Removal of Sodium Ascorbate from Water by Adsorption onto composite Beads (calcium-Alginate/Activated carbon)

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Abstract

A biomaterial was prepared by encapsulating an activated carbon powder with sodium alginate, thus forming composite beads. These composite gel beads have been studied in terms of their adsorption capacity on the food additive Sodium Ascorbate in aqueous solution. For this, several parameters were evaluated using UV-visible spectroscopy. The maximum retention of SA is for an average time of 3 hours with a very small quantity of adsorbent m= 0.25g, and the sorption mechanism is described by pseudo-first-order. The adsorption isotherm is compatible with Langmuir's theoretical adsorption model. The thermodynamic parameters showed that the adsorption process is spontaneous, disordered and endothermic ($\Delta G < 0$, $\Delta S > 0$, $\Delta H>0$). The process thus obtained is of a physical nature (physisorption). Finally, the pH of the acidic medium favors the increase in the adsorption capacity, this effect is due to the formation of hydrogen bonds. On the other hand, the increase in pH inversely influences the adsorption capacity by the repellent effect of the functional groups with the same negative charge present on the adsorbent and the adsorbate.

Keywords: Composite beads, Activated carbon, Alginate, Adsorption, Biomaterial, Sodium ascorbate.

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1. Introduction

Water constitutes an essential element for all existence. In fact, water is fundamental for the economy of humanity. Unfortunately, this source is affected by all types of pollution including natural, industrial and chemical pollution [1]. This sounding issue brings suffering to millions of inhabitants around the world who experience water shortages and struggle daily to find their needs of drinking water.

Researchers have applied several solutions to remedy these harmful effects. Among these solutions, the use of biomaterials has become the green key to reducing pollution given their low cost, availability, and compatibility with the environment [2]. These biomaterials have effectively shown the possibility of eliminating organic and / or inorganic pollutants.

The application of the adsorption phenomenon has been widely used in several works using adsorbent materials. In various works, researchers opted to use activated carbon, alginate, clay, etc. [3, 4]. As for activated carbon, it is one of the most common biomaterials used to purify water and liquids. It is obtained from various plant sources such as: wood, coconut shells, almond shells, hazelnuts and walnuts, apple pulp, apricot kernels, peach kernels as well as the kernels of olives [5, 6]. Further, it is one of the most widely used materials in environmental work as an instrument for the removal of dye, heavy metals, waste, and pharmaceuticals [7, 8].

In addition, alginate is also a biomaterial used in adsorption generally extracted from seaweed such as Laminaria, Macrocystis, Fucus, Phaeophyceae, Ascophyllum…etc. Alginate is very interesting because of its ability to form porous gels in the presence of divalent cations such as the calcium ion Ca^{2+} [9]. Researchers have taken this important characteristic into account in various studies dealing with the elimination of pollutants. In their work, Veglio's team was able to use calcium alginate beads to eliminate copper (II) ions [10]. In another experiment, Asthana et al [11] used a similar system to adsorb nickel (II) cations. Finally, the adsorption of some organic molecules has also been studied: nitrophenol [12], tannery waste [13] or methylene violet [14].

The combination of these two materials, namely activated carbon and alginate, makes it possible to combine the encapsulating properties and the mechanical properties of the polymer matrix. This dual function is often chosen so as to provide binding sites for the pollutants. Simple and efficient composite balls in adsorption are thus obtained, thus having a high capacity to fix or adsorb organic or inorganic pollutants, and also heavy metal cations such as nickel Ni, lead Pb, and cobalt Co [15, 16].

Given the above, we were interested in preparing composite beads based on alginate and activated carbon, in order to adsorb an organic pollutant, in our case the food additive sodium ascorbate SA under number (E301). The latter is widely used in various food and industrial fields such as beverages and pharmaceutical products [16]. Combined with dopamine, it could lead to nervous system disorders. According to a study in 1998, the findings showed that the association of sodium ascorbate and dopamine could increase the risk of onset of Parkinson's disease. At high doses (over 1000 mg per day), this combination can cause gastrointestinal disorders (nausea, diarrhea, bloating). These inconveniences can vary from person to person [17]. In addition, its ingestion could be a risk factor for oxalo-calcium lithiasis (kidney stones) [18].

