



Investigation of kinetics of Cr(VI)–fired brick clay interaction

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ABSTRACT

Fired brick clay is an excellent sorbent for the removal of heavy metal ions from waste water, owing to the availability of pores and interlayer spacing. Consequently, heat treatment of brick clay significantly affects the extent of interaction between the brick clay sorbent and adsorbates. The interaction between Cr(VI), available as $\text{Cr}_2\text{O}_7^{2-}$, and brick clay particles fired at temperatures between 200 °C and 600 °C follows pseudo second order kinetics, and the method of initial rates leads to the estimation of the average rate of the interaction process. Kinetics modeling suggests that the mass transfer of the interaction be mainly controlled by time-dependent intraparticle diffusion, as well as immobilization of Cr(VI) species within interlayer structure of the brick clay matrix and interparticle diffusion, both of which are time-independent.

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1. Introduction

Industrial activities have no doubt accelerated the pollution of the environment in an irreproducible way. Different types of pollutants are added to the environment due to industrial and anthropogenic activities, causing significant damage to the equilibrium of the ecosystem. When pollutants such as pigments, dyes, metal ions, acids and bases are released to natural waters, the aquatic ecological system breaks down as a result of decreased dissolved oxygen levels and increased amounts of toxic substances. One of the most hazardous water pollutants are the group of heavy metals, such as Pb, Cd, Cr, Sn and Cu [1–3]. Among many studies, much attention has been paid on water pollution due to chromium species as they are heavily used in the industrial sector.

Cr(VI) is used in many industries, such as leather tanning, battery manufacturing, electroplating, cement and photography [4,5]. Therefore, effluents released by these industries contain Cr(VI), which should be removed before disposing of effluents to the natural drainage system. Several conventional techniques, including adsorption, electrochemical precipitation and reverse osmosis are used for treatment of effluents containing metal ions [6]. As chromium species are not biodegradable, they lead to bioaccumulation in living organisms causing health problems in animals, plants and human being. Further, chromium is a carcinogenic element,

which affects the change in DNA replication, causing problems in the next generation [7,8].

Many natural and synthetic sorbents, such as fungi, rice husk, maize cob, fruit waste and different types of clay are used to remove heavy metals from effluents [9–15]. Equilibrium and kinetics studies of sorption of many heavy metals on these adsorbents have already been reported. For example, it has been demonstrated that adsorption of Cu and Cd on rice husk, and Cr(III) on modified bentonite clay obey both Langmuir and Freundlich isotherm models [16,17]. Among adsorption studies of Cr(VI) on adsorbents, adsorption of Cr(VI) on *Rhizopus cohnii* biomass and carbon nanotubes is more accurately explained by the Langmuir model [18,19], while that on kaolinite and its modified forms show a good fit with both isotherms [20].

Kinetics of Cr(VI) sorption on adsorbents is a complex issue, and the mode of interaction, and hence the order of sorption reaction depends on the type of the adsorbent. For instance, Cr(VI) adsorption on carbon nanotubes follows pseudo second order kinetics [19], while that on zeoliteNaX follows first order reversible kinetics [6]. The low value of the experimentally determined rate constant for the reverse reaction of the Cr(VI)/zeoliteNaX system indicates that the adsorption process of Cr(VI) on the adsorbent is highly favorable. Therefore, this adsorbent can be used for treatment of potable water as well as industrial effluents for the removal of Cr(VI). Although kinetics data are useful for design and fabrication of waste water treatment plants and for investigation of the efficiency of removal of hazardous substances from the environment, kinetics studies on normal and modified clay types for sorption of Cr(VI) have been limited [20,21]. Further, effect of heat treatment of clay on adsorption kinetics has not been widely addressed.

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Table 1
Surface area of fired brick clay.

Firing temperature (°C)	Surface area (m ² g ⁻¹)
200	0.844
400	0.225
600	0.214

Therefore, it is important to investigate the kinetics of adsorption of Cr(VI) on effective adsorbents, such as clay types.

