

Thermodynamic Study of Isothermal Adsorption of Aluminum Ion from Water Using Activated Carbon Adsorbent

Mohammad Ali Takassi^{*1}, ParisaGhashghaee pour², Asadolah Farhadi³, Touba Hamule⁴

^{*1, 3, 4}The department of science, Petroleum University of Technology, Ahwaz, Iran 6198144471

²Khozestzn regional electrical company, Ahwaz, Iran 6198144475

¹takassi@put.ac.ir; ²p.ghashghaeipor@yahoo.com; ³farhadichem@put.ac.ir; ⁴t.hamoule@put.ac.ir

Abstract-In this study, the thermodynamic property of isothermal adsorption of aluminum ion from aqueous solutions was investigated with activated carbon adsorbent. The isothermal adsorption of aluminum ion by activated carbon adsorbent was found to be an endothermic process. The adsorption of ion increases when temperature is elevated. Thermodynamic parameters were obtained. The values of ΔG , ΔH and ΔS are -1127.3, 4716.5, 19.6 J/mol. g_(adsorbent) respectively. The adsorption was observed to be a spontaneous process. The adsorption of aluminum ion on activated carbon did not follow the Langmuir isotherm for liquid adsorbate on solid adsorbent. However, the adsorption follows the Freundlich isotherm. The nature of adsorption is physisorption. This investigation studied all effective parameters involved in the adsorption process: concentration of adsorbate, level of adsorbent, contact time, pH, and temperature. It was found that the adsorption of aluminum ion from aqueous solutions increases by increasing the concentration of adsorbate. The study concluded that the amount of adsorption increases by increasing the time of contact between adsorbate and adsorbent and also by increasing the level of adsorbent. The study also revealed that maximum adsorption occurs at pH 5, and adsorption decreases at pH levels lower and higher than 5.

Keywords- Aluminum; Activated Carbon; Adsorption; Isotherm; Physisorption

I. INTRODUCTION

Activated carbon as an adsorbent has numerous applications. It is widely used for adsorption of gases and liquids: carbon dioxide [1, 2], oxygen [3], hydrogen sulfide [4, 5], ammonia [6], hydrocarbons and its chlorinated derivatives [7-9], methyl-tert-butyl ether (MTBE) [10], phenol and its derivatives [11,12] and pesticides [13]. Activated carbon is also used in the adsorptive removal of harmful metal ions, anions and other poly anions from water solutions: nickel [14], chromium [15], lead and cadmium [16], uranium [17], arsenic [18, 19], copper [20], fluoride [21], bromate [22] and sulfate [23]. The present investigation studies the isothermal adsorption of aluminum ions from aqueous solutions with the use of activated carbon as an adsorbent. The presence of aluminum ions in a body seems to have no positive impacts on living cells. In high quantities, aluminum affects the nerve systems and blood circulation [24]. Aluminum is absorbed more from food stuffs than water [25]. A few studies have revealed that consumption of acidic food and liquids containing aluminum could result a considerable increment of aluminum absorption [26]. Aluminum sulfate (Alum) and poly aluminum chloride (PAC) have long been used as primary mineral coagulants are used to remove color and turbidity in the water treatment industry [27-30]. Typically, a portion of these coagulants dissolve and remain in the final treated water. Even trivial amounts of aluminum in potable water cause numerous health problems that include Alzheimer's disease and dialysis encephalopathy. The Environmental Protection Agency (EPA) has set the maximum acceptable limit for aluminum in drinking water as 0.2 mg/L (milligram per liter). Ideally, the concentration of aluminum in drinking water should be less than 0.05 mg/L and no more than 0.2 mg/L. Having access to safe drinking water is considered among the essential needs of any community. Growing human population, developing cities and increasing industrialization have polluted the environment, and sources of drinking water in particular [31-32]. Preserving the quality of water in terms of aluminum levels and controlling potential contaminations by resources requires planning and research; aluminum extent was, therefore, measured on a very small scale while attempts were simultaneously made to reduce or remove it from industrial effluents [33].

