LETTER TO THE EDITOR

Discussion on the Comments of Slobodan K. Milonjić on the article entitled "Adsorption of strontium on different sodium-enriched bentonites" by Sanja R. Marinović, Marija J. Ajduković, Nataša P. Jović-Jovičić, Tihana M. Mudrinić, Bojana N. Nedić-Vasiljević, Predrag T. Banković and Aleksandra D. Milutinović-Nikolić, published in the *Journal of the Serbian Chemical Society*, Vol. 82, Issue 4, 2017, pp. 449–463

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Abstract: A thorough discussion on the Comments on the article "Adsorption of strontium on different sodium-enriched bentonites", by Sanja R. Marinović, Marija J. Ajduković, Nataša P. Jović-Jovičić, Tihana M. Mudrinić, Bojana N. Nedić-Vasiljević, Predrag T. Banković and Aleksandra D. Milutinović-Nikolić published in the Journal of the Serbian Chemical Society, Volume 82, Issue 4, Pages: 449-463 (2017), given as Letter to the Editor by S. K. Milonjić, is provided in this letter. The authors of the commented paper have considered all the comments, and responded to each of them, point by point.

Keywords: adsorption; bentonites; analysis of problematic interpretation.

After the scientific paper entitled "Adsorption of strontium on different sodium-enriched bentonites", by Marinović *et al.*[1] had been published, it was commented on by Milonjić.[2] The authors of the paper[1] have thoroughly considered all the comments.[2] There are two typing errors that were, unfortunately, overlooked during the reviewing process and the proof reading. These accidental mistakes were, however, discussed by the critic as fundamental. Beside them,

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other comments are questionable and imply superficial approach of the critic to the evaluation. This may be due to the specificity of the scientific field of clays and clay minerals, that perhaps has not been taken into consideration. The authors of the paper hereby address the Editorial office of the Journal of the Serbian Chemical Society, with the detailed discussion that provides the relevant scientific data, and offers the references of the renowned authors and from the competitive scientific journals, aimed to prove the Comments[2] wrong, and to support their position. The authors have responded to each of the comments,[2] point by point.

In the Eq. (1)[1] the authors accidentally omitted one factor, namely volume (*V*), from the formula. However, and it is important to be stressed, they used the correct formula for the calculation of the amount of Sr^{2+} adsorbed after time *t* (q_t). The values of q_t in Tables II and III[1] are calculated using the correct formula and the units are appropriate (mg g^{-1}). Therefore, the recalculating is redundant because the calculated data are certainly valid. Consequently, the drawn conclusions can be based on the data, and should not be regarded as questionable. Moreover, it should be noted that the authors are well aware of the correct form of the formula and have reported it previously in several scientific publications.[3–6]

The comment: "From Fig. 4 (Ref. 1), it is evident that the adsorbed amounts of Sr^{2+} on Na-T, Na- W and Na-B bentonites in the initial pH_i range ~4 to ~9 are constant because the final pH_f values are constant" is unnecessary, because the authors commented the obtained results in the similar manner. In Fig. 4, in the published paper, two aspects of the influence of the initial pH (pH_i) are presented. The first set of curves represents the influence of pH_i on Sr^{2+} uptake. The other one represents the influence of pH_i on the final pH (pH_f) with the goal of determining the pH_i range for which pH_f is almost constant, exhibited as the plateau in the diagram. This plateau results from the constant ratio of the quantities of negative and positive charges on the surface of adsorbent. The direct consequence of this effect is the constant value of pH_f, which leads to the constant Sr^{2+} uptake within the corresponding pH_i range. One of the goals of this part of investigation was the determination of the acidity range within which pH_i for further adsorption experiments should be chosen. Accordingly, it is not important whether the constant ratio of the quantities of negative and positive charges on the surface of adsorbent was elaborated, as the relevant phenomenon (as the authors did in the published paper) or its direct consequence was evidenced as constant pH_f value.

The remark that refers to the lack of the experimental proof of the ion exchange mechanism, as the dominant one, can be addressed as follows. The main property of smectites – a group of clay minerals – is the cation exchange ability, expressed through the high values of the cation exchange capacity (*CEC*). This property is well described in literature[7] as well as the fact that the ion

exchange mechanism is considered to be the governing mechanism for the adsorption of cations. Therefore, in the research area of clays and clay minerals, additional experimental proofs for the ion exchange mechanism are not a common practice. It was legitimate, though, for the reviewers of the submitted text, to request additional experimental proofs, which did not happen. Otherwise, the authors would have readily provided additional data. Beside the ion exchange mechanism, the mechanism of adsorption on clays is the surface adsorption. Surface adsorption should be favoured by the developed specific surface area, which was not the case, and in the criticized paper[1] a discussion on this topic was originally provided.

