



PHYSICAL CHEMISTRY 2008

Proceedings

*of the 9th International Conference on Fundamental
and Applied Aspects of Physical Chemistry*

Volume II

The Conference is dedicated to the 200th Anniversary of the University in Belgrade



September 24-26, 2008,
Belgrade, Serbia



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ISBN 978-86-82475-13-2
Title: Physical Chemistry 2008. (Proceedings)
Editor: Prof. dr A. Antić-Jovanović
Published by: The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For publisher: Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia
Printed by: "Jovan" Printing and Published Comp;
250 Copies; Number of Pages: x + 301 (469-770);
Format B5; Printing finished in September 2008.
Text and Layout: Aleksandar Nikolić
250 – copy printing

THE ROLE OF INTRAPARTICLE DIFFUSION IN THE SORPTION OF Cu^{2+} IONS ONTO HYDROXYAPATITE

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Abstract

The Cu^{2+} sorption onto HAP was investigated as a function of time, in the concentration range $5 \cdot 10^{-4}$ - $5 \cdot 10^{-3}$ mol/dm³. The experimentally obtained kinetic data were fitted with the intraparticle diffusion model. The correlation coefficients were low considering the overall reaction period. However, q versus $t^{0.5}$ plots could be divided into three segments, out of which the second linear segment can be attributed to the intraparticle diffusion. Intraparticle diffusion rate constants (k_i) increased from $3.57 \cdot 10^{-3}$ to $7.80 \cdot 10^{-3}$ mmol/g min^{0.5} with the increase of the initial Cu^{2+} concentration. As the lines did not pass through the origin it was concluded that intraparticle diffusion is not the only rate-controlling step.

Introduction

It is generally accepted that the sorption dynamics consists of three consecutive steps: (1) transport of sorbate particles from the bulk solution to the external surface of the sorbent by diffusion through the liquid boundary layer, (2) diffusion of the sorbate from the external surface into the pores of the sorbent and (3) sorption of the sorbate on the active sites on the internal surface of the pores [1]. The overall rate of sorption may be controlled by each process or by their combination. It has been noticed in many studies that boundary layer diffusion is dominant during the initial sorbate uptake, and then gradually, after the sorbent's external surface is loaded, the sorption rate becomes controlled by intraparticle diffusion.

In this paper, the role of intraparticle diffusion in the kinetics of Cu^{2+} sorption from the aqueous solution by hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP) was studied.

Materials and Methods

As a sorbent, synthetic HAP, prepared by neutralization of $\text{Ca}(\text{OH})_2$ with H_3PO_4 , was used [2]. The sorbent was shaken (120 rpm) with $\text{Cu}(\text{NO}_3)_2$ solutions (solid to liquid ratio 1:200), at room temperature ($20 \pm 1^\circ\text{C}$). The contact times were varied in the range 5 min. - 48 h. The initial concentrations of Cu^{2+} were $5 \cdot 10^{-4}$, $1 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$ mol/dm³, while initial pH values were adjusted to 5. After filtration, the Cu^{2+} concentrations were measured by a Perkin Elmer Analyst 200 Atomic Absorption Spectrometer.

Results and Discussion

The intraparticle diffusion model, proposed by Weber and Morris [3], can be expressed by following equation:

$$q = k_i t^{0.5} + c \quad (1)$$

where q is the amount of Cu^{2+} sorbed (mmol/g) at time t , k_i is intraparticle diffusion rate constant ($\text{mmol/g min}^{0.5}$), and c is constant related to the boundary layer thickness. According to this model, the plot of uptake, q versus the square root of time, should be linear if intraparticle diffusion is involved in the adsorption process. Furthermore, if these lines pass through the origin then the intraparticle diffusion is the rate controlling step.

The plots of the amounts of Cu^{2+} sorbed by HAP against the square root of time, for various initial sorbate concentrations, are presented in Fig. 1.