In this study, activated carbon was used to adsorb aluminum ions from aqueous solutions. Parameters affecting the adsorption process are temperature, concentration of aluminum ion, contact time, pH of the solution and level of adsorbent. Thermodynamic parameters ΔG , ΔH and ΔS are obtained. Langmuir isotherm for adsorption of adsorbate from the solution and Freundlich isotherm were studied.

II. EXPERIMENTAL

A. Materials and Reagents

Hydrochloric acid (Merck), sulfuric acid (Merck), sodium chloride (Merck), ethylenediaminetetraacetic acid, widely abbreviated as EDTA (Merck), buffer (sodium acetate, Merck), Eriochrome Cyanine R (Merck); tetrazole aluminum (Merck); aluminum (III) chloride salt in water, equivalent to 1000 micrograms aluminum was used to produce the standard aluminum

ion solution). All solutions were made of deionized water with less than one micro Siemens electrical conductivity. Activated carbon in mesh size of 20 was used in all experiments.

B. Instrumental Setup and Method

A standard procedure was followed to prepare the aluminum ion solutions in all experiments. 1 g of activated carbon was added to 50 ml of aluminum ion solution with a specific concentration. The container was mixed for one minute using a stirrer at a speed of 360 rpm. Then the content of the container was filtered, and the solid residue was removed. The remaining aluminum in filtrate was measured through aluminum measurement standard number 3500-A 1B (Erio chrome Cyanine R Method) using a spectrophotometer at a wavelength of 535nm. Jar test apparatus equipped with a stirrer model LOVIBIND was used for sample preparation; uv-vis spectrophotometer (Thermo Fisher scientific / GIOS UV-VIS) was used to determine the amount of aluminum ion left in the solution after the adsorption process.

III. RESULTS AND DISCUSSION

There are many studies that deal with the removal of harmful materials from water [34-39]. However, few studies have been reported about the removal of aluminum from water [40]. An isothermal adsorption describes the equilibrium of the adsorption of an adsorbate from the surface of an adsorbent at constant temperature. It represents the amount of adsorbate bound on the surface of adsorbent as a function of the adsorbate present in the solution. The adsorption process is either endothermic or exothermic. Endothermic adsorption occurs when the system absorbs energy from its surroundings in the form of heat. In contrast, during exothermic adsorption the system releases energy in the form of heat. This study investigated the isothermal adsorption of aluminum ion on activated carbon adsorbent. Effective parameters involved in the adsorption process are concentration of aluminum ion, level of adsorbent, contact time, pH, and temperature.