Apparatus

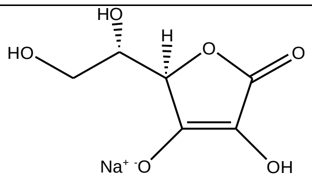
Spectrophotometric measurements were carried out on a OptizenPoP UV-visible spectrometer in the 200–400 nm range using 1cm matched quartz cells. The pH measurements were conducted with a Bante-instrument PHS-3BW with a combined glass electrode. The temperature measurements were carried out using a thermostated shaker bath (WSB Daihan).

2. Materials and Methods

2.1. Chemicals

The alginate sodium salt, Calcium chloride ($CaCl_2$) and the activated carbon were obtained from Sigma-Aldrich. As adsorbate, food additive sodium L(+) ascorbate was used in the research and was purchased from BiochemChemopharma. The activated carbon used was in the form of a powder -100 mesh particle size and high temperature resistance. The basic parameters characterizing the physicochemical properties of selected adsorbate is collected in Table 1.

Table 1. The physicochemical properties of the studied adsorbates [19].

Adsorbate	Chemical Formula	Molecular Weight [g/mol]	Water Solubility [mg/L at 25°C]	Ionization Constant pKa	Melting Point [°C]
sodium L(+) ascorbate		198,11	0,62	4,7	218

2.2. Biopolymer Composite beads production

Spherical calcium alginate-activated carbon composites gels were obtained by adding an amount of 3g of activated carbon into 2,0%(w/v) of sodium alginate aqueous solution that was previously prepared. The mixture was thoroughly agited for 30 mn and then were poured dropwise by syringe into a magnetically stirred of 0,3M calcium chloride aqueous solution. After 24 hours of aging in calcium solution, the beads were then collected by filtration, washed several times with distilled water and stored in at room temperature. they take a spherical form approximately 2,0mm in diameter measured by vernier caliper. This experience condition was reported in several works [20-22].

Adsorption procedure

Composites beads of calcium alginate-activated carbon were employed for their capacity of adsorption of sodium ascorbate (SA) using a batch system according to the literature [3]. To determine time and concentration effect required for the adsorption equilibrium of SA, the experiments were carried out at 50mL of solutions with different initial concentration of SA at 10, 35 and 60 mg/L respectively with 0,25g weight of beads at different time intervals with 5-300 nm at room temperature. The isotherm was studied in the same condition applied above at different interval initial concentrations at 2-60 mg/L for 180mn (3h) time. In addition, the pH effect on the adsorption kinetics of SA onto composite beads was conducted with different pH 3; 4; 5,03; 6; 7,02; 8; 9,04 and 10,03 solutions respectively below ambient temperature. These pH were adjusted by NaOH and HCl of solution (0,1M and 0,01M) for acidic and basic media respectively. Experiments for temperature effect were carried out at 298, 308 and 318 K respectively. All the adsorption experiments were conducted at condition similar of volume at 50mL, weight of adsorbent at 0,25g, and the concentration is 10mg/L for both experiments pH and temperature effect under agitation speed 250 rpm. At equilibrium, SA concentration in solutions was measured by a UV-visible spectrophotometer at λmax = 272 nm. The amount adsorbed of SA at equilibrium (qe) was calculated using the following equation **1** [23]:

$$qe = (C_0 - C_e)V/W \quad \textbf{(1)}$$

Where qe is the amount adsorbed (mg/g), C_0 (mg/L) is the initial food additive SA concentration, C_e (mg/L) is the food additive SA concentration at any time, V is the solution volume (L), and W is the weight of adsorbent (g).

Results And Discussion

Adsorption Dynamics

The curves kinetic study of three SA concentrations onto composite beads are represented in Figure 1.

