## Applicability of shrinking core model on the adsorption of heavy metals by clarified sludge from aqueous solution

 $k_0^*$ 

T.K. Naiya · A.K. Bhattacharjee · D. Sarkar · S.K. Das

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**Abstract** Shrinking Core model, widely accepted in the solid-fluid non-catalytic reaction system was applied to analyze the adsorption of metal ions like Zn(II), Cr(VI), Cd(II) and Pb(II) from the aqueous solutions onto the clarified sludge (CLS). The diffusivities of different metal ions in clarified sludge were determined by global optimization. The depth of penetration was also estimated for different initial concentrations. The experimental concentration profiles at various initial concentrations for all these four different metal ions matched well with the model predictions.

Keywords Clarified sludge · Diffusivity · Film mass transfer · Shrinking core · Linear parameter

 $E(D_0)$ 

 $k_0$ 

Nomen	clature		
C	Metal concentration in the bulk solution at any		
	time		
$C_0$	Initial metal concentration in the bulk solution		
$C^*$	Dimensionless concentration in the bulk (= $\frac{C}{C_0}$ )		
$C_{ij}^{*model}$	Dimensionless concentration parameter according		
,	to model		
$C_{ij}^{*\exp}$	Dimensionless concentration parameter according		
, and the second	to experiment		
CLS	Clarified sludge		
$D_0$	Effective pore diffusion coefficient		
$d_n$	Volume surface mean diameter		

Objective function for global optimization

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Parameter defined in the Sect. 5.3

Langmuir isotherm constant

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	$(=k_0C_0)$
N(t)	Flux of the metal in CLS at time <i>t</i>
PCM	Progressive conversion model
R	Mean radius of the CLS particles $(=\frac{d_p}{2})$
$R_f$	Radial distance of penetration front at time t
SCM	Shrinking Core Model
r	Dimensionless radial distance of penetration front
	at time $t = \frac{R_f}{R}$
t	Time
$t^*$	Dimensionless time $(=\frac{D_0t}{R^2})$
V	Volume of stirred solution
W	Mass of CLS added
$W^*$	Dimensionless mass of CLS added (= $\frac{W}{VC_0}$ )
$Y_{s}$	Langmuir isotherm constant
$Y_s^*$	Dimensionless Langmuir isotherm constant
	$(=Y_SC_0)$
$Y_{et}$	Adsorbed amount in equilibrium with bulk
	concentration at time t
$\rho$	Density of CLS

Dimensionless density of CLS

Dimensionless Langmuir isotherm constant

### 1 Introduction

Metals are considered to be non-biodegradable and have great environmental, public health and economic impacts (Brower et al. 1997; Cay et al. 2004). Beyond the permissible limits, they are generally toxic and some are even hazardous in nature. Chromium, cadmium, lead and zinc are often present in industrial waste water, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refineries, paint manufacture, pesticides, pigment manufacture, printing and photographic in-



dustries etc. (Kadirvelu and Namasivayam 2000). A variety of technologies have been developed for the treatment of heavy metal from waste water. Conventional technologies for the removal of heavy metal from waste water are chemical precipitation, ion exchange, electrochemical precipitation, solvent extraction, membrane separation, concentration, evaporation, reverse osmosis, emulsion per traction and adsorption (Zhou et al. 1993; Chakravarti et al. 1995; Kongsricharoern and Polprasert 1996; Ortiz et al. 2003; Trgo et al. 2006; Gupta et al. 2001; Gupta and Sharma 2002; Srivastava et al. 2006). Among these technologies, adsorption is a cost-effective and user friendly technique for the removal of heavy metal (Bhattacharya et al. 2006).

Efforts have been made to develop low-cost adsorbents, for the removal of heavy metal from waste water, are well documented (Pollard et al. 1992). These adsorbents are waste slurry, kaolinite clay, clarified sludge, bentonite, red mud washed with water, red mud acid treated, blast furnace sludge, phosphatic clay, red mud, paper mill sludge, bagasse clarified sludge, coffee residues binding with clay, calcined phosphate etc. (Srivastava et al. 1989, 1997; Degodo et al. 1998; Lopez et al. 1998; Pehlivan et al. 2006).