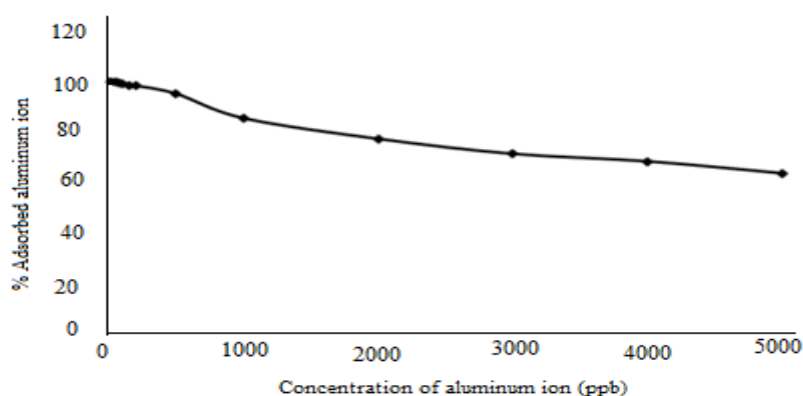


Fig. 1 The effect of aluminum ion concentration on adsorption process

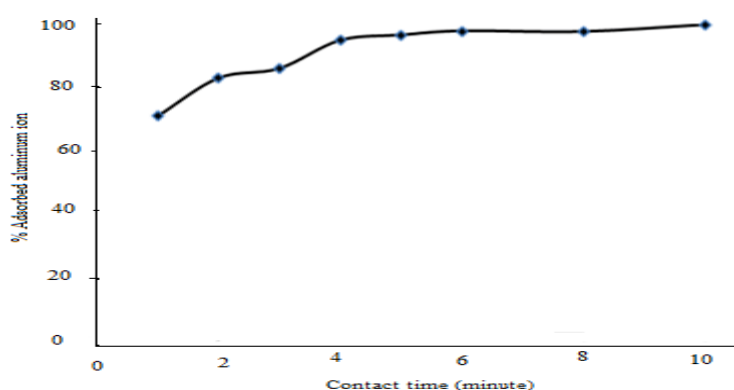


Fig. 2 The effect of time of contact between the adsorbate and adsorbent in adsorption process

At a very low concentration (1-10 ppb) all aluminum ions were absorbed by the adsorbent. When the concentration of aluminum ion was raised to 20, 50, 80 and 100 ppb; 99.5%, 99.3%, 98.8% and 98.5% of aluminum ion were adsorbed and removed from the solutions. At a very high concentration (5000 ppb) 62.7% of aluminum ion was adsorbed from the solution. Fig.1 demonstrates the effect of adsorbate concentration on the adsorption process. Next, the effect of contact time on the adsorption process was studied. The contact time between one gram of activated carbon and 50 milli liter of solution having an

aluminum ion concentration of 3 milligrams per liter was varied between one to ten minutes. Fig. 2 demonstrates that a contact time of five minutes a mixing velocity of 360 rpm suffices for the completion of the operation of aluminum adsorption. In order to investigate the pH effect on the adsorption of aluminum ion process; the experiments were carried out at different pH levels varying from 2 to 10.

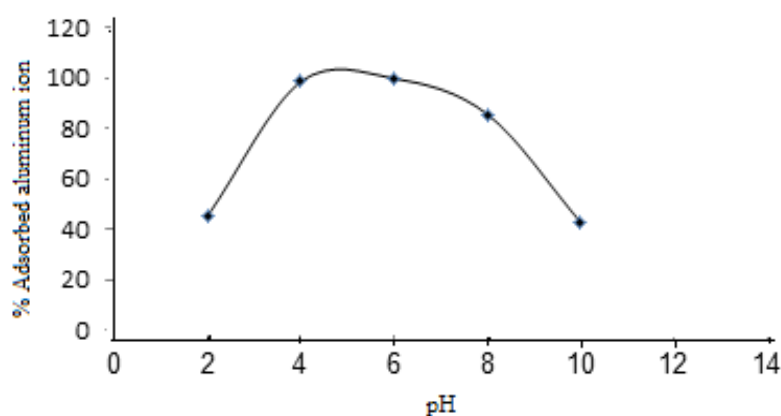


Fig. 3 The effect of pH of solutions on adsorption process

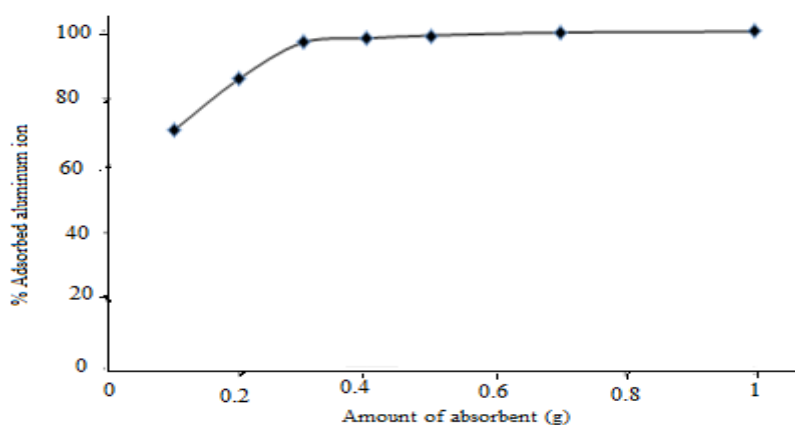
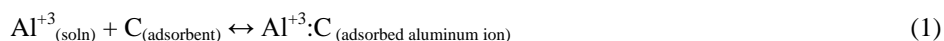


