



## Discussion

## Authors' response to comments on "Factors influencing the removal of divalent cations by hydroxyapatite"

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## ABSTRACT

Recently, it has come to our attention, that a polemical note by Milonjić [S.K. Milonjić, Comments on "factors influencing the removal of divalent cations by hydroxyapatite", J. Hazard. Mater. 162 (2009) 1588–1589], has been published raising several critical comments on some experimental procedures, as well as the presentation and interpretation of some data found in the cited paper by Smičiklas et al. [I. Smičiklas, A. Onjia, S. Raičević, Dj. Janačković, M. Mitrić, Factors influencing the removal of divalent cations by hydroxyapatite, J. Hazard. Mater. 152 (2008) 876–884]. Since we have not received any prior copy of this discussion through the process involved in the acceptance of these comments, we now take the opportunity of responding. We have reviewed some scientific papers dealing with cation sorption, in order to demonstrate variety of experimental approaches used for batch sorption tests, regarding solution pH. Finally, we justified experimental methods and data interpretation methods we chose to perform in the mentioned manuscript.

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### 1. Discussion

In the comments reported by Milonjić [1], our paper [2] was criticized from several aspects, including: point of zero charge ( $\text{pH}_{\text{PZC}}$ ) determination, experimental procedure and interpretation of kinetic and isotherm sorption data and repetition of the previously published results. It was stated that "...the determination of  $\text{pH}_{\text{PZC}}$  by any method should be performed using three different concentrations of an electrolyte". In our opinion, repetition of  $\text{pH}_{\text{PZC}}$  determination, using solutions of different concentrations of the same electrolyte, is certainly initially necessary in order to determine whether the electrolyte is inert in respect to a certain sorbent surface, or not. The  $\text{pH}_{\text{PZC}}$  value of hydroxyapatite (HAP) sample studied in the commented paper was determined using  $0.1 \text{ mol/dm}^3 \text{ KNO}_3$ , because it was already well documented that  $\text{KNO}_3$  is an *inert* electrolyte in respect to HAP surface [3–5].  $\text{pH}_{\text{PZC}}$  value of HAP is independent on  $\text{KNO}_3$  concentration, i.e. no specific sorption of either  $\text{K}^+$  or  $\text{NO}_3^-$  ions occurs at HAP surface. What's more, Milonjić was the author of papers where  $\text{pH}_{\text{PZC}}$  values of HAP and other solids were determined using one [6] or two [7,8] concentrations of *inert* electrolyte. Specific sorption of ions, on the other hand, shifts the  $\text{pH}_{\text{PZC}}$  in respect to the value obtained in inert electrolyte solutions [9]. When the cations are sorbed specifically, i.e. when they exhibit chemical affinity to the examined surface, the

PZC shifts to a lower pH [10]. Once this shift is observed—specific sorption is recognized. Each repetition of the experiment, with different concentration of electrolyte will give a different  $\text{pH}_{\text{PZC}}$  value, because it is concentration dependent. Therefore, the repetition is not necessary to prove the existence of specific sorption; it is enough to compare the results with the ones obtained in inert electrolyte. Finally, the purpose of our experiment was not to investigate the influence of electrolyte concentration on the position of  $\text{pH}_{\text{PZC}}$ , but, as indicated by the title of the section ("Effect of pH"), to determine and compare the effect of pH on the amount of divalent cations removed from the solution. Observed PZC shifts to lower pH, in respect to  $\text{pH}_{\text{PZC}}$  obtained in  $\text{KNO}_3$  solution, were used as a confirmation of a specific cation sorption. Other authors have applied the same experimental procedure, using only one electrolyte concentration in the "effect of pH" studies and made the same remark considering the position of  $\text{pH}_{\text{PZC}}$  [11,12]. Milonjić himself was the author of papers where the  $\text{pH}_{\text{PZC}}$  shift and specific sorption of cations were recognized using only one electrolyte concentration:  $1 \times 10^{-5} \text{ mol/dm}^3 \text{ Zn(NO}_3)_2$  or  $\text{Cd(NO}_3)_2$  [8] or  $0.01 \text{ mol/dm}^3$  of  $\text{Pb(NO}_3)_2$ ,  $\text{Cd(NO}_3)_2$  and  $\text{Sr(NO}_3)_2$  [13].

In the comment, it was also stated that sorption equilibrium and kinetic studies conducted under uncontrolled pH are incorrect, as well as all calculations based on these data. At this point we would like to make a short review regarding definitions of sorption, sorption isotherm and especially experimental procedures used for sorption studies. Sorption, in contrast to adsorption, is a general term used to describe several physical and chemical processes (adsorption, ion-exchange, surface precipitation, surface

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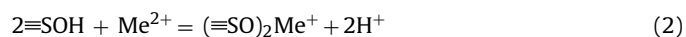
complexation, diffusion, dissolution/precipitation, etc.) that result in a sorbate being retained by a sorbent [14]. Thus, the sorption is defined as the *net* accumulation of a sorbate at an interface between a sorbent and the solution, caused by *any* mechanism. Sorption process can be quantified using mathematical equations that relate the amount of sorbate retained by the sorbent to the concentration of sorbate in solution, at equilibrium. By definition, a sorption isotherm describes this equilibrium, at *constant temperature*.