In steel production using a Basic Oxygen Furnace, for every ton of crude steel produced about 100–150 kg of slag/sludge is generated in the form of waste depending upon the hot metal quality and steel making practice. The current capacity of crude steel production in India is 26 mtpa through basic oxygen furnace route and it generates about 3.9 million-ton of sludge waste every year. The sludge initially in the dust form in the Basic Oxygen Furnace arrested by hydro jetting and then by venture scrubbers and collected in clarifier for settling. In most steel plants this sludge is creating problems related to disposal. Presently it is only partially reprocessed and a significant proportion is either dumped or used for land filling (Reddy et al. 2006).

The present study deals with a series of batch adsorption experiments to investigate and explore the feasibility of clarified sludge as low cost and readily available adsorbent for removal of the heavy metals from aqueous solutions. Studies in agitated finite batch mode is important because of the fact that it yields equilibrium as well as the kinetic data, from which, parameters like the effective pore diffusivity of the adsorbate can be extracted that becomes useful for further analysis like the modeling of industrial packed bed absorber performance. Generally in adsorption two mass transfer resistances acts in series, namely the external liquid film resistance and the pore diffusion resistance. As in the present study the experiments were conducted under vigorous agitation, the liquid film resistance was assumed to be negligible in comparison to the pore diffusion resistance, characterized by concentration independent effective pore diffusion coefficient  $(D_0)$  of the adsorbate. The mechanism of pore diffusion was assumed to be in accordance to the mechanism proposed by Shrinking Core Model (SCM) widely accepted in the study of non-catalytic solid-fluid reaction (Fogler 1997). A generalized shrinking core model was applied by Jena et al. (2003) for batch adsorption of a few organics from aqueous solutions in porous silica and active carbon particles. In the present work SCM was applied to generate the time evolution equation for bulk concentration and radius of penetration in terms of different system parameters including unknown effective pore diffusivity, followed by a global optimization of the same parameter giving the closest match between experimental findings and the model prediction. The final outcome of the analysis was the pore diffusivity values for different systems of metal ions and clarified sludge, along with the characterization and performance evaluation of clarified sludge as a potential adsorbent for heavy metals. In addition to that the outcome of SCM was also compared with the predictions of other diffusion models in order to establish the gross effectiveness of the proposed model in analyzing the behavior of the present system.

#### 2 Theoretical analysis

The clarified sludge as adsorbent is assumed to have a spherical shape with diameter same as that of volume-surface mean diameter of the distribution obtained by screen analysis. Pseudo-steady state diffusion of the adsorbed heavy metal, i.e., Zn(II), Cr(VI), Cd(II) and Pb(II) through a spherical shell in a particle of clarified sludge (Fig. 1) is assumed. The rate of uptake of the metal at any instant is equated to the rate of removal of the same from the solution. Liquid side resistance to mass transfer has been neglected as the solution is vigorously shaken. Theoretical analysis and computation of the diffusivity has been done for all the cases with different initial concentrations of the metal in the solution.

The shrinking core model is schematically depicted in Fig. 1. If C is the metal concentration in the bulk solution at any time t, the flux of the metal in the spherical clarified sludge particle can be obtained by integrating the diffusion equation at pseudo-steady state taking diffusivity as a constant, concentration independent parameter of the system.

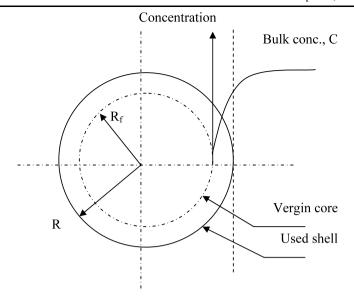
$$N(t) = \frac{4\pi D_0.C}{\left(\frac{1}{R_f} - \frac{1}{R}\right)}$$
 (1)

The following mass balance equation relates the shrinking rate of the virgin core and rate of change of the solid phase concentration to the instantaneous flux of the metal.