It has been reported that brick clay is a strong adsorbent for heavy metals. Nature of brick clay, surface area and surface charge affect the extent of interaction of adsorbates. As brick clay particles are negatively charged [21], cations are strongly attached to brick clay particles. Heavy metal cations present in contaminated water can easily be removed by such adsorbents. Further, equilibrium studies of sorption of Cr(VI) on brick clay (fired and unfired), investigated under optimized conditions, indicate that the removal of Cr(VI) is about 60% by brick clay [22]. Kinetics aspects of Cr(VI) adsorption on fired brick clay would thus provide valuable information in order to understand the mechanism of the Cr(VI) sorption process and other applications.

Among many kinetics models reported, the intraparticle diffusion model is helpful in understanding the kinetics of interaction of heavy metals and adsorbents at microscopic level [15,16]. In this research, time dependence of the extent of sorption of Cr(VI) was used as a measure of the rate of interaction of Cr(VI) with brick clay particles, fired at different temperatures. Such kinetics measurements were continuously obtained until the system reached equilibrium, and used to investigate the validity of kinetics models. The method of initial rates was also employed with different initial concentrations to determine the rate of interaction of the above process.

2. Methods and materials

2.1. Materials

Standard solutions of Cr(VI) of concentrations varying from 5 ppm to 40 ppm were prepared using analytical grade K₂Cr₂O₇ (BDH Chemicals). This concentration range covers typical Cr(VI) levels in untreated industrial effluents. Brick clay samples fired in the laboratory at the predetermined temperatures (200 °C, 400 °C and 600 °C) were used for all experiments. After firing, the samples were separated into appropriate sizes using a set of sieves. All experiments were conducted with fired brick clay particles of diameter (*d*) <1 mm at ambient temperature. Surface area of this material fired at different temperatures, as estimated by methylene blue adsorption experiments, is shown in Table 1 [23]. Brick clay used in this investigation consists of aluminosilicates containing other metals such as Na, Mg, Ca, Al and Fe, and quartz based on XRD measurements [23].

2.2. Instrumentation

The Carbolite CTF 12/100/900 furnace (Thermal Engineering Services, UK) was used to fire brick clay samples. Spectro-Electronic M Series atomic absorption spectrophotometer (Thermo Electron Corporation, UK) was used to measure metal ion concentrations.

2.3. Research design

Brick clay, being a natural substance having variable composition, reflects many difficulties in quantitative analysis. Consequently, the method of sampling and the number of trials selected should be given sufficient attention. Representative sam-

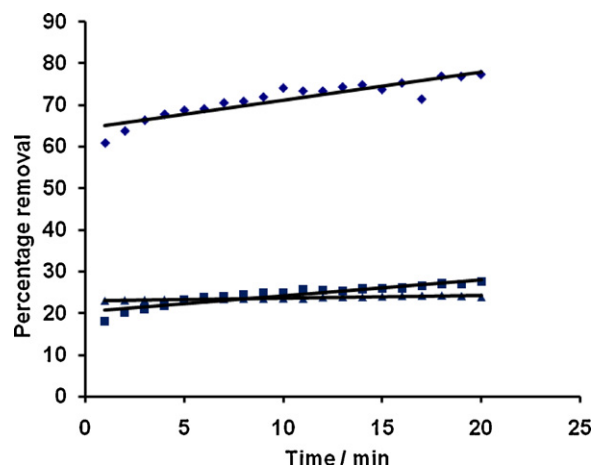


Fig. 1. Percentage removal of Cr(VI) by brick clay fired at 200 °C (◆), 400 °C (■) and 600 °C (▲) at different stirring times (*t*) [50 g brick clay, 500 cm³ of 20 ppm Cr(VI) solution, *d* <1 mm].

ples were thus prepared by grinding many pieces of brick clay samples randomly obtained from a bulk, followed by firing at each predetermined temperature. Firing was conducted using the method reported elsewhere [22]. Cr(VI) solutions of 20 ppm were used in order to investigate the validity of kinetics models. For this purpose, mixtures of fired brick clay and aqueous Cr(VI) solutions in 1:10 (w/v) ratio were stirred and 10.00 cm³ aliquots were withdrawn in one minute time interval up to a time period of 20 min. Then, the amount of Cr(VI) sorbed by brick clay samples, each of which was fired at 200 °C, 400 °C and 600 °C, was determined.