It can be noted that the curves recognize an almost linear and rapid increase from the first minutes of contact, then stabilizes when approaching equilibrium. The equilibrium time is attained after approximately 3 hours for the three concentrations. This variation can be explained by the more massive presence of active sites at the surface of the material for short times. Subsequently, the adsorption at equilibrium becomes almost similar due tothe reduction of the active sites or their localization, or the competition between the molecules and the existence of the forces of repulsion between the molecules of SA adsorbed by the composite of the beads and those in solution [24]. It is also evident that in the concentration range studied (10; 35 and 60 mg/L) the increase in the initial concentration of SA contributed to the increase in the amount of adsorption of the additive (qe mg/g) by the composite beads of alginate/activated carbon. This phenomenon is explained by the presence of a strong solute concentration gradient between the solution and the surface of the adsorbent solid [25, 26].

The adsorption kinetic data were analyzed using the pseudo-first-order and pseudo-second-order models, as described in Eqs. **2** and **3** respectively [27-29].and as represented in Figure 2.

$$\boldsymbol{log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t} \qquad (2)$$

$$\frac{t}{q_t}=\frac{1}{k_2 q_{e2}^2}+\frac{1}{q_{e2}}t(3)$$

Here, k_1 (min^{-1}) and k_2 (g/mg·min) are the pseudo-first and pseudo-second-order adsorption rate constants, respectively. The fitted model parameters are given in Table 2.

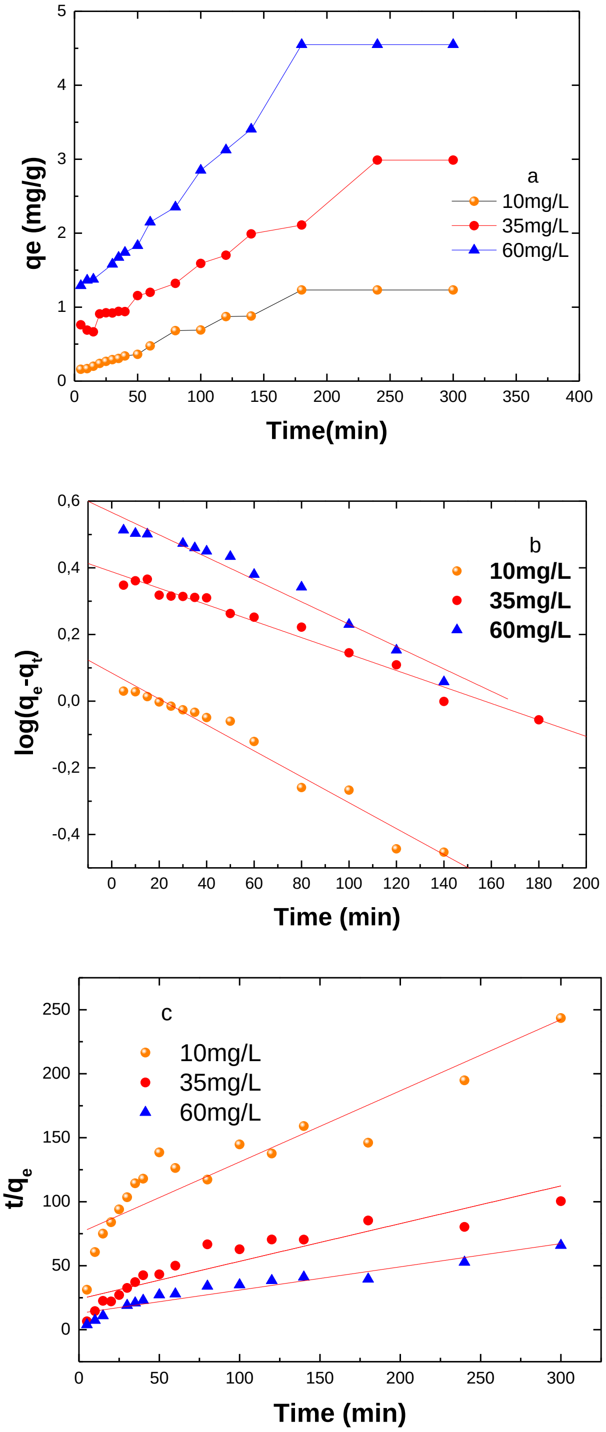


Figure 1 : (a) effect of time contact on SA adsorption by composite beads at different concentrations (10; 35; 60mg/L). The kinetic model and their fitting by using (b) pseudo-first-order and (c) pseudo-second-order.