Fig. 4 The effect of adsorbent levels on adsorption process

The results (Fig. 3) revealed that adsorption of aluminum ions would be more efficiently carried out at pH 5. At a higher pH the adsorption decreases because aluminum ion (Al^{+3}) may be converted to aluminate $[Al(OH)_4]^{-}$ -ion. At a pH lower than 5 the adsorption of aluminum ion decreases again. This could be due to a competition that occurs between adsorption of aluminum ions and hydrogen ions with positive charges. In addition, in the decrease in adsorption process could also be due to the change in morphology of adsorbent which may occur at a lower pH. The effect of changing adsorbent levels was studied for adsorption of on centration of aluminum ion in aqueous solutions. Fig. 4 demonstrates that up to a certain level adsorption increases with increasing adsorbent levels, but after that adsorption remains constant. Furthermore, investigations were carried out on the heat o a specific cf adsorption of aluminum ions on activated carbon. The effect of temperature on the adsorption process was studied for a certain concentration of aluminum ions on one gram of activated carbon in the range of 298°K and 353°K. It was found that the amount of adsorption increases with elevated temperature. Therefore the adsorption of aluminum ions on activated carbon is an endothermic process. The adsorption process is depicted in Equation (1).



When C_0 is the initial concentration of aluminum ion in aqueous solution; C_e the concentration of remaining aluminum ion after adsorption process (equilibrium concentration); the distribution constant K_d between adsorbed aluminum ion and the remaining aluminum ion can be obtained using Equation (2).

$$K_d = \frac{C_0 - C_e}{C_e} \quad (2)$$

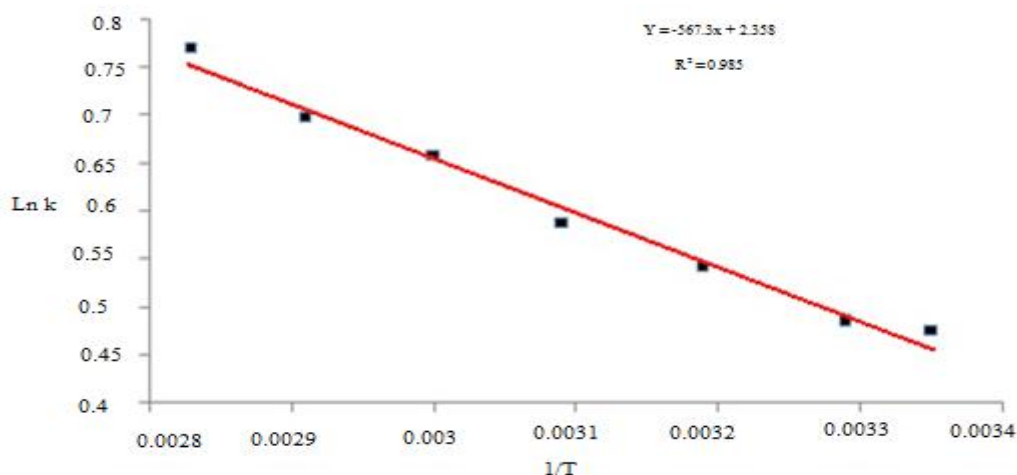


Fig. 5 The plot of Ln K versus 1/T

The distribution constant was measured for all temperatures (298°K-353°K). Gibbs free energy yields the change of free energy of adsorption process ΔG_{ads} as seen in Equation (3).

$$\Delta G_{ads} = -RT \ln K_d \quad (3)$$

$$\Delta G_{ads} = \Delta H_{ads} + T \Delta S_{ads} - RT \ln K_d = \Delta H_{ads} - T \Delta S_{ads} \quad (4)$$

$$\ln K_d = -\frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} \quad (5)$$

The plot of $\ln K_d$ versus $1/T$ was obtained, the values of ΔH_{ads} and ΔS_{ads} were determined from the slope and intercept of the line, Fig. 5.