In order to use the method of initial rates, kinetics experiments were conducted using Cr(VI) solutions of initial concentrations varying from 5 ppm to 40 ppm. At each initial concentration, the suspension of Cr(VI) solution and brick clay fired at 200 °C was stirred for 30 s. The solution was quickly separated by filtration, and atomic absorption measurements were recorded in triplicate. Three brick clay samples were used for each set of experimental conditions, and hence a measurement used for calculations was an average of nine measurements.

3. Results and discussion

3.1. Preliminary kinetics studies

For investigation of kinetics of interaction of Cr(VI) species with fired brick clay particles, it is important to monitor how fast the interaction takes place under different experimental conditions. Percentage removal of Cr(VI) from solution by brick clay particles is a measure of the extent of interaction which can be monitored as a function of time. Fig. 1 shows how the percentage removal of Cr(VI) changes with stirring time for brick clay fired at different temperatures. Percentage removal is marginally increased with stirring time by brick clay fired at 200 °C and 400 °C, while the extent of removal by brick clay fired at 600 °C shows weaker time dependence. Brick clay fired at 200 °C shows the highest removal at all stirring time periods (*t*) attempted as compared to that fired at 400 °C and 600 °C. This is expected based on earlier findings that Cr(VI) shows the maximum sorption at 10 min stirring time followed by 2 h equilibration with brick clay fired at 200 °C, among the firing temperatures from unfired to 900 °C, owing to the presence of chemical species at 200 °C that attract Cr(VI) species [22]. Further, the percentage removal graphs obtained for clay fired at 200 °C and 400 °C are almost parallel to each other according to Fig. 1, indicating that the rate of interaction of Cr(VI) on brick clay fired at these two temperatures, which is the rate of change in percentage

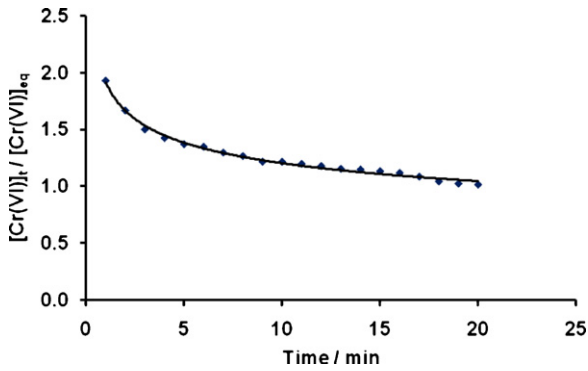


Fig. 2. Concentration of Cr(VI) in solution with respect to the equilibrium concentration at different stirring times (*t*). Other conditions are as stated in Fig. 1.

removal, is approximately equal. This subsequently implies that the rate constant of the rate determining step of the Cr(VI)–brick clay interaction is approximately equal for clay fired at these two temperatures.

Further kinetics analysis in terms of models would be necessary in order to obtain a clear understanding of the overall approach of Cr(VI) species toward active sites of fired brick clay particles for its interaction. As the concentration of solution Cr(VI) species at any given time with respect to the equilibrium concentration ($[Cr(VI)]_t/[Cr(VI)]_{eq}$) shows a negative exponential decay (Fig. 2) as expected, reaching a plateau at 20 min, it is clear that sorption of Cr(VI) on brick clay particles reaches equilibrium at 20 min. Thus, experiments for kinetics modeling should be completed within this time frame.

3.2. Determination of the order of sorption

For better understanding of the rate process, Cr(VI) soption was first visualized by simple kinetics models. This approach can be initiated with the generalized rate law for a single reactant, assuming that the activity of brick clay particles is constant, as shown below

Table 2

Regression coefficients of linearized integrated rate laws for different reaction orders for the interaction of Cr(VI) with brick clay fired at different temperatures.

