University of Belgrade, Technical Faculty in Bor

29th International Conference Ecological Truth & Environmental Research

EcoTER'22

Proceedings

Editor
Prof. Dr Snežana Šerbula

21-24 June 2022, Hotel Sunce, Sokobanja, Serbia

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29th INTERNATIONAL CONFERENCE

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PREFACE

In today's world, the environment has been endangered by the use of outdated technology, fossil fuels and environmental law violations. Therefore, environmental and many other scientists all over the world have been concerned about finding sustainable technology in resolving these issues. That is why environmental research and ecological truth are at the focus of the 29th International Conference Ecological Truth & Environmental Research 2022 (EcoTER'22), which will be held in Sokobanja, Serbia, 21–24 June 2022. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 29th International Conference Ecological Truth & Environmental Research 2022 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These proceedings include 85 papers from the authors coming from the universities, research institutes and industries in 6 countries: Bulgaria, Italia, Albania, Bosnia and Herzegovina, Montenegro and Serbia.

As a part of this year's conference, the 4th Student section – EcoTERS'22 is being held. We appreciate the contribution of the students and their mentors who have also participated in the Conference.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged by the Organizing Committee of the EcoTER'22 conference.

The support of the Platinum donor and their willingness and ability to cooperate have been of great importance for the success of EcoTER'22. The Organizing Committee would like to extend their appreciation and gratitude to the Platinum donor of the Conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to EcoTER'22. Sincere thanks go to all the people who have contributed to the successful organization of EcoTER'22.

Prof. Snežana Šerbula,

President of the Organizing Committee

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ARSENITE–SOIL HUMIC ACID BINDING BY ISOTHERMAL TITRATION CALORIMETRY: THERMODYNAMICS AND MNIS MODEL

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Abstract

Arsenite–humic acid-binding process was investigated using the Isothermal Titration Calorimetry (ITC). The ITC data were successfully (R^2=0.996-0.936) interpreted by applying the MNIS model, enabling thermodynamic parameters to be determined. The MNIS model was adjusted to the arsenite–HA binding process assuming hydrogen bonding as the dominant type of interaction in the system. Negative enthalpy change values indicated the arsenite–HAs binding as an exothermic process. Negative ΔG values (-(27.85-26.83) kJ mol^{-1}) pointed out to spontaneous binding reaction, leading to the formation of the arsenite–HA complexes. High binding constants values ((7.57-5.02)10^5 M^{-1}) clearly demonstrated pronounced binding affinity. As ΔS values (0.041-0.027) kJ mol^{-1} K^{-1}) were apparently positive, but close to zero, and ΔH>ΔS, the reaction could be considered enthalpy driven. Reaction heats and ΔH values (-(18.96-15.64) kJ mol^{-1}) confirmed hydrogen bonds as the most ascendant interaction type in the arsenite–HA complex. Thermodynamic and reaction parameters clearly indicated that arsenite–HA complexes are formed at common soil pH values, confirming the possible influence of humic acids on increased As mobility, and its reduced bioavailability.

Keywords: humic acid, arsenate, enthalpy, reaction coefficient

INTRODUCTION

Arsenic (As) as one of the inorganic contaminants is an extremely toxic metalloid that reaches soil and water as a result of anthropogenic activities or mobilization from natural sources [1]. Arsenic toxicity toxicity is directly related to its chemical form. The inorganic species are generally more toxic than the organic ones. Considering the inorganic forms, arsenate (As(III)) is more toxic in comparison to arsenite (As(V)) [2]. Arsenic toxicity is highly dependent on its speciation, which could be influenced by various environmental conditions such as pH, redox potential and the presence of organic and inorganic compounds and microorganisms [3]. Natural organic matter (NOM) plays a significant role in regulating As speciation, reactivity, mobility, bioavailability, and related toxicity [2,3].

Humic substances, including humic acids (HAs), are the most abundant fractions of NOM. HAs are the most reactive compounds in soil having the capacity for various chemical and physical reactions in the environment. HAs have a complex structure and contain active

functional groups, such as carboxyl and hydroxyl, having an important impact on transformation and migration of metal and metalloids in soil [4]. Thus, toxic metalloid arsenic interacts with HAs and forms As–HA complexes, further influencing As adsorption on the mineral solid phase surfaces, its solubility, and mobility [5].