Table 2 : Parameters of pseudo-first-order and pseudo-second-order kinetic models for adsorption of SA onto composite beads.

		Pseudo-premier d'ordre			Pseudo-second d'ordre		
C_0	qe(exp)	qe (calc)	k_1	R^2	qe (calc)	k_2	R^2
10	1,23	1,214	0.00896	**0,983**	1,87	0.00367	**0,916**
35	2,98	2,443	0.00576	**0,988**	3,44	0.00347	**0,920**
60	4,55	3,681	0,00715	**0,983**	5,49	0.0026	**0,952**

According to the results, it was found that the elimination of sodium ascorbate is better described by the pseudo-first-order model explained by the values of the correlation coefficients found approximately (R^2 = 0,98) with an optimum time of 3 hours. On the other hand, the pseudo-second-order model does not describe the adsorption of SA proved by the values of the reduced correlation coefficients between (0,91 and 0,95).

Adsorption isotherm

Adsorption isotherms are essential for describing the mechanism of solutes interact with adsorbents. Figure 2 shows the amounts adsorption of different SA concentrations adsorbed onto beads composite alginate/activated carbon. In this study, two isotherm models: Langmuir and Freundlich were used to correlate our experimental equilibrium data. These two theoretical models are given by equations 4 and 5 respectively [30, 31].

$$\frac{1}{q_e} = \frac{1}{q_{max}.k_L.C_e} + \frac{1}{q_{max}} \qquad (4)$$

$$\log q_e = logK_F + {}^{1}/_{n_F}\, logC_e \qquad (5)$$

$$R_L = \frac{1}{1+K_L.C_0} \qquad (6)$$

Noted that qmax (mg/g) is the maximum adsorption capacity, k_L (L/mg) is the Langmuir constants. In equation 5, n_F and K_F (mg/g) is the Freundlich constants about the adsorption intensity and the Freundlich constants respectively. R_L is a dimensionless separation factor in the Langmuir isotherm model used to assess the adsorption behavior, and is showed from equation 6.