Further comments[2] refer to the adsorption kinetics data analysis. According to the reference,[8] recommended by the critic, results for longer adsorption times should be taken into account for porous materials (such as the investigated clays), which is opposed to the suggestions of the critic. Tran *et al.*[8] propose for this type of materials the extended adsorption times, even longer than 24 h. However, after receiving the remarks,[2] the authors performed an additional calculation using fewer points, only for shorter times, than the one presented in the published paper. The equation for the pseudo-second order kinetics:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

was again used for the calculation. The newly obtained results for q_e, differed for up to 5 % in comparison with the published ones. Therefore, the conclusions in the published manuscript, based on the calculated data, are not erroneous. In addition, the distinguished experts in the field of clays and clay minerals published the kinetic analysis for the adsorption of Cs^+ onto the porous clay mineral sepiolite, using times that exceed the equilibrium time.[9]

The dimension of the Freundlich adsorption constant, given in Table II as K_F in $dm^3\ mg^{-1}$, is a typing error. The authors are well aware of the correct unit, and the proof for this are the publications that preceded the commented one.[4,5] The correct form of the unit is presented in corrections on the paper[1] at the end of this text; however it differs from the one suggested by Milonjić.[2] Here, the authors provide the dimensional analysis that explains how the unit is derived when the correct analytic form of the Freundlich equation[10–12] is used, as presented in Eq. (3):

$$q_e = K_F c_e^{\frac{1}{n}} \tag{3}$$

The unit for K_F is derived in Eq. (4):

$$K_\mathrm{F}(=)\mathrm{mg\ g^{-1}}\left(\mathrm{dm^3\ mg^{-1}}\right)^{\frac{1}{n}} \tag{4}$$

The Langmuir, Freundlich and Dubinin–Raduskevich isotherm models were applied on the experimentally obtained data for the adsorption of Sr^{2+} onto different bentonites. Low values of the coefficient of determination (R^2) obtained for the Freundlich model suggested that the Freundlich model is not appropriate for the investigated system. Therefore, the Freundlich adsorption constant (n) was not taken into consideration in the paper by Marinović *et al.*[1] for the determination of the nature of the investigated process. Hence, the conclusions drawn from the isotherm analysis were not in disagreement, as stated by the critic.

However, the corrections and the reformulated discussion on the mechanism of Sr^{2+} uptake is given at the end of this text.

The authors believe that the discussion given in the text above have completely addressed all the remarks given in the Comments by Milonjić.[2] It is worth emphasizing that the original paper was already revised in the manner suggested by the Reviewers and the Editor of the Journal of the Serbian Chemical Society. Therefore, the authors will avoid potential further polemics with Dr Milonjić regarding the Marinović *et al.*[1] paper that might become excessive.

Corrections on the paper published in the *Journal of the Serbian Chemical Society*, Volume 82, Issue 4, Pages: 449-463 (2017)

- The correct equation on Page 452 is:

$$q_t = \frac{(c_0 - c_t)V}{m_\mathrm{ads}} \tag{1}$$

where c_0 and c_t are the concentrations (mg dm^{-3}) of Sr^{2+} in a solution initially and after adsorption time t, respectively, V is the volume of solution (dm^3) and m_ads is the adsorbent mass.

The correct unit for K_F in Table II is mg g^{-1} (dm^3 mg^{-1})$^{1/n}$.

The discussion in the paragraph following the Table III, Page 460, is reformulated as follows:

The squared correlation coefficients (R^2) showed that the experimental data were in good agreement with the Dubinin–Radushkevich isotherm model (Table III). The calculated E values were similar for all the investigated adsorbents and slightly higher than 8 kJ mol^{-1}, within the range of the adsorption energy characteristic for the systems in which ion exchange is the dominant mechanism (8–16 kJ mol^{-1}).[13] Consequently, the sentence in the Conclusion, Page 461, where this result is emphasized, should be:

The value obtained for the adsorption energy was slightly above 8 kJ mol^{-1}. This indicated the ion exchange as the dominant adsorption mechanism.

И З В О Д

ДИСКУСИЈА КОМЕНТАРА СЛОБОДАНА К. МИЛОЊИЋА НА РАД ПОД НАСЛОВОМ АДСОРПЦИЈА СТРОНЦИЈУМА НА РАЗЛИЧИТИМ НАТРИЈУМОМ ИЗМЕЊЕНИМ БЕНТОНИТИМА, АУТОРИ: САЊА МАРИНОВИЋ, МАРИЈА АЈДУКОВИЋ, НАТАША ЈОВИЋ-ЈОВИЧИЋ, ПРЕДРАГ БАНКОВИЋ, ТИХАНА МУДРИНИЋ, БОЈАНА НЕДИЋ- -ВАСИЉЕВИЋ и АЛЕКСАНДРА МИЛУТИНОВИЋ-НИКОЛИЋ, ОБЈАВЉЕНОГ У *JOURNAL OF THE SERBIAN CHEMICAL SOCIETY*, ВОЛУМЕН **82**, БРОЈ 4, 2017, СТР. 449–463

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У овом тексту дата је детаљна дискусија која се односи на коментаре у писму С. К. Милоњића уреднику часописа *J. Serb. Chem. Soc.*: *Comments on the article entitled "Adsorption of strontium on different sodium-enriched bentonites", by Sanja R. Marinović, Marija J. Ajduković, Nataša P. Jović-Jovičić, Tihana M. Mudrinić, Bojana N. Nedić-Vasiljević, Predrag T. Banković and Aleksandra D. Milutinović-Nikolić, published in the Journal of the Serbian Chemical Society, Volume 82, Issue 4, 2017, pp. 449–463.* Аутори коментарисаног рада су размотрили све коментаре и на сваки од њих одговорили.

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