$$N(t) = \frac{d}{dt} \left[ \frac{4}{3} \pi (R^3 - R_f^3) \rho Y_{et} \right]$$
 (2)



**Fig. 1** Schematic diagram of the diffusion system



The average solid phase concentration based on the entire volume of the particle as a function of solid phase concentration in the outer shell and radius of the core.

$$\overline{Y_t} = Y_{et} \left[ 1 - \left( \frac{R_f}{R} \right)^3 \right] \tag{3}$$

The mass balance equation for the entire system in terms of bulk concentration of the metal solution of volume V and average solid phase concentration:

$$-V\frac{dC}{dt} = W\frac{d\bar{Y}_t}{dt} \tag{4}$$

where W = mass of clarified sludge added to V volume of stirred solution. Now we introduce the following dimensionless variables and parameters.

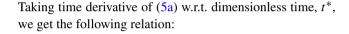
$$C^* = \frac{C}{C_0}, \qquad r = \frac{R_f}{R}, \qquad t^* = \frac{D_0 t}{R^2},$$
  $W^* = \frac{W}{VC_0}, \qquad \rho^* = \frac{\rho}{C_0}$ 

In order to represent the equilibrium relation between solid and liquid phase concentration Langmuir isotherm is used in its dimensionless form as:

$$Y_{et} = \frac{Y_S^* C^*}{1 + k_0^* C^*} \tag{5a}$$

where  $k_0^* = k_0 C_0$  and  $Y_S^* = Y_S C_0$ . Here  $k_0$  and  $Y_S$  are constant parameters in the actual Langmuir isotherm (Langmuir 1918) expressed as:

$$Y_{et} = \frac{Y_S C}{1 + k_0 C} \tag{5b}$$



$$\frac{dY_{et}}{dt^*} = \frac{Y_S^*}{(1 + k_0^* C^*)^2} \cdot \frac{dC^*}{dt^*}$$
 (5c)

Simplifying (1) and (2) in terms of parameters in dimensionless parameters:

$$\frac{C^*}{\rho^*(\frac{1}{r}-1)} = -\frac{r^2 Y_S^* C^*}{(1+k_0^* C^*)} \cdot \frac{dr}{dt^*} + \frac{(1-r^3)}{3} \frac{d}{dt^*} \left(\frac{C_t^* Y_S^*}{1+k_0^* C^*}\right)$$
(6)

Incorporating (5c) in (6),

$$\frac{C^*}{\rho^*(\frac{1}{r}-1)} = -\frac{r^2 Y_S^* C^*}{(1+k_0^* C^*)} \cdot \frac{dr}{dt^*} + \frac{(1-r^3)Y_S^*}{3(1+k_0^* C^*)^2} \frac{dC^*}{dt^*} \tag{7}$$

Again simplifying (4) using (3) and (5):

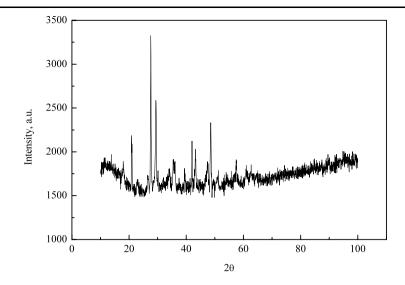
$$\frac{dr}{dt^*} = \left[ \frac{\frac{1}{W^*} + \frac{(1-r^3)Y_S^*}{(1+k_0^*C^*)^2}}{\frac{3r^2Y_S^*C^*}{(1+k_0^*C^*)}} \right] \frac{dC^*}{dt^*}$$
(8)

Finally, solving (7) and (8), the time evolution equation for both bulk concentration and radius of the unreacted core in their dimensionless form are as obtained:

$$\frac{dC^*}{dt^*} = -\frac{3W^*C^*}{\rho^*(\frac{1}{r} - 1)} \tag{9}$$



**Fig. 2** XRD study of Clarified sludge



and

$$\frac{dr}{dt^*} = -\left[\frac{1 + \frac{W^*(1-r^3)Y_S^*}{(1+k_0^*C^*)^2}}{\rho^*r(1-r) \cdot \frac{Y_S^*}{(1+k_0^*C^*)}}\right]$$
(10)

Initial conditions for (9) and (10) are taken as:  $C^* = 1.0$  and r = 0.999 (rather than r = 1 in order to avoid singularity in the process of computation) at  $t^* = 0.0$ . Equations (9) and (10) can be solved simultaneously to find the time evolution of bulk concentration, provided all the process parameters are known. The unknown constant parameter in the expression namely the diffusivity  $D_0$  can be estimated by a global optimization technique in order to achieve best fit condition of model predictions with experimental results.