The isothermal titration calorimetry (ITC) is a physical technique used to determine the thermodynamic parameters of interactions in solution. ITC has been widely used to study the binding of both organic and inorganic compounds to humic acids [6–8]. To the authors' knowledge, there are no literature data on As-HA binding process using ITC technique. Martin *et al*., [9] are the only ones using ITC to inspect the thermodynamics and kinetics of arsenic adsorption on ferrihydrite-kaolinite as influenced by the presence of humic acid coverage.

To better understand arsenic-soil HA binding process, in this study the system containing arsenite solution and soil humic acid suspension only was investigated by ITC technique. Row ITC data were interpreted by Multiple Non-Interacting Sites (MNIS) theoretical model adjusted for binding of charge-neutral molecular species to humic acid. Applying this model, thermodynamic parameters of arsenite–HA interaction were determined.

MATERIALS AND METHODS

Three soil humic acids (LPHA, TCHA and ESHA) of different origin were investigated. LPHA was isolated from Leptosol, originating from Negotin, E Serbia; TCHA was isolated from Technosol originating from Serbia ZiJin Bor Copper mine, formed on reclaimed copper post-flotation tailings; ESHA is the IHSS standard humic acid isolated from Elliott Soil [10]. LPHA and TCHA samples were isolated using a modified IHSS method [10] (HA gel was dried at 35 °C, powdered, and sieved using a 0.05 mm sieve).

Stock humic acid suspensions of LPHA, TCHA and ESHA (2 g dm^{-3}) were prepared in 0.01 M KOH and stored at 4 °C. Working HA suspensions (0.8 g dm^{-3}) were prepared before each titration by mixing stock suspensions and 0.1 M KNO_3 solution (1:1.5). Initial pH of working HA suspensions was adjusted to 5. Arsenate solution (5 mM) was prepared using sodiumhydroxoarsenate (III) ($NaAsO_2$) (Merck, Darmstadt, Germany) in 0.1 M KNO_3.

Thermal events were monitored by the Thermal Activity Monitor (227, LKB Bromma, Sweden) using a perfusion cell (227-401/402, Sweden) as a measuring device. Titrations were performed using Radiometer Automatic Titrator (ABU 80, Denmark). Prior to titration experiments, the measuring cell of the perfusion system was filled with 2.5 ml of HA suspension, thermally equilibrated in four steps and calibrated (10 μW range) using both static and dynamic calibration procedures. The working temperature was 298.15 K. Titration experiments started after the stable baseline was obtained.

Titrant (5 mM arsenite solution) was added in 30 μl portions at every 30 minutes with titration speed and mixing rate of 50 μl/min and 120 min^{-1}, respectively. For each titration, the output signal, power (μW) versus time (min), was recorded by the TAM assistant software and thermograms were obtained. Software used for titration control and data acquisition, as well as software for thermogram peak area determination, was developed in the laboratory.

Under the experimental conditions used for ITC titrations, pH-metric titration was performed as well. The HA suspension (10 ml) was titrated by 120 µl of 5 mM arsenite solution using Radiometer TTT85 titrator at 298 K. Titration speed was 12.5 µl min^{-1}. The next titration step was started after the pH value was stable for 7 s with pH units drift not exceeding ±0.001.

The plot of the heat of exchange (dQ/dn) as a function of the molar charge ratio Z ([As]m/[HA]m), where [As]m and [HA]m are the arsenate and humic acid molar charge concentrations, respectively, is fitted with the MNIS model [8,11]. The MNIS model is chosen because neutral arsenite species ($As(OH)_3$ and $HAsO_2$) were the only ones present in the titration range. The MNIS constant fitting parameters for carboxyl and phenolic HA functional groups (maximum charge densities, dissociation constants, and empirical parameters) were adopted from Ritchie and Perdue [12]. The MNIS model was adjusted assuming hydrogen bonds as dominant in the arsenate–HA interaction. Arsenite–HA binding enthalpy change (ΔH [kJ mol^{-1}]), affinity constant (K [M^{-1}]) and reaction stoichiometry (n) were obtained from the MNIS fit. K and ΔH values obtained by the fitting procedure applied were used to calculate binding Gibbs free energy ΔG [KJ mol^{-1}] and entrophy ΔS [kJ K^{-1} mol^{-1}] change.

RESULTS AND DISCUSSION

Thermograms generated by the ITC measurements are illustrated in Fig. 1a. The respective integrated heat data (dQ/d[As]) as a function of molar charge ratio ($[As]_m/[HA]_m$) fitted by the MNIS model are presented in Fig. 1b. By inspecting R^2 values, which ranged from 0.996 to 0.936, it is obvious that the MNIS model can be used to successfully interpret the arsenite–HAs binding process. As a result of the fitting procedure performed, ΔH, K and n were obtained and reported in Table 1. Also, ΔG and ΔS values are calculated and given in Table 1.