Order of reaction	Temperature of firing (°C)		
	200	400	600
First order	0.343	0.827	0.558
Second order	0.721	0.318	0.674
Pseudo second order	0.999	0.972	0.973

[15].

$$\frac{dq_t}{dt} = k'(q_e - q_t)^n \tag{1}$$

where, *k'* is the apparent rate constant, *t* is contact time, *q_e* and *q_t* are the masses of Cr(VI) sorbed by unit mass of sorbent at equilibrium and at time *t*, respectively, and *n* is the order of the reaction with respect to Cr(VI) species. As *q_t* is more conveniently expressed in mg of Cr(VI) sorbed by 1 g of brick clay, the apparent rate constant *k'* is estimated in s⁻¹ for first order reactions and g mg⁻¹ s⁻¹ for second order reactions. The integrated forms of the rate law given in Eq. (1) are linearized as

$$\log(q_e - q_t) = -\frac{k'}{2.303}t + \log q_e \tag{2}$$

for first order,

$$\frac{1}{q_e - q_t} = k't + \frac{1}{q_e} \tag{3}$$

for second order, and

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{(k'q_e^2)} \tag{4}$$

for pseudo second order kinetics.

Eqs. (2)–(4), when plotted for brick clay fired at different temperatures are shown in Fig. 3. The regression coefficient (*R*²) of each graph is given in Table 2. Low *R*² values obtained for the first order and second order rate equations suggest that these two

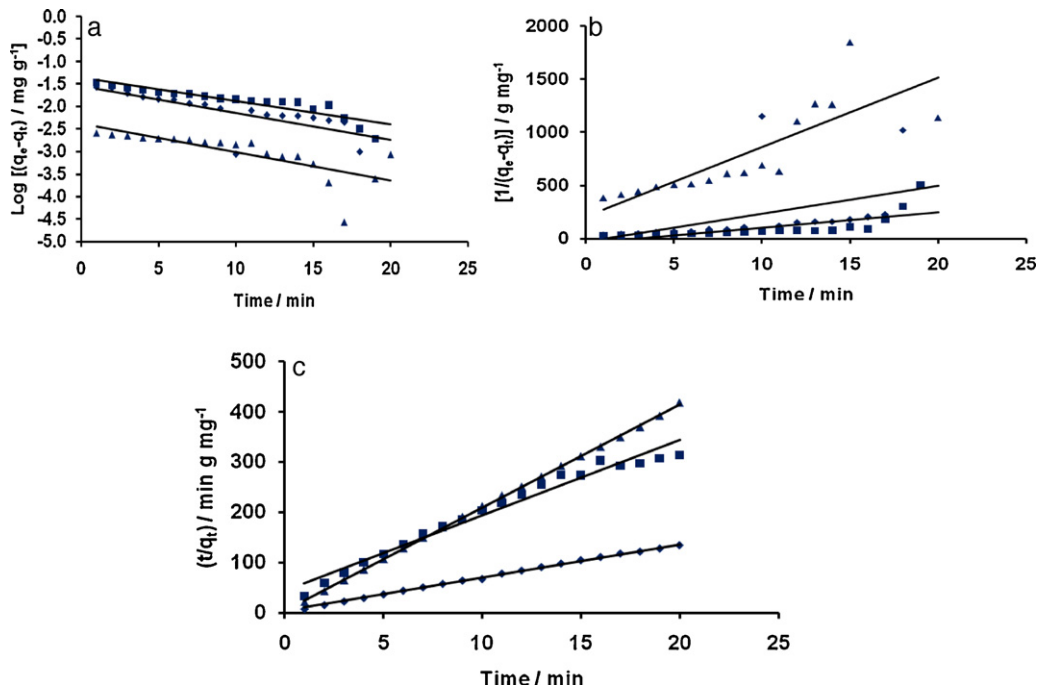


Fig. 3. Kinetics models for the interaction of Cr(VI) with brick clay fired at 200 °C (◆), 400 °C (■) and 600 °C (▲) (a) first order kinetics model, (b) second order kinetics model, (c) pseudo second order kinetics model.

orders for the interaction of Cr(VI) species with brick clay particles be ruled out. Having high regression coefficients, the most probable approach of Cr(VI) species on fired brick particles thus follows the pseudo second order regardless of firing temperatures attempted. Among the three temperatures employed for firing brick clay, the best fit ($R^2 = 0.999$) is observed for 200 °C, which is the firing temperature which leads to the maximum interaction, according to previous studies [22]. The apparent rate constants of the sorption process on brick clay fired at 200 °C, 400 °C and 600 °C (pseudo second order) are determined to be 11.4 g mg⁻¹ min⁻¹, 5.1 g mg⁻¹ min⁻¹ and 99.2 g mg⁻¹ min⁻¹, respectively. For these calculations, the presence of brick in the reaction mixture was not considered although the composition of brick strongly affects the sorption process. Consequently, the apparent rate constant does not reflect the actual rate of the sorption process.