#### 3 Computational method

Equations (9) and (10) are numerically solved by forth order Runge-Kutta method with step size of  $\Delta t^* = 10^{-5}$  with a simultaneous global optimization of diffusivity  $D_0$ . The objective function for global optimization is

$$E(D_0) = \frac{1}{3} \cdot \sum_{j=1}^{3} \sum_{i=1}^{7} \left( C_{ij}^{*\text{model}} - C_{ij}^{*\text{exp}} \right)^2$$
 (11)

Seven experimental data points (i = 1, 6) distributed over the time span of 1.5 hrs, sufficient enough for the system to reach equilibrium are compared with theoretical counterpart at the same instant of time and calculated error, after squaring is summed and subsequently averaged for three different runs (j = 1, 3), characterized by three different initial concentrations. As the optimization problem is one di-

 Table 1
 Chemical composition of clarified sludge

Constituent	Percent by weight %		
Fe <sub>2</sub> O <sub>3</sub>	48		
CaO	23.4		
MgO	2.5		
MnO	0.2		
SiO <sub>2</sub>	12.6		
Na <sub>2</sub> O	0.7		
K <sub>2</sub> O	0.5		
Loss on ignition	12		

mensional, it is solved by simple Fibonacci search technique (Beveridge and Schecter 1970).

#### 4 Materials and methods

The clarified sludge was collected from the sludge thickener of Basic Oxygen Furnace of Rourkela Steel Plant, Rourkela, Orissa, India. The sludge, initially present in the dust form in the basic oxygen furnace was arrested by hydro jetting followed by venturi scrubbers and then collected in a clarifier for settling. The sample was subjected to characterization by a variety of methods such as X-ray diffraction (XRD), chemical analysis, thermo gravimetric analysis (TGA), particle size, BET surface area, and scanning electron microscope (SEM). The sludge, after collection was ground, homogenized and dried at  $105 \pm 5\,^{\circ}\text{C}$  for 3 hr and there after cooled to ambient temperature in a desiccators.

The XRD sample was scanned at  $2^{\circ}$   $2\theta$ /min with CuK $\alpha$  radiation. The corresponding diffraction pattern is shown in the Fig. 2 and it conforms the peaks of 2CaSiO<sub>2</sub>, 2CaOFe<sub>2</sub>O<sub>3</sub>, 3CaOSiO<sub>2</sub>, and some traces of complex phases of CaO.MgO.SiO<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> and FeO. The



<b>Table 2</b> Particle size distribution of the clarified sludge $(-44 + 52 \text{ mesh: } 250-350 \mu\text{m})$							
250–275 μm	275–285 μm	285–295 μm	295–305 μm	305–315 μm	315–325 μm	325–335 μm	335–350 μm
0.9%	18.3%	25.1%	10.7%	16.5%	17.2%	8.7%	2.6%