The values of ΔG_{ads} , ΔH_{ads} and ΔS_{ads} are -1127.3, 4716.5, 19.6 J/mol. $g_{(adsorbent)}$ respectively. Since ΔG_{ads} is a negative value and ΔS_{ads} is a positive value the adsorption is a spontaneous process. The positive value of ΔH_{ads} states that the adsorption is an endothermic process. The Langmuir isotherm for adsorption from liquid solution is described in Equation (6):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_{ads}} \quad (6)$$

Where C_e is the amount of adsorbate in the solution (after adsorption process or equilibrium concentration) $\frac{mg}{L}$; q_e is the amount of adsorbed adsorbate on solid adsorbent $\frac{mg}{L}$; q_m is the amount of adsorbate necessary for formation of a monolayer $\frac{mg}{L}$; and k_{ads} is an adsorption constant.

$$q_e = (C_o - C_e) \times \frac{v}{m} \quad (7)$$

Where v is volume of the solution L; and m is mass of adsorbent mg. Langmuir isotherm was obtained by plotting $\frac{C_e}{q_e}$ versus C_e . This study demonstrated that the adsorption of aluminum ions on activated carbon does not follow Langmuir isotherm. The Freundlich isotherm [41] is one of the equations that relate the amount of material adsorbed to the concentration of material in the solution.

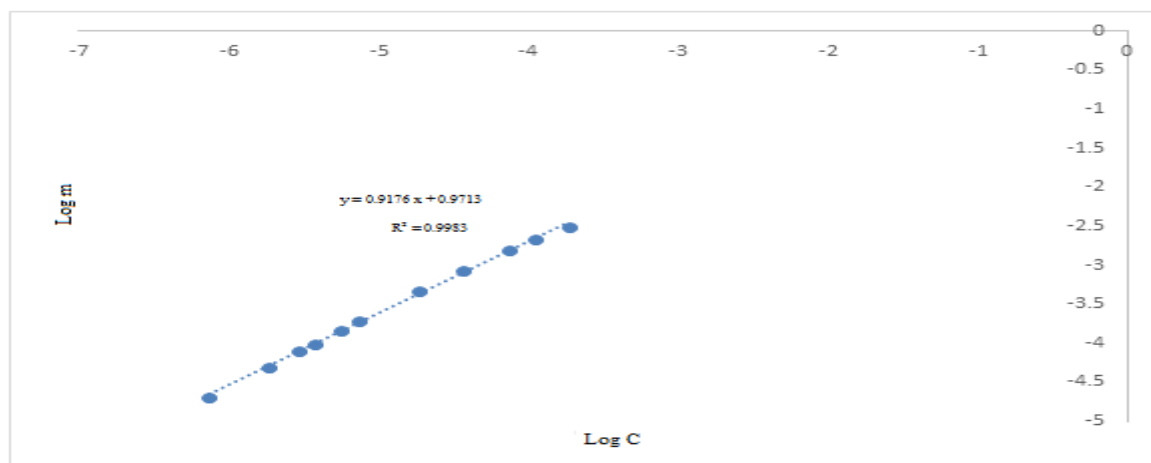


Fig. 6 The plot of Log m versus Log C

The Freundlich isotherm equation is shown in Equation (8):

$$m = K_{\text{ads}} C^{1/n} \quad (8)$$

Here m is the number of grams adsorbed per gram of adsorbent; C is the concentration; K_{ads} and n are constant. By measuring m as a function of C and plotting $\text{Log } m$ versus $\text{Log } C$, the values of n and K_{ads} can be determined from the slope and intercept of the line. The Freundlich isotherm was studied for adsorption of aluminum ion solution on one gram of activated carbon. The result is presented in Figure 6. The adsorption of aluminum ions on activated carbon follows Freundlich isotherm with $n = 1.09$ and $K_{\text{ads}} = 9.36$. Since n is a positive number, a physisorption of aluminum ions occurred on activated carbon. Rajan has reported a similar study about in vitro adsorption of aluminum by an edible biopolymer (Y-glutamic acid) [42]. The following similarities were observed when our results of adsorption of aluminum on activated carbon were compared with those reported by Ranjan. The adsorption process is very fast. Low adsorption occurs at low pH. Maximum adsorption occurs at moderate pH.