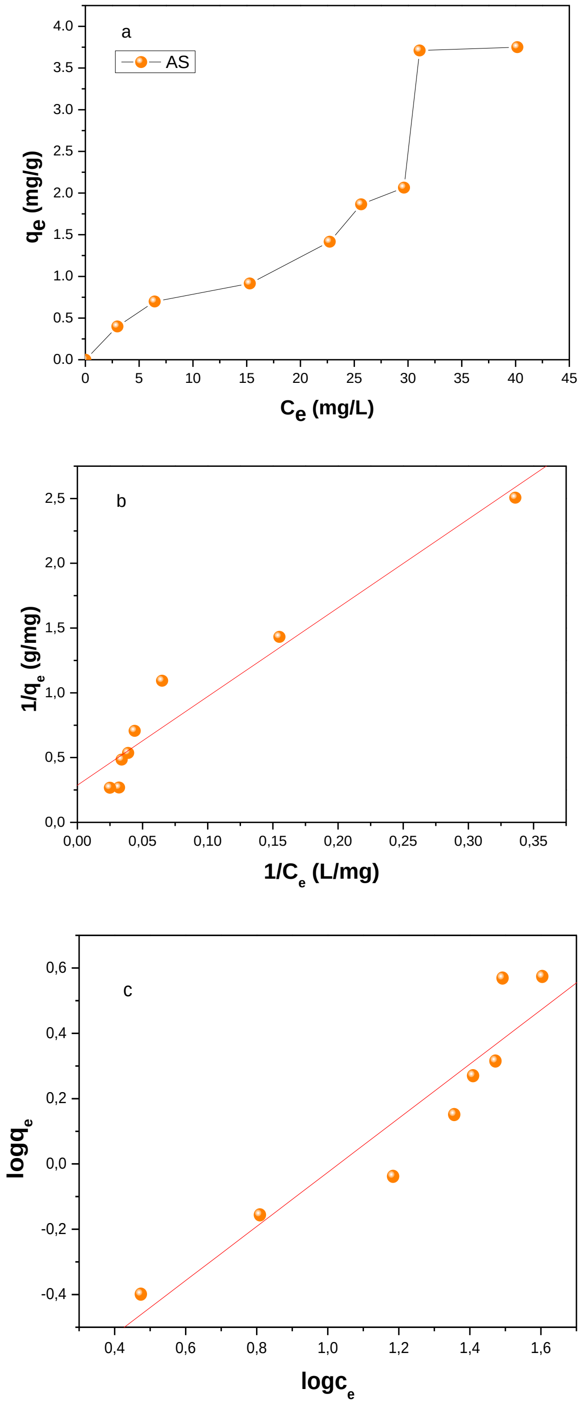


Figure 2 :(a) Adsorption isotherm of SA by composite beads, and their linear modeling and fitting of (b) Langmuir and (c) Freundlich.

The graph indicates that the amount adsorbed increases as a function of the initial concentration of SA, which is related to the existence of vacant sites on the surface of the adsorbent. The state of equilibrium indicated that the adsorbent is saturated by adsorbate, with amount of adsorption attained the maximum value of 3,75 mg/g. This high value of adsorption is probably explained by the low molecular size of the additive used. The isotherm presents a concavity facing upwards, due to the packing of the molecules from each other on the surface of the adsorbent.

The results of the parameters of both models: Langmuir and Freundlich are illustrated in Table 3. The study of the adsorption isotherms showed that the Langmuir model is suitably adapted for the experimental isotherms according to the high correlation coefficient R^2= 0,9683. The R_L values obtained by Table 4 are between 0 and 1, corresponding to the spontaneous and favorable adsorption process [32].

Table 3: Parameters of the sodium ascorbate adsorption isotherms according to the Langmuir and Freundlich models.

Langmuir isotherm			Freundlich isotherm		
q_{emax}(mg/g)	K_L (L/mg)	R^2	n	K_F(mg/g)	R^2
3,484	4,19x 10^{-2}	**0,9683**	1,208	0,139	**0,9407**

Table 4: R_L values for adsorption of SA on composite beads based on the Langmuir model

C_0	5	10	20	30	35	40	50	60
R_L	0,83	0,70	0,54	0,44	0,40	0,37	0,32	0,28

The influence of pH on SA adsorption

pH is an essential parameter to consider in adsorption processes. This parameter acts both on the solubility and on the ionization state of the adsorbent. The effect of the pH of the solution on the adsorption capacity of sodium ascorbate at 10mg/L initial concentration was studied on the composite beads at different pH values is given in Figure 3.

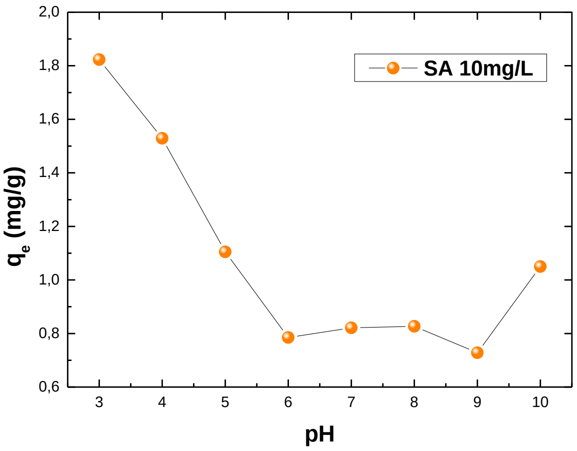


Figure 3: Effect of pH on SA adsorption on composite beads.

According to the spectrum, a very interesting phenomenon on the adsorption capacity of sodium ascorbate at different pH was noticed. Adsorption is high in acid media (pH= 3 and 4) approximately (1,82 and 1,52 mg/g), then decreases until reaching low sorption for neutral and basic pH (pH= 6 to 10) about 0,72 mg/g. This can be interpreted by the behavior of the carboxylate groups present on the surface of the alginate beads which are protonated in the acid medium, thus promoting the formation of hydrogen bonds with sodium ascorbate. The latter being rich in hydroxyl functional groups (-OH). On the other hand, in the neutral and basic medium, the carboxylate ions of the adsorbent and the enolate ions of the adsorbate (SA) have the same negative charges, which causes the repulsion and therefore the delay in the adsorption capacity [33, 34].