Considering solid/liquid systems, it is difficult to find exact and explicit instruction on how sorption isotherm should be obtained. Isotherm data published in relevant scientific literature were generally obtained by reacting sorbent with solutions ranging in initial sorbate concentrations, over a time period sufficient for reaching equilibrium, at constant temperature. However, different approaches have been applied regarding some other sorption parameters, especially solution pH. Using apatite based materials, as well as other sorbents, batch sorption experiments were conducted in different ways, for example:

- pH value of the solution was not mentioned in the manuscript [15–17],
- initial pH values were neither measured nor adjusted, final pH values were measured [18,19],
- initial and final pH values were measured [20,21],
- initial pH values were adjusted, final pH values were not mentioned [13,22–26],
- initial pH values were adjusted, final pH values were measured [27–30],
- initial and final pH values were adjusted [31],
- the pH was controlled several times in the course of the reaction [32],
- the pH was maintained constant throughout the equilibration time, by addition of acidic or alkaline solutions [33–35],
- experiments were conducted at constant pH, using buffered solutions [36–38].

The various experimental concepts were used also for sorption kinetic studies.

In our manuscript [2], final pH decrease (in respect to  $\text{pH}_{\text{PZC}}$ , in  $\text{KNO}_3$ ) with the increase of the amount of cation sorbed by HAP was reported. This phenomenon was connected with the formation of surface complexes, when protonated surface functional groups ( $\equiv\text{SOH}$ ) interact with cations from the solution with 1:1 or 1:2 stoichiometry [39]:



By keeping constant pH along cation sorption, the sorbent/(sorbate solution) system is artificially maintained under forced conditions. Since the purpose of our experiments is to evaluate certain sorbent as a metal removing agent, these conditions will not be realistic if the sorbent is applied on actual contaminated water, where maintaining constant pH is not reasonable or not possible at all. In our opinion, conducting the experiments at constant pH would suppress the mechanism described by Eqs. (1) and (2). As a result, the obtained capacities would not represent the *net* accumulation caused by *any* mechanism, but a part of it. What's more, both ways of keeping pH constant exhibit certain drawbacks. Addition of acidic or alkaline solutions can often change the volume, composition and consequently concentration of the solution. It was, for example, reported that adding either  $0.1 \text{ mol/dm}^3$  NaOH or HCl was not successful in maintaining constant pH, which always tended to drop gradually, especially at high metal ion concentrations even after the addition of large quantities of alkaline solution [36]. On the other hand, if the pH is controlled by buffer solution, its' components can

interfere with the reaction species in several ways, and observed sorption capacities are dependent on the applied buffering system [37,38]. In conclusion, all experimental techniques for obtaining sorption isotherm have pros and cons and, in our belief, it is the most important that authors are precise in describing experimental conditions.

General purpose adsorption isotherms (Langmuir, Freundlich, ...) are often used for interpretation of experimental data, as empirical models which do not make statements about the underlying mechanisms [40]. The Langmuir isotherm was originally developed to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature [41]. Although this model is based on the assumptions that are usually not applicable, a large number of studies considering sorption of solutes from a liquid phase have revealed that Langmuir isotherm can fit the experimental points, obtained even when pH was not maintained constant (Refs. [15,20,22–24,27,28,33], for example). The fact that numerous sorption data, obtained for different systems and different sorption mechanisms, actually met the mathematical criteria necessitated by Langmuir equation makes it evident that sorption isotherm equations should be regarded simply as curve fitting devices [39]. The clear identification of the sorption mechanism is usually only possible by application of various spectroscopic methods, nevertheless isotherm equations enable comparison of sorption capacities among sorbents or sorbates, or changes in sorbate retention due to varying sorption conditions.

The statement made in the Comment [2], that a linear relationship between  $\text{Ca}^{2+}$  released from HAP crystal lattice and the amount of divalent metal-ions sorbed has already been reported by the same authors, is not correct. Fig. 5b, Ref. [2] describes relationship between the amounts of divalent cations sorbed by sample HAP3, from the solutions of different initial sorbate concentrations, vs. amounts of released  $\text{Ca}^{2+}$ . Figs. 2a and b, from the previously published paper [42] represent, on the other hand, relationship between the amounts of divalent cations sorbed from one single metal and one mixed metal solution, by 10 different HAP samples, and the corresponding  $\text{Ca}^{2+}$  concentrations in the solutions. The experiments related to synthesis and characteristics of the HAP sample studied in commented paper, were in deed previously published, and that was the reason why we referred to our previous work in the Introduction, as well as in Section 2.1. Starting material [2].

As a final point, the authors do agree with the remark that, on page 881, Ref. [2], it was erroneously written that the constants ( $K$  and  $X_m$ ) in the Langmuir equation were obtained from the experimental data given in Fig. 3b, instead of Fig. 4. However, the constants were determined from the slope and the intercept of the linear plot  $C_e/q_e$  as a function of  $C_e$ . The author of the comments wrote that the relationship  $C_e/q_e$  vs.  $C_e/X_m$  should be used, proving that such unintended error may happen to anyone.

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