IV. CONCLUSION

In this study the isothermal adsorption of aluminum ions in aqueous solutions was investigated using activated carbon as an adsorbent. The adsorption did not follow Langmuir isotherm in the solution, but it followed the Freundlich isotherm. The Freundlich isotherm revealed that the nature of adsorption is physisorption. Thermodynamically this adsorption is a spontaneous and endothermic process, adsorption increases when the temperature is elevated. All parameters involved in the adsorption process were examined. Since this adsorption is an endothermic process, temperature elevation causes an increase in adsorption. A contact time of five minutes suffices for the completion of the adsorption process. The pH level of the solution affects the adsorption of aluminum ions on adsorbent. The maximum adsorption occurred at pH 5. Adsorption decreases when pH levels of the solution increased or decreased. We conclude that activated carbon is a suitable adsorbent for the removal of aluminum ions from aqueous solutions.

ACKNOWLEDGEMENT

We would like to acknowledge Mrs. Razieh Asrari of Ramin Power Plant, for technical support.

REFERENCES

- [1] N.P. Wickramaratne, J. Jaro, "Activated Carbon Spheres for CO₂ Adsorption", *ACS Appl. Mater. Interfaces*, 5 (5), pp.1849–1855, 2013.
- [2] B.B.Saha, S.Jribi, S. Koyama, I.I. El-Sharkawy, "Carbon Dioxide Adsorption Isotherms on Activated Carbons", *J. Chem. Eng. Data*, 56 (5), pp.1974–1981, 2011.
- [3] Y.Zhou, L. Wei, J. Yang, Y.Sun, L. Zhou, "Adsorption of Oxygen on Super activated Carbon", *J. Chem. Eng. Data*, 50 (3), pp. 1068–1072, 2005.
- [4] R.Yan, T.Chin, Y. Ling Ng, H. Duan, D. Tee Liang, J.H.Tay, "Influence of Surface Properties on the Mechanism of H₂S Removal by Alkaline Activated Carbons", *Environ. Sci. Technol.*, 38 (1), pp 316–323, 2004.
- [5] F.Adib, A.Bagreev, T. J. Badosz, "Analysis of the Relationship between H₂S Removal Capacity and Surface Properties of Unimpregnated Activated Carbons", *Environ. Sci. Technol.* 34 (4), 686–692, 2000.
- [6] M.Gonçalves, L.Sánchez-García, E.de Oliveira Jardim, J. Silvestre-Albero, F. Rodríguez-Reinoso, "Ammonia Removal Using Activated Carbons, Effect of the Surface Chemistry in Dry and Moist Conditions", *Environ. Sci. Technol.*, 45 (24), 10605–10610, 2011.