Effect of temperature on the adsorption process

Several studies were carried out on the influence of temperature on the adsorption of organic compounds [35, 36]. These studies have shown that the relationship between temperature and adsorption essentially depends on the adsorbent/adsorbate couple. As a result, it can be assumed that an increase in temperature affects physical adsorption much more than chemical adsorption. Generally, the absolute magnitude of the free energy change for physical adsorption is less than that for chemisorption. The first varies from -20 to 0 kJ/mol, and the second from -80 to -400 kJ/mol [37].

The thermodynamic parameters of adsorption, such as standard free energy ($\Delta G°$, KJ/mol), standard enthalpy ($\Delta H°$, KJ/mol) and standard entropy ($\Delta S°$, J/mol. K), present the influence of temperature on adsorption. In general, the determination of the thermodynamic parameter has been established from the Van't Hoff [38] equation 7 as follows:

$$\boldsymbol{\ln D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}} \qquad (7)$$

Where D is the distribution ratio (mm^3/g), R is universal gas constant ($8.314\ J.\ mol^{-1}\ .K^{-1}$) and T the absolute temperature (K).

The distribution ratio is defined for the concentrations of adsorbed molecules as follows in equation **8** [39]:

$$\boldsymbol{D = \frac{(C_0 - C_e)V}{C_e.m.1000}} (8)$$

The ΔG (KJ/mol) can be obtained from the famous equation **9** [40]:

$$\boldsymbol{\Delta G° = \Delta H - T\Delta S} \qquad (9)$$

The thermodynamic parameters of SA adsorption by the composite gel beads were taken into consideration by varying the temperature at 25, 35 and 45°C. This study is illustrated in the graph shown in Figure 4. The results are calculated by the linear line obtained by fitting and are given by Table 4.

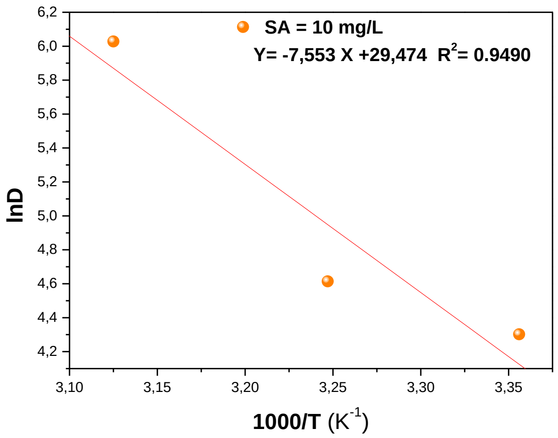


Figure 4: Evolution of LnD as a function of 1000/T for the adsorption of sodium ascorbate

Table 4: the values of the thermodynamic parameters of sodium ascorbate adsorption.

ΔG			ΔH	ΔS
T= 298 K	T= 308 K	T= 318 K		
-10,25	-12,69	-15,15	62,74	244,93

The analysis of the thermodynamic parameters shows that the adsorption process on the adsorbate is carried out by a spontaneous and favorable reaction (ΔG < 0). The variation of the free energy between -20 and 0 KJ/mol involves physical adsorption [37, 41]. This result implied that the adsorption between SA-composite beads gels is rather caused by electrostatic interactions and hydrogen bonds but not chemical bonds. The standard enthalpy (ΔH° >0) of the system is positive which indicates that the reaction between adsorbent and adsorbate is endothermic. Moreover, the positive value of the entropy (ΔS° > 0) describes that the system is disordered between the solid/solution interface.

Conclusion:

In this work, composite beads (calcium alginate-activated carbon) were prepared (2:3) and used for their adsorption capacity of organic pollutant, which is sodium ascorbate SA on different parameters. Adsorption of composite-SA beads is comfortably adequate for Langmuir's theory and follows pseudo-first-order kinetics. They have a high adsorption capacity in acid medium at 1,82 mg/g for 10mg/L of SA, for a minimum amount of 0,25g, due to the functional groups constituting their surface, which form hydrogen bonds and electrostatic interactions.