Table 1 *ΔH, K, and n values obtained by the MNIS fit of row ITC data and calculated ΔG and ΔS values*

	LPHA	TCHA	ESHA
ΔH (kJ mol^{-1})	-(16.25±0.26)	-(15.64±0.36)	-(18.96±0.19)
$K10^5$ (M^{-1})	5.02±0.85	7.57±212	5.36±0.51
n	0.629±0.005	0.586±0.006	0.448±0.002
ΔG (kJ mol^{-1})	-26.83	-27.85	-27.00
ΔS (kJ mol^{-1} K^{-1})	0.035	0.041	0.027

Negative peaks in the ITC thermograms and negative enthalpy change values indicate the arsenite–HAs binding as an exothermic process. Regarding negative ΔG values, it can be concluded that the binding reaction is spontaneous, leading to the formation of arsenite–HA complexes. High binding constants values ((7.57–5.02)10^5 M^{-1}) clearly demonstrated pronounced binding affinity. As ΔS values ((0.041–0.027) kJ mol^{-1} K^{-1}) were apparently positive, but close to zero, and ΔH>ΔS, the reaction could be considered enthalpy driven.

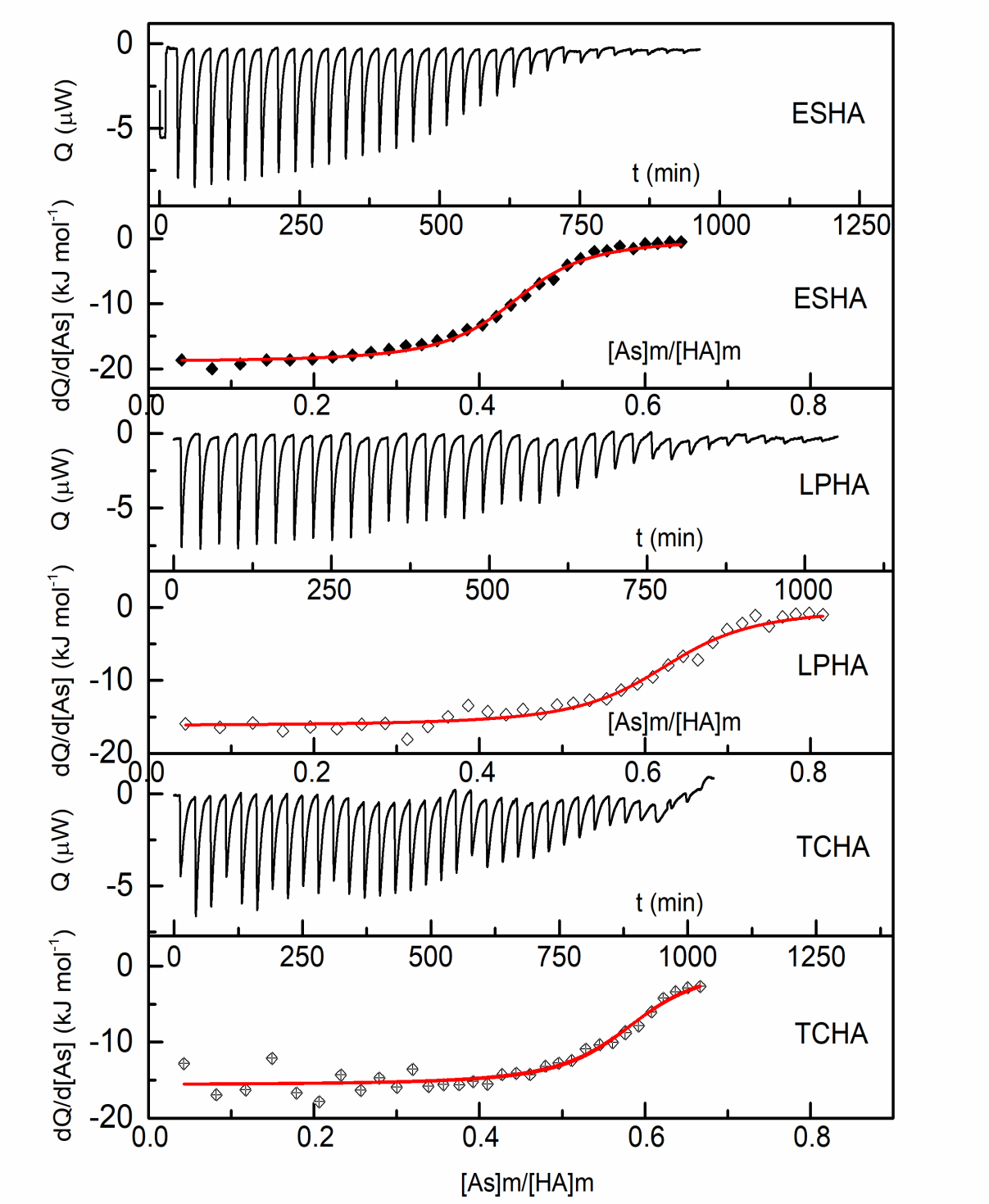

Figure 1 *(a) ITC thermograms; (b) integrated heat data (dQ/d[As]) as a function of molar charge ratio ($[As]_m/[HA]_m$) for LPHA, TCHA and ESHA; solid lines - the MNIS fit*

In this study, initial pH at the titration start was 5, not exceeding 8 for LPHA and 9 for ESHA and TCHA at the end of titration. Since As(III) forms stable neutral hydroxo complexes ($As(OH)_3$ and $HAsO_2$) at pH under 8 [13], these compounds are the only ones present in the sample solution. At pH above 8, anions AsO_2^- are formed and one can expect that an ionic exchange reaction exists, causing the MNIS model not fit the data obtained in

this pH range. Over the reaction stoichiometry range (0.629–0.448), where titration can be considered as completed, the MNIS model obviously fitted the experimental points successfully (Figure 1b), suggesting arsenate–HA hydrogen bonds remain as the dominant reaction type.

Previously reported data [3,14,15] did not include reaction heat measurements. Considering the results of this study, reaction heats measured by ITC and ΔH values (-(18.96–15.64) kJ mol^{-1}) obtained by the MNIS fit, confirm hydrogen bonds (typical bond strength from 10 to 40 kJ mol^{-1}) as the only interaction type in the arsenate–HA complex for both carboxyl and phenolic functional groups.