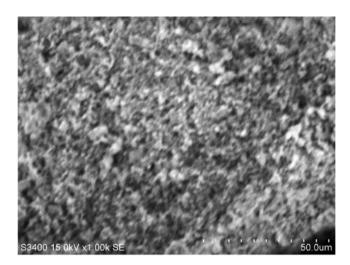


Fig. 3 Scanning Electron Micrographs (SEM) of clarified sludge

formation of Fe<sub>2</sub>O<sub>3</sub> is likely to be on account of the oxidation of the entrapped steel in the sludge due to water quenching. It was also observed that the dicalcium silicate present in the sludge has both  $\alpha$  and  $\beta$  forms. The large number of humps in the pattern indicates some incomplete crystallization in the sludge due to very rapid quenching (Reddy et al. 2006). Table 1 shows the chemical analysis of the clarified sludge. Thermo gravimetric analysis was carried out in Perkin Elmer TGA analyzer (Model TGA6, Perkin Elmer, USA) in nitrogen atmosphere between 50-900°C using a scanning rate of 20°C per minute using 3.72 mg of sample. The result indicates that the sample contains a high percentage (88%) of ash (Metal oxide and silica). The ignition loss might have been resulted due to the presence of hydroxides in clarified sludge, which get converted into the respective oxides. The particle of 250–350 µm size was analyzed in a standard Particle Size Distribution analyzer (Model 117.08, MALVERN Instruments, USA) and the corresponding results are shown in Table 2. Using the distribution data the corresponding volume-surface mean diameter  $(\overline{d}_p)$  was calculated to be 302.298 µm. In addition to the particle size distribution the specific surface area was also determined by BET method using a surface area analyzer (Model 1750 SORPTY, Carlo Erba, Italy) and was found to be 78.55 m<sup>2</sup>/g. Figure 3 shows the SEM micrographs (Model S415A, Hitachi, Japan) of the clarified sludge, which clearly indicates the irregular and highly porous structure of the sample.

All the necessary chemicals used in the study were of analytical grade. Zinc sulphate [ZnSO<sub>4</sub>, 7H<sub>2</sub>O], potas-

sium dichromate [K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>], cadmium nitrate tetrahydrate [Cd(NO<sub>3</sub>)<sub>2</sub>, 4H<sub>2</sub>O] and lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] were obtained from E. Merck India Limited, Mumbai, India. Stock solution of the above heavy metals was made by dissolving exact amount of respective the metal salt. The range of concentration of the metal components prepared from the stock solution was varied between 3 mg/L to 300 mg/L. The test solutions were prepared by diluting 1 g/L of stock metal solution with double distilled water.

The necessary amount of clarified sludge was taken in a 250 ml stopper conical flask containing 100 ml of desired concentration of the test solution for the batch adsorption studies at the desired pH value. Different initial concentration of metal solutions was prepared by proper dilution from stock 1000-ppm metal standard. pH of the solution was monitored in a 5500 EUTECH pH Meter using FET solid electrode (calibrated with standard buffer solutions) by adding 0.1 M HCl and NaOH solutions as per the required pH value. Necessary amount of clarified sludge was then added and the contents in the flask were shaken for the desired contact time in an electrically thermo stated reciprocating shaker operating at the rate of 120-130 strokes/minute under a constant temperature condition of  $30 \pm 2$  °C (room temperature). The time required for reaching the equilibrium condition was estimated by drawing samples at a regular interval of time till the equilibrium was reached. The contents of the flask were then filtered with standard filter paper and the filtrate was analyzed for the residual metal present in the sample using Atomic Absorption Spectrophotometer (Varian SpetraAA 55, USA) as per the procedure laid down in APHA, AWWA standard methods for testing water and wastewater, 1998 edition (APHA, AWNA Standard Methods 1998).

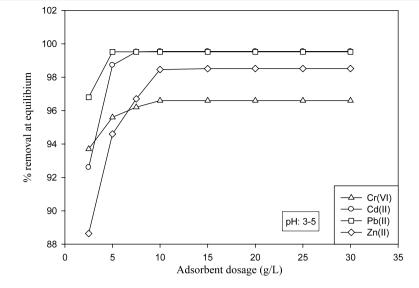
#### 5 Results and discussion

# 5.1 Optimum operating conditions and the adsorption isotherms

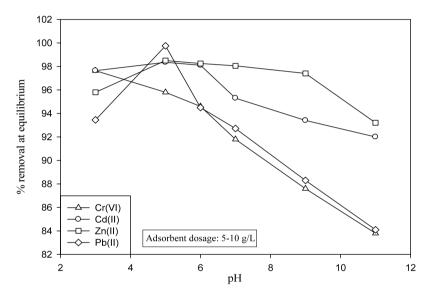
Initially, the parametric studies, i.e., to find the effect of different parameters like the initial concentration of the metal salts, the adsorbent dosage, pH, and the contact time on the equilibrium percentage removal were carried out to determine the operating conditions. It was found that percentage removal of the heavy metals monotonically decreases with the increase of initial concentration where as on the other