Furthermore, the solid-liquid interface (composite-SA) is described by physical and spontaneous sorption.

References

[1] Peng, J., Song, Y., Yuan, P., Xiao, S., Han, L. An novel identification method of the environmental risk sources for surface water pollution accidents in chemical industrial parks. Journal of Environmental sciences, 25(7), 1441-1449, 2013.

[2] Quesada, H.B.; de Araújo, T.P., Vareschini D.T., de Barros, M.A.S.D., Gomes, R.G.; Bergamasco, R. Chitosan, alginate and other macromolecules as activated carbon immobilizing agents: A review on composite adsorbents for the removal of water contaminants. Int. J. Biol. Macromol, 1640, 2535–2549, 2020.

[3] Ullah, N., Zarshad, A., Ullah, S., Khan, A.S., Adalat, B., et al. Synthesis of activated carbon-surfactant modified montmorillonite clay-alginate composite membrane for methylene blue adsorption. Chemosphere, 309, 136623, 2022.

[4] Ai, L., Ming Li, and Long Li. Adsorption of methylene blue from aqueous solution with activated carbon/cobalt ferrite/alginate composite beads: kinetics, isotherms, and thermodynamics. Journal of Chemical & Engineering Data 56.8: 3475-3483, 2011.

[5] Caturla, F., Molina-Sabio, M., and Rodriguez-Reinoso, F. Preparation of activated carbon by chemical activation with ZnCl2. Carbon, 29, 7, 999-1007, 1991.

[6] Reza, M.S., Yun, C.S., Radenahmad, N., Bakar, MSA, Saidur, R., Taweekun, J., Azad, AK. Preparation of activated carbon from biomass and its' applications in water and gas purification, a review. Arab Journal of Basic and Applied Sciences, 27, 1, 208-238, 2020.

[7] Bhatnagar, A., Hogland, W., Marques, M., et al. An overview of the modification methods of activated carbon for its water treatment applications. Chemical Engineering Journal, 219, 499-511, 2013.

[8] Kobya, M., Demirbas, E., Senturk, E., et al. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresource technology, 96, 13, 1518-1521, 2005.

[9] Papageorgiou, S.K.; Katsaros, F.K.; Kouvelos, E.P.; Nolan, J.W.; Le Deit, H.; Kanellopoulos, N.K. Heavy metal sorption by calcium alginate beads from Laminaria digitata. J. Hazard. Mater, 137, 1765–1772, 2006.

[10] Veglio, Francesco et Beolchini, F. Removal of metals by biosorption: a review. Hydrometallurgy, 44, 3, 301-316, 1997.

[11] Asthana, R. K., Chatterjee, S., and Singh, S. P. Investigations on nickel biosorption and its remobilization. Process Biochemistry, 30, 8, 729-734, 1995.

[12] Peretz, S. and Cinteza, O. Removal of some nitrophenol contaminants using alginate gel beads. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 319, 1-3, 165-172, 2008.

[13] Annadurai, G., Juang, R.S. and LEE, D. J. Factorial design analysis for adsorption of dye on activated carbon beads incorporated with calcium alginate. Advances in Environmental Research, 6, 2, 191-198, 2002.

[14] Asadi, S., Eris, S., Azizian, S. Alginate-based hydrogel beads as a biocompatible and efficient adsorbent for dye removal from aqueous solutions. ACS omega, 3, 11, 15140-15148, 2018.

[15] kuyucak, N. and Volesky, B. Biosorbents for recovery of metals from industrial solutions. Biotechnology letters, 10, 137-142, 1988.

[16] Mees, D. R., Pysto, W., and Tarcha, P. J. Formation of selenium colloids using sodium ascorbate as the reducing agent. Journal of colloid and interface science, 170, 1, 254-260, 1995.

[17] Sakagami, H., Satoh, K., Ida, Y., Hosaka, M., Arakawa, H., Maeda, M. Interaction between sodium ascorbate and dopamine. Free Radical Biology and Medicine, 25(9), 1013-1020, 1998.

[18] Massey, L. K., Liebman, M., Kynast-Gales, S. A. Ascorbate Increases Human Oxaluria and Kidney Stone Risk. The Journal of Nutrition, 135(7), 1673–1677, 2005.