- [7] M.Mofarahi, M. Sadrameli, J. Towfighi, "Characterization of Activated Carbon by Propane and Propylene Adsorption", *J. Chem. Eng. Data*, 48 (5), pp. 1256–1261, 2003.
- [8] C.Borkar, D. Tomar, S. Gumma, "Adsorption of Dichloromethane on Activated Carbon" *J. Chem. Eng. Data*, 55 (4), pp. 1640–1644, 2010.
- [9] J.Zhang, W.Zhu, M.Makkee, B. Van der Linden, F.Kapteijn, J.A. Moulijn "Adsorption of 1,2-Dichloropropane on Activated Carbon", *J. Chem. Eng. Data*, 46 (3), pp. 662–664, 2001.
- [10] F.Gironi, C.Capparucci, L.Marrelli, "Adsorption of MTBE Vapors onto Activated Carbon" *J. Chem. Eng. Data*, 48 (4), pp. 783–788, 2003.
- [11] L.Khenniche, F.Benissad-Aissani, "Adsorptive Removal of Phenol by Coffee Residue Activated Carbon and Commercial Activated Carbon: Equilibrium, Kinetics, and Thermodynamics" *J. Chem. Eng. Data*, 55 (11), pp. 4677–4686, 2010.
- [12] C.Ruiz, E. Mena, P. Cañizares, J. A. Villaseñor, M.A. Rodrigo, "Removal of 2,4,6-Trichlorophenol from Spiked Clay Soils by Electrokinetic Soil Flushing Assisted with Granular Activated Carbon Permeable Reactive Barrier" *Ind. Eng. Chem. Res.* 53 (2), pp. 840–846, 2014.
- [13] H.G. Schwartz, "Adsorption of selected pesticides on activated carbon and mineral surfaces" *Environ. Sci. Technol.* 1 (4), pp. 332–337, 1967.
- [14] C.Aydiner, M.Bayramoglu, B. Bulent Keskinler, O.Ince "Nickel Removal from Waters Using a Surfactant-Enhanced Hybrid Powdered Activated Carbon/Microfiltration Process II, the Influence of Process Variables", *Ind. Eng. Chem. Res.* 48 (2), pp. 903–913, 2009.
- [15] J. Fang, Z. Gu, D. Gang, C. Liu, E.S. Ilton, B. Deng, "Cr(VI) Removal from Aqueous Solution by Activated Carbon Coated with Quaternized Poly(4-vinylpyridine)", *Environ. Sci. Technol.* 41 (13), pp. 4748–4753, 2007.
- [16] F. Boudrahem, A.Soualah, F. Aissani-Benissad, "Pb(II) and Cd(II) Removal from Aqueous Solutions Using Activated Carbon Developed from Coffee Residue Activated with Phosphoric Acid and Zinc Chloride" *J. Chem. Eng. Data*, 56 (5), pp. 1946–1955, 2011.
- [17] S.J.Coleman, P.R.Coronado, R.S., Maxwell, J.G. Reynolds, "Granulated Activated Carbon Modified with Hydrophobic Silica Aerogel-Potential Composite Materials for the Removal of Uranium from Aqueous Solutions" *Environ. Sci. Technol.*, 37 (10), pp. 2286–2290, 2003.
- [18] B. Deng, M. Caviness, Z. Gu "Arsenic Removal by Activated Carbon-Based Materials" *Advances in Arsenic Research*, Chapter 20, 284–293, 2005.
- [19] T.Budinova, N.Petrov, M.Razvigorova, J.Parra, P. Galiatsatou "Removal of Arsenic(III) from Aqueous Solution by Activated Carbons Prepared from Solvent Extracted Olive Pulp and Olive Stones" *Ind. Eng. Chem. Res.*, 45 (6), pp. 1896–1904, 2006.
- [20] M.D.Gutiérrez-Valero, M.Luz Godino-Salido, P.Arranz-Mascarós, R.López-Garzón, R.Cuesta, J. García-Martín "Adsorption of Designed Pyrimidine Derivative Ligands on an Activated Carbon for the Removal of Cu(II) Ions from Aqueous Solution" *Langmuir*, 23 (11), pp. 5995–6003, 2007.
- [21] A. K.Gupta, D. Deva, A. Sharma, N. Nishith-Verma, "Adsorptive Removal of Fluoride by Micro-nano-hierarchical Web of Activated Carbon Fibers" *Ind. Eng. Chem. Res.*, 48 (21), pp. 9697–9707, 2009.
- [22] Kishimoto N., Matsuda, N., Bromate Ion Removal by Electrochemical Reduction Using an Activated Carbon Felt Electrode, *Environ. Sci. Technol.*, 43 (6), 2054–2059, 2009.
- [23] F. Zhao, N.Rahunen, J.R. Varcoe, A.Chandra, C.A. Vignone-Rossa, E. Alfred, A.E. Thumser, R.C.T.Slade, "Activated carbon cloth as anode for sulfate removal in a microbial fuel cell" *Environ. Sci. Technol.*, 42 (13), pp. 4971–4976, 2008.
- [24] W.A. Banks, J. Kastin, "Aluminum-Induced neurotoxicity: Alterations in membrane function at the blood-brain barrier", *Neurosci. Biobehav. Rev.* 13, pp. 47–53, 1989.
- [25] R.A.Yokel, C.L. Hicks, R.L.Florence, "Aluminum bioavailability from basic sodium aluminum phosphate, an approved food additive emulsifying agent, incorporated in cheese", *Food Chem. Toxicol.*, 46, pp. 2261–2266, 2008.
- [26] P. Slanina, W. French, L.G. Ekström, L.Löf, S. Slorach, A. Cedergren "Dietary citric acid enhances absorption of aluminum in antacids", *Clin. Chem.* 32, 539–541, 1986.
- [27] C.W.K. Chow, J.A. van Leeuwen, R.Fabris, M. Drikas, "Optimized Coagulation Using Aluminum Sulfate for the Removal of Dissolved Organic Carbon, Desalination", 245, pp. 120–134, 2009.
- [28] K. Ching-Jey, L.A. Gary, W.B. Curtis, "Factors affecting coagulation with aluminum sulfate—I. Particle formation and growth," *Water Res.*, 22, pp. 853–862, 1988.
- [29] S. Ghafari, A.A. Hamidi, A.A. Zinatizadeh, "Application of response surface methodology (RSM) to optimize coagulation–flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum", *J. Hazard. Mater.* 163, pp. 650–656, 2009.
- [30] G. Baoyu, Y. Qinyan, "Effect of SO₄²⁻/Al³⁺ ratio and OH⁻/Al³⁺ value on the characterization of coagulant poly-aluminum-chloride-sulfate (PACS) and its coagulation performance in water treatment, *Chemosphere*", 61, pp. 579–584, 2005.
- [31] A. Joseph and P.E. Salvato, *Environmental Engineering and sanitation*, 4th Ed. John Wiley & Sons, Inc, New York, 1993.
- [32] S.V.S. Rana, "Environmental Pollution: Health and Toxicology", Narosa Publishing House, New Delhi, India, 2006.
- [33] I. Karadjova, B. Izgi, S. Gucer, "Fractionation and speciation of Cu, Zn and Fe in wine samples by atomic absorption spectrometry", *Spectrochim. Acta Part B.*, 57, pp. 581–590, 2002.
- [34] S. Jagtap, M. K. Yenkie, N. Labhsetwar, S. Rayalu, "Fluoride in Drinking Water and Defluoridation of Water", *Chem. Rev.*, 112 (4), 2454–2466, 2012.
- [35] Ge F., Shu H., Dai Y., (2007), "Removal of bromide by aluminum chloride coagulant in the presence of humic acid", *J. Hazard.*