**Fig. 4** Variation of equilibrium % removal with adsorbent dosage (pH range: 3–5)



**Fig. 5** Variation of equilibrium % removal with pH (adsorbent dosage: 5–10 g/L)



hand it increases with the adsorbent dosage up to a definite limiting value, different for different metals after which it remains constant. The variation of % removal with respect to adsorbent dosage for four different heavy metals is shown in Fig. 4. On the other hand the variation of % removal with respect to pH at a fixed adsorbent dosage for four different heavy metals is shown in Fig. 5. It can be clearly observed from the figure that except Cr(VI) the maximum % removal takes place at pH = 5, where for Cr(VI) is shifts to 3. In order to be more informative the optimum operating conditions (pH and adsorbent dosage) for four different heavy metals are given in Table 3.

In order to determine the Langmuir adsorption isotherm parameters ( $k_0$  and  $Y_S$ ) equilibrium studies were conducted under the corresponding optimum operating conditions. The linear representation of the isotherm i.e., the  $\frac{C}{Y_{et}}$  vs C plot for four different heavy metals are shown in Fig. 6 [Cr(VI)

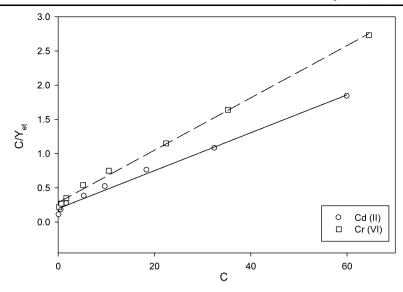
**Table 3** Optimum operating conditions for equilibrium as well as dynamic adsorption study

Metal ion	Initial pH	Adsorbent dosage (g/L)	Contact time (hr.)
Zn(II)	5	10	3
Cr(VI)	3	10	3
Cd(II)	5	7.5	2
Pb(II)	5	5	2

& Cd(II)] and 7 [Zn(II) & Pb(II)]. The Langmuir constants determined from the slope and intercept of the linear plots are shown in Table 4. The listed correlation coefficients as well as the corresponding standard deviations clearly indicate that the Langmuir isotherm can well describe the equilibrium adsorption characteristics of the present system.



Fig. 6 Langmuir plot for Cr(VI) and Cd(II) at optimum operating conditions



**Fig. 7** Langmuir plot for Zn(II) and Pb(II) at optimum operating conditions

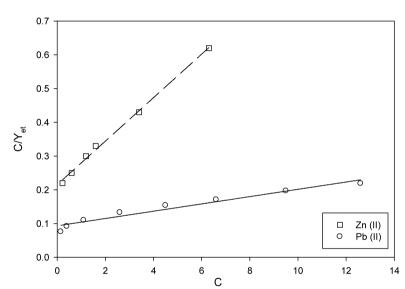


Table 4 Langmuir constants at optimum operating condition

Metal ion	Langmuir constant				
	$\overline{k_0}$	$Y_s$	$R^2$	SD	
	(L/mg)	(L/g)			
Zn(II)	0.299	4.641	0.9986	0.0089	
Cr(VI)	0.134	3.505	0.9761	0.0119	
Cd(II)	0.14	5.055	0.9986	0.0497	
Pb(II)	0.116	10.713	0.9962	0.0547	