3.3. Intraparticle diffusion model

The transfer of adsorbate species from the bulk solution phase to solid sorbent phase is expected to occur through many steps. Some processes that would take place during this transfer are:

1. Mass transfer of adsorbate from the bulk solution to particle surface.
2. Deposition on the surface of sorbent particles.
3. Interparticle diffusion.
4. Immobilization in interlayer regions.
5. Intraparticle diffusion within the pores of adsorbent particles.
6. Adsorption at internal sites.

The simple kinetics models discussed in earlier sections account for the entire process as a whole, which provide concentration dependence relationships of the overall rate. Therefore, to obtain microscopic level information, the intraparticle diffusion model can be employed.

The simplified mathematical relationship for the intraparticle diffusion model can be derived from the Fick's second law of diffusion modified for spherical particles [Eq. (5)].

$$\left(\frac{\partial C_t}{\partial t}\right)_x = D \left(\frac{\partial^2 C_t}{\partial x^2}\right)_t \quad (5)$$

where C_t is the concentration of adsorbate in solution at time t , D is the diffusion coefficient of adsorbate and x is the distance in the direction of diffusion. The above equation is converted to the concentration of the adsorbate through Laplace transform, as shown below [24].

$$C_t = C_0 \operatorname{erfc} \frac{x}{2(Dt)^{1/2}} \quad (6)$$

where C_0 is the concentration at $t=0$ (initial concentration). Eq. (6) can be simplified to result in the relationship that the fractional concentration of sorption $(C_0 - C_t)/C_0$ varies with the function, $(Dt/r^2)^{1/2}$, where r is the radius of an adsorbate particle. Therefore, the amount adsorbed, $q_t = C_0 - C_t \frac{V}{W}$ where V is the volume of the adsorbate solution and W is the mass of brick clay, is proportional to $t^{1/2}$, which can simply be written as [15,16],

$$k = \frac{1}{t^{1/2}} \times q_t \quad (7)$$

where the parameter, k , which is not a rate constant, can be correlated to intraparticle diffusion rate [16,24].

The validity of the intraparticle diffusion model has been demonstrated for sorption of heavy metal ions on various biosorbents [15]. However, due to the layered structure of brick clay, in addition to intraparticle diffusion, several other mass transfer processes would be responsible for the transfer of Cr(VI) to the solid

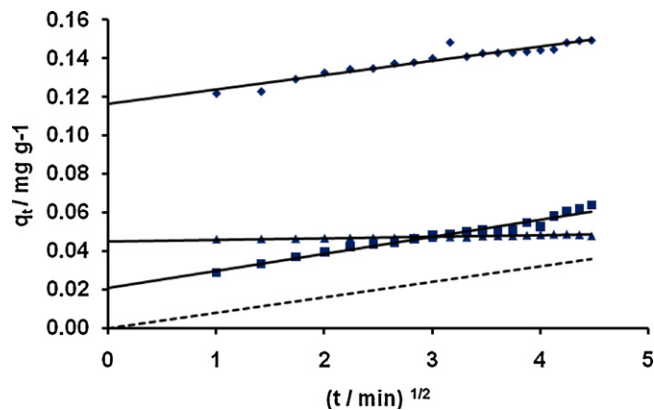


Fig. 4. Modified intraparticle diffusion model: Variation of the amount of Cr(VI) adsorbed on brick clay (q_t) fired at 200 °C (◆), 400 °C (■) and 600 °C (▲) as a function of $t^{1/2}$. The dotted line is the hypothetical intraparticle diffusion line for brick clay fired at 200 °C and 400 °C.

brick clay phase. Immobilization of Cr(VI) species through deposition between layers of the brick clay matrix and interparticle diffusion would be predominant processes that are not considered in the intraparticle diffusion model. As the interlayer spacing depends on the temperature of firing, the above stated modes of mass transfer, and hence the kinetics of Cr(VI) removal is highly dependent on firing temperature. The layered structure of clay is not much destroyed when brick clay is fired at 200 °C, indicating the highest contribution to the sorption process. Increase in firing temperature would decrease the interlayer spacing, thereby decreasing the extent of Cr(VI) removal.