[19] Available online: pubchem.ncbi.nlm.nih.gov (accessed on 12 Juin 2023)

[20] Bousher, A., Shen, X., Edyvean, R. G. J. Removal of coloured organic matter by adsorption onto low-cost waste materials. Water Res. 31, 2084, 1997.

[21] Yang, S. A., and Pyle, D. L., J. Chem. Technol. Biotechnol. 74, 216, 1999.

[22] Sankar, M., Sekaran, G., Sadalla, S., and Ramasami, T., J. Chem. Technol. Biotechnol. 74, 337, 1999.

[23] Torres, E.; Mata, Y.N.; Blázquez, M.L.; Muñoz, J.A.; González, F.; Ballester, A. Gold and silver uptake and nanoprecipitation on calcium alginate beads. Langmuir, 21, 7951–7958, 2005.

[24] Smidsrød, O., Molecular basis for some physical properties of alginates in the gel state. Faraday discussions of the Chemical Society, 57, 263-274, 1974.

[25] Lian, L., Guo, L., Guo, C., Adsorption of Congo red from aqueous solutions onto Ca-bentonite. Journal of Hazardous Materials, 161, 126–131, 2009.

[26] Hameed, B.H., Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. Journal of Hazardous Materials, 161, 753-759, 2009.

[27] Ho, Y.S., Ofomaja, A.E., Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber. J Hazard Mater 129(1–3):137–142, 2006.

[28] Jin S., Sen A., Sandvik A.W., Ashkin-Teller criticality and pseudo-first-order behavior in a frustrated ising model on the square lattice. Phys Rev Lett 108(4). 2012.

[29] El-khaiary, M. I., Malash, G. F., and HO, Y. S., On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems. Desalination, 257, 1-3, 93-101, 2010.

[30] Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40(9), 1361–1403, 1918.

[31] Freundlich, H.: Uber die adsorption in loesungen. J. Phys. Chem. 57, 385–470, 1907.

[32] Jin S, Sen A, Sandvik AW Ashkin-Teller criticality and pseudo-first-order behavior in a frustrated ising model on the square lattice. Phys Rev Lett 108(4), 2012.

[33] Wasilewska, M., Deryło-Marczewska, A, Adsorption of non-steroidal anti-inflammatory drugs on alginate-carbon composites-equilibrium and kinetics. Materials, 15(17), 6049, 2022.

[34] Sun, X., Hu, D., Yang, L. Y., Wang, N., Wang, Y. G., Ouyang, X. K., Efficient adsorption of Levofloxacin from aqueous solution using calcium alginate/metal organic frameworks composite beads. Journal of Sol-Gel Science and Technology, 91, 353-363, 2019

[35] Machado, F. M., Bergmann, C. P., Fernandes, T. H., Lima, E. C., Royer, B., Calvete, T., Fagan, S. B, Adsorption of Reactive Red M-2BE dye from water solutions by multi-walled carbon nanotubes and activated carbon. Journal of hazardous materials, 192(3), 1122-1131, 2011.

[36] Ghosh, D. and Bhattacharyya, K.G. Adsorption of Methylene Blue on Kaolinite. Applied Clay Science, 20, 295-300, 2002.

[37] Jaycock, M.J. and Parfitt, G.D. Chemistry of Interfaces. Ellis Horwood Ltd., Chichester. 1981.

[38] Lima, E. C., Gomes, A. A., and Tran, H. N. Comparison of the nonlinear and linear forms of the Van't Hoff equation for calculation of adsorption thermodynamic parameters ($\Delta S°$ and $\Delta H°$). Journal of Molecular Liquids, 311, 113315, 2020.

[39] Khan, S.A., Rehman, R. U, Khan, M.A., Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite. Waste Management. 15, 271-282, 1995.

[40] Atkins, P. W, and De Paula, J., Physical Chemistry, W. H. Freeman and Company, New York, 9th edition. 2010.

[41] Yu, Y., Zhuang, Y. Y., Wang, Z. H., Adsorption of Water-Soluble Dye onto Functionalized Resin. Journal of Colloid and Interface Science, 242(2), 288-293, 2001.