Mat., 147 (1-2), 457-462

- [36] S. Vasudevan, G. Sozhan, S. Ravichandran, J. Jayaraj, J. Lakshmi, S. M, Sheela, "Studies on the Removal of Phosphate from Drinking Water by Electrocoagulation Process" Ind. Eng. Chem. Res., 47 (6), pp. 2018–2023, 2008.
- [37] E. A. Vik and B. Eikebrok, Coagulation Process for Removal of Humic Substances from Drinking Water, Aquatic Humic Substances, Chapter 24, pp. 385-408, 1988.
- [38] .H. Elcik, M. Cakmakci, E. Sahinkaya, B. Ozkaya, "Arsenic Removal from Drinking Water Using Low Pressure Membranes" Ind. Eng. Chem. Res., 52 (29), pp. 9958–9964, 2013.
- [39] S. B. Applebaum, M. E. Bretschger, "Removal of Iron and Manganese from Water", Ind. Eng. Chem. 26 (9), pp. 925–931, 1934.
- [40] M. Cherifi, S. Hazourli, M. Ziati, "Initial Water Content Temperature Effects on Electrokinetic Removal of Aluminum in Drinking Water Sludge", Physics Procedia, 2 (3), pp. 1021-1030, 2009.
- [41] G.W. Castellan, Physical Chemistry, Addison-Wiley Publishing Company, Reading, Massachusetts, USA, 1983.
- [42] Y. C. Rajan, B. S. Inbaraj, B. H. Chen, "In Vitro Adsorption of Aluminum by an Edible Biopolymer Poly(γ -glutamic acid)", J. Agric. Food Chem., 62 (20), pp. 4803–4811, 2014.