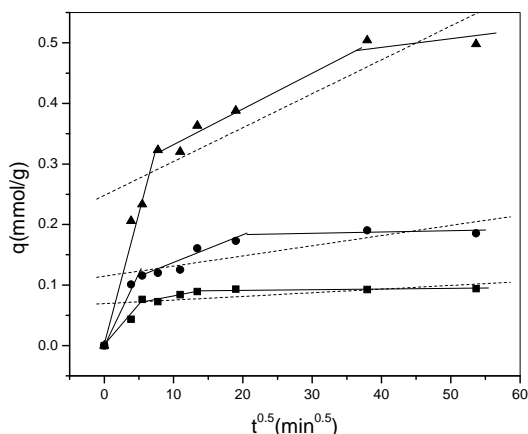


Fig. 1. Dependency between the amount of Cu^{2+} sorbed by HAP and square root of time. Cu^{2+} concentrations (mol/dm^3): $5 \cdot 10^{-4}$ (■), $1 \cdot 10^{-3}$ (●) and $5 \cdot 10^{-3}$ (▲). Linear data fitting for overall process (--) and different process stages (—).

Considering the overall reaction period, the intraparticle diffusion model has shown low correlation with experimental data (Table 1). Owing to the varying extent of sorption in the initial and final stages, plots of q versus $t^{0.5}$ often demonstrate multilinearity, signifying that different types of mechanisms are operating in the various stages of the sorption [4].

In the case of Cu^{2+} sorption by HAP (Fig. 1), at the beginning of sorption there is a region representing more rapid diffusion through the boundary layer, followed by the second stage representing diffusion of the sorbate molecules by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism [5]. The third segment corresponds to equilibrium [5]. The rates of the first two stages increase with initial concentration increase, since the driving force for the mass transfer increase in the same way. The equilibrium was achieved faster (about 6 h) in the systems with lower metal concentrations, while approximately 24 h was needed in the case of the highest studied Cu^{2+} concentration. The intraparticle diffusion step (Stage 2) approximately takes place in the time ranges 25 min-3

h, 25 min-6 h and 60 min-22 h for initial concentrations $5 \cdot 10^{-4}$, $1 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$ mol/dm³, respectively.

The correlation coefficients for the second linear segments (Table 1) are relatively high, while the calculated intraparticle diffusion rate (k_i) increases from $3.57 \cdot 10^{-3}$ to $7.80 \cdot 10^{-3}$ mmol/g min^{0.5} with the initial concentration increase. The increased initial Cu²⁺ concentration create a lower intraparticle diffusion resistance and accordingly give higher internal diffusion coefficient. However, the plots indicated that the intraparticle diffusion is not the only rate controlling step because the lines did not pass through the origin.

Table 1. Linear regression coefficients for the overall sorption process and the stage involving intraparticle diffusion, and calculated intraparticle diffusion rate constants.

Initial Cu ²⁺ concentration (mol/dm ³)	Overall process R	Stage 2	
		R	$k_i \cdot 10^3$ (mmol g ⁻¹ min ^{-0.5})
$5 \cdot 10^{-4}$	0.63	1.00	3.57
$1 \cdot 10^{-3}$	0.85	0.93	5.10
$5 \cdot 10^{-3}$	0.91	0.93	7.80

Conclusion

The intraparticle diffusion model was found to be inappropriate for the description of the overall process of Cu²⁺ sorption by HAP. However, intraparticle diffusion which can be attributed to the second linear segment of the q vs, $t^{1/2}$ plots, takes place in the time ranges 60 min-22 h for Cu²⁺ concentration $5 \cdot 10^{-3}$ mol/dm³, 25 min-6 h for $1 \cdot 10^{-3}$ mol/dm³ and 25 min-3h for $5 \cdot 10^{-4}$ mol/dm³ solution. The calculated k_i values were found to increase with the increase of initial Cu²⁺ concentration. The results imply that both boundary layer and intraparticle diffusion might be involved in this removal process.

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