Due to the extensive presence of toxic arsenic species in the environment, their interaction with NOM is comprehensively studied in the literature. HA as a NOM fraction, binding arsenic species present in soils and sediments, enhance their mobilization and release into the soil solution. Increased As mobility can lead to groundwater contamination, but it can also be useful in soil remediation processes [5]. Besides the HA role in As mobility increases, forming the HA-As complexes can have a positive impact on the environment by reducing the bioavailability of toxic arsenic species [2]. Thermodynamic and reaction parameters obtained in this study clearly indicate that arsenite–HA complexes are formed at common soil pH values, confirming the possible influence of humic acids on increased As mobility, as well as reduced bioavailability.

CONCLUSION

The arsenate-humic acid binding process was investigated using the ITC technique. The ITC data were successfully interpreted applying the MNIS model, enabling thermodynamic parameters of the arsenite–HA interaction to be determined. Negative enthalpy change values (-(18.96–15.64) kJ mol^{-1}) indicated the arsenite–HAs binding as an exothermic process. Negative ΔG values (-(27.85–26.83) kJ mol^{-1}) pointed out to spontaneous binding reaction, leading to the formation of the arsenite–HA complexes. High binding constants values ((7.57–5.02)10^5 M^{-1}) clearly demonstrated pronounced binding affinity. As ΔS values (0.041–0.027) kJ mol^{-1} K^{-1}) were apparently positive, but close to zero, and ΔH>ΔS, the reaction could be considered enthalpy driven.

The MNIS model applied was adjusted to the arsenate–HA binding process assuming that hydrogen bonding is the dominant type of interaction in the system. Reaction heats measured by ITC and ΔH values (-(18.96–15.64) kJ mol^{-1}) obtained by the MNIS fit, confirm hydrogen bonds (typical bond strength from 10 to 40 kJ mol^{-1}) as the most ascendant interaction type in the arsenate–HA complex for both carboxyl and phenolic functional groups. The assumption validity was confirmed by good MNIS fit (R^2 = 0.996–0.936) as well.

Thermodynamic and reaction parameters obtained in this study clearly indicate that arsenite–HA complexes are formed at common soil pH values, confirming possible influence of humic acids on increased As mobility, as well as reduced its bioavailability.

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