Among different factors of mass transfer, effect of immobilization of Cr(VI) ions within the layered structure is probably much quicker than intraparticle diffusion. Hence it is proposed that immobilization within layers and intraparticle diffusion be time-independent, while interparticle diffusion be time-dependent. Eq. (7) is then modified as,

$$q_t = k t^{1/2} + I \quad (8)$$

where I is the contribution from the immobilization of Cr(VI) and interparticle diffusion, both of which depend on the layered structure of brick clay, to the overall extent of Cr(VI) removal. Hence, Eq. (8), the modified intraparticle diffusion model can be used to model Cr(VI) sorption on brick clay. The plots of q_t vs $t^{1/2}$ obtained for Cr(VI) sorption on brick clay fired at different temperatures are shown in Fig. 4. From these plots, the intraparticle diffusion component [Eq. (7)] can be extracted by drawing a parallel line going through the origin. The difference between the experimental line and the hypothetical intraparticle diffusion line (broken line) can be taken as the time independent mass transfer component of Cr(VI) from the solution phase to the solid brick clay phase.

The validity of the modified intraparticle diffusion model for sorption interaction of Cr(VI) on brick clay is further supported by obtaining high regression coefficients for Eq. (8) (Table 3).

Table 3
Regression coefficients of intraparticle diffusion model for Cr(VI) sorption on brick clay particles.

Firing temperature of brick clay	Regression coefficient (R^2) [Eq. (8)]
200 °C	0.909
400 °C	0.966
600 °C	0.882

Table 4
Initial rates determined for the interaction of Cr(VI) with fired brick clay particles.

Initial concentration (ppm)	Initial rate (ppm min ⁻¹)
5.0	4.4
8.0	5.1
14.0	5.2
30.0	9.7
37.0	10.8
Average	7.0

3.4. Method of initial rates

The method of initial rates is widely applied for the determination of kinetics of a chemical reaction, which is often used in conjunction with the isolation method. During the investigation of kinetics of Cr(IV)–brick clay interaction, Cr(VI) species should be isolated for the determination of its concentration independently, as it is not appropriate to change the concentration of the solid brick clay sorbent.

The initial rates determined for different initial concentrations of Cr(VI) for brick clay fired at 200 °C are shown in Table 4. The average rate over the concentration range of 5.0–37.0 ppm Cr(VI) is 7.0 ppm min⁻¹.

4. Conclusion

The interaction between Cr(VI) ions and brick clay particles fired at temperatures between 200 °C and 600 °C follows pseudo second order kinetics. The best fit ($R^2=0.999$) is obtained for brick clay fired at 200 °C, the firing temperature which shows the strongest attraction. For brick clay fired at this temperature, the pseudo second order model leads to an apparent rate constant of 11.4 g mg⁻¹ min⁻¹, while the method of initial rates provides an average rate of 7.0 ppm min⁻¹ over the concentration of range from 5.0 ppm to 37.0 ppm. It is important that kinetics measurements be obtained within 20 min at which the system reaches equilibrium. Further, the mass transfer of Cr(VI) ions from the solution to the solid sorbent phase is not solely controlled by intraparticle diffusion, which is time dependant. It is suggested that an additional time independent term responsible for immobilization of Cr(VI) species within the layered structure of the brick clay matrix and interparticle diffusion be introduced to the intraparticle diffusion model. The validity of the use of the additional term in the intraparticle diffusion model is demonstrated for Cr(VI)–fired brick clay interaction. However, this modification is yet to be investigated for other adsorbents having layered or pore structures.

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