#### 5.2 Dynamic concentration profile

Dimensionless concentration  $(\frac{C}{C_0})$  vs time data generated numerically after solving (9) and (10) with simultaneous optimization of pore diffusion coefficient  $(D_0)$  were compared with experimental values. Figures 8 to 11 shows a com-

parative plot of model prediction and experimental data at three different initial concentrations of 10, 25 and 50 mg/L for four different metal ions, i.e., Zn(II), Cr(VI), Cd(II) and Pb(II) in combination with clarified sludge as the sole adsorbent. All these figures show a very good agreement of the model prediction with experimental data, with a maximum standard deviation well within 0.13, which establishes the general validity of SCM in describing the adsorption of different metals on clarified sludge. The necessary outcome of the present work can be finally summarized in terms of pore diffusivity values of different metal ions in clarified sludge as given in Table 5. In terms of increasing order of pore diffusivity the stated metal ions can be arranged as follows: Cr(VI), Cd(II), Zn(II), Pb(II). In addition to the pore diffusivities degree of penetrations of different metal ions in the clarified sludge were also evaluated as shown in Fig. 12, in order to avoid the redundancy the trend of penetration vs



Fig. 8 Variation of dimensionless concentration with time for three different initial concentrations of Cr(VI)

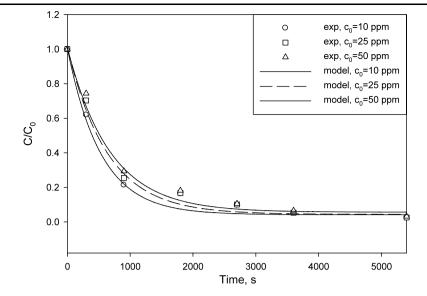
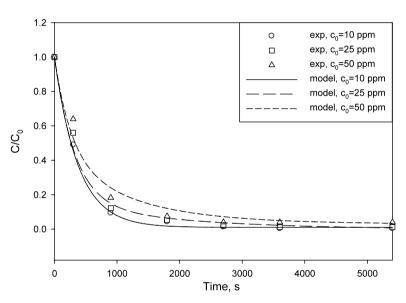


Fig. 9 Variation of dimensionless concentration with time for three different initial concentrations of Cd(II)



**Fig. 10** Variation of dimensionless concentration with time for three different initial concentrations of Zn(II)

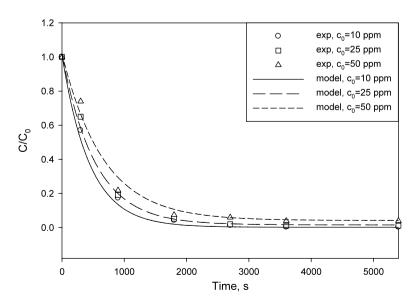
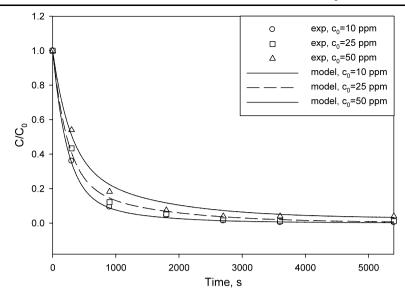




Fig. 11 Variation of dimensionless concentration with time for three different initial concentrations of Pb(II)



**Fig. 12** Degree of penetration of Pb(II) ions in clarified sludge particles

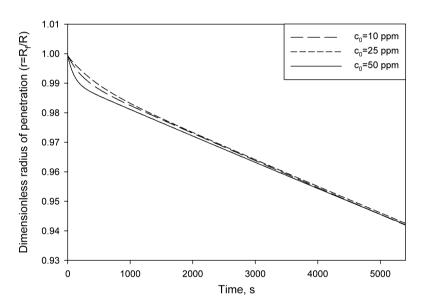


Table 5 Value of diffusivity obtained by the SC model

Metal ion	Diffusivity (cm <sup>2</sup> /s)	SD
Zn(II)	$4.7 \times 10^{-7}$	0.11
Cr(VI)	$1.8 \times 10^{-7}$	0.09
Cd(II)	$2.3 \times 10^{-7}$	0.13
Pb(II)	$7.3 \times 10^{-7}$	0.06

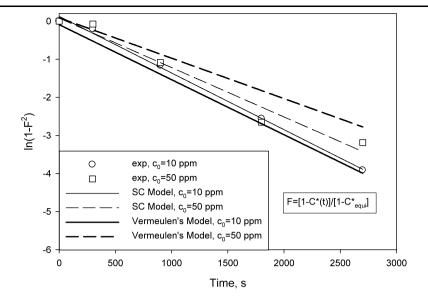
time is only given for Pb(II)-Clarified Sludge system. The outcome of this work may be very much useful in the design and simulation of the actual packed bed adsorption column and it also establishes the utility of clarified sludge as a potential adsorbent for the treatment of industrial effluents containing toxic metal ions.

