69	-23.84
S004	AIC	38.47	12.66	26.26
	AICC	39.22	15.06	27.06
	BIC	40.36	14.58	28.04
	HIC	38.79	12.48	26.51
S005	AIC	31.26	55.74	-6.66
	AICC	32.01	57.34	-5.86
	BIC	33.15	58.57	-4.88
	HIC	31.58	56.22	-6.41
S006	AIC	-14.29	0.08	8.60
	AICC	-12.79	4.08	10.31
	BIC	-13.50	0.98	9.20
	HIC	-14.79	-0.92	7.93

Table 6
Values of AIC, AICc, BIC, HIC from Langmuir and Freundlich adsorption models

		Henry's	Freundlich	Langmuir
S001	AIC	8.73	-4.11	-9.29
	AICC	9.53	-1.11	-6.29
	BIC	8.68	-4.21	-9.40
	HIC	8.07	-5.44	-10.63
S002	AIC	31.96	16.15	5.44
	AICC	32.76	19.15	8.44
	BIC	31.91	16.04	5.33
	HIC	31.29	14.82	4.10
S003	AIC	25.56	7.72	-4.74
	AICC	26.36	10.72	-1.74
	BIC	25.51	7.61	-4.84
	HIC	24.89	6.38	-6.07
S004	AIC	45.81	28.52	37.94
	AICC	46.61	31.52	40.94
	BIC	45.76	28.41	37.83
	HIC	45.14	27.18	36.61
S005	AIC	56.62	27.53	42.17
	AICC	57.42	30.53	45.17
	BIC	56.56	27.42	42.06
	HIC	55.95	26.19	40.84
S006	AIC	31.75	16.46	24.86
	AICC	32.55	19.46	27.86
	BIC	31.69	16.35	24.75
	HIC	31.08	15.12	23.53

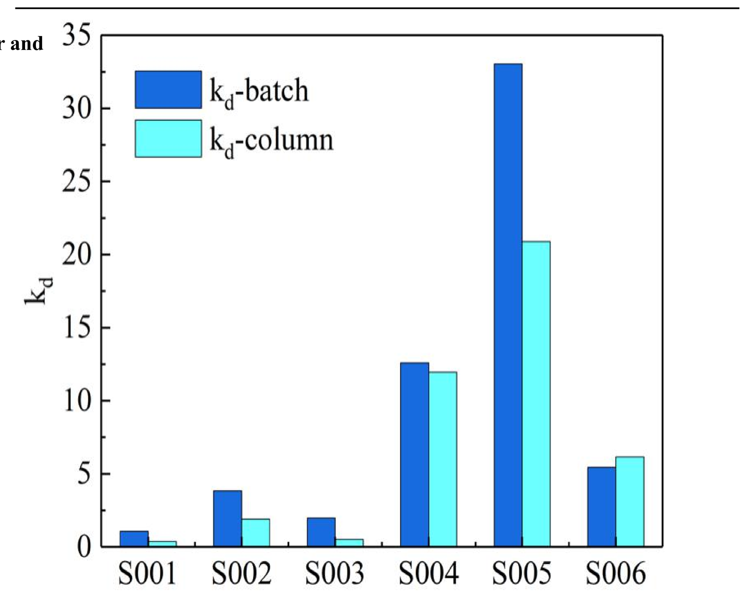

Figure 2. Comparison of the distribution coefficient derived from batch and column experiments.

According to the parameters obtained from model fitting, in both batch and column studies, particle size distribution and the clay mineral contents were the most important factors affecting adsorption capacity and adsorption rate.

Conclusions

- the adsorption capacity increased as a function of particle specific surface area and the clay mineral contents
- The mobility of Cr(VI) in different sediments has a sequence of: Loamy sand, sandy loam, silty loam clay, loam.
- model selection criteria were superior to the error equations when comparing kinetic and equilibrium models because they took into account the quality of data and the complexity of the model.

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