5.3 Comparison of the proposed shrinking core model with other diffusion models

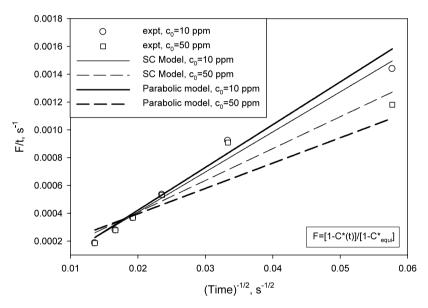
For noncatalytic reactions of particle with surrounding fluid, two idealized group of models are generally used, the progressive conversion model (PCM) and the shrinking core model (SCM). Both can be easily extended to analyze the solid-liquid adsorption system. The PCM extended for adsorption studies visualizes that the adsorbate enters and get adsorbed throughout the solid adsorbent at all times, most likely at different rates at different locations within the particle (Fogler 1997). In order to establish the gross effectiveness of SCM the predictions of the proposed model was compared with two standard forms of PCM, namely the diffusion model according to Vermeulen's approximation (In-



Fig. 13 Comparison of the proposed SC model with the diffusion model according to Vermeulen for Zn(II)-Clarified sludge system



**Fig. 14** Comparison of the proposed SC model with parabolic diffusion model for Zn(II)-Clarified sludge system



glezakis and Grigoropoulous 2001) and the parabolic diffusion model (Aharoni et al. 1998).

According to Vermeulen's approximation impregnated diffusion model  $\ln(1-F^2)$  vs t should give a straight line with a slope of  $\frac{\pi^2 D_0}{R}$ , where  $F = \frac{1-C^*(t)}{1-C^*(t)|_{\text{equi}}}$  and  $C^*(t)|_{\text{equi}}$  is the dimensionless concentration at equilibrium. Figure 13 shows the comparative plot of two models (Vermeulen's and the proposed one) with respect to discrete experimental data points for CLS-Zn(II) system. It can be clearly noted that the proposed SCM gives much better result that its PCM counterpart, which is being confirmed by the corresponding standard deviations found to be 0.35 and 0.13 for Vermeulen's and the proposed SCM respectively.

On the other hand the parabolic diffusion model predicts a linear relationship between  $\frac{F}{t}$  and  $\frac{1}{t^{\frac{1}{2}}}$ . Once again the cor-

responding comparative plot is shown in Fig. 14 for CLS-Zn(II) system, which clearly reflects the general superiority of SCM over PCM in describing the dynamic response of the present system. The standard deviation for the parabolic model was calculated to be 0.21, whereas for the proposed SCM it is well within 0.09.

The comparative analysis clearly reflects the general applicability of SCM over PCM in describing the dynamic behavior of the present system under different parametric conditions.

#### 6 Conclusion

In the present work, performance of clarified sludge obtained from industrial waste was analyzed as an adsorbent



for the removal of metal ions from aqueous solution. An extensive characterization of the sludge was conducted in terms of physical properties, composition and the surface characteristics. Batch adsorption studies were conducted to generate experimental time evolution data of concentration, which as a basis were used to validate Shrinking Core Model formulated to simulate the process of adsorption. This was followed by a global optimization in order to extract the pore diffusivity data for different metal ions in the clarified sludge. Additionally the performance of SCM was also compared with that of two other diffusion models, which clearly indicates a gross effectiveness of SCM over other models in analyzing the behavior of the present system. The outcome of the present analysis, in particular the pore diffusivity values can be used in the modeling and simulation of the actual industrial adsorption column, where from the optimum operating conditions or efficient control strategy can be extracted.

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