

Al(III) removal from wastewater by natural clay and coconut shell

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Abstract

This paper describes the adsorption of Al³⁺ ions from aqueous solutions, by natural clay (from Sakarya's Yenigün district) and coconut shell modified by means of acid treatment. Batch experiments were carried out to determine the effect of various factors such as initial pH (4-9), temperature (20, 40, 70 °C), initial concentration (10 to 200 mg L⁻¹) and contact time (1-120 minute) on the adsorption process. The adsorption experiments were performed at a temperature of 20 ±2 °C, at 200 rpm agitation rate, with an adsorbent level of 1 g L⁻¹, produced 98.95% (at pH 6) and 92.83% (at pH 7) maximum Al³⁺ removal efficiency for clay and coconut shell based adsorbents respectively. Furthermore, the process was found to be exothermic for clay and endothermic for coconut. XRF and XRD analyses of the clay variety used in adsorption analyses revealed it to be saponite clay, within the larger group of smectite clay minerals. The application of Langmuir revealed maximum adsorption capacity of 149.25 mg g⁻¹ for natural clay adsorbent (NCA), and 120.482 mg g⁻¹ for coconut shell adsorbent (CSA). Moreover, adsorption kinetics were found to be consistent with the second order kinetics (R² > 0.95). The result shows that, natural clay and coconut shell adsorbents are effective adsorbents to remove Al³⁺ from aqueous solutions with good adsorption rate (>92.8%).

Keywords: Adsorption, aluminium, clay, coconut shell, kinetic.

1. Introduction

When released to the receiving environment, wastewater with a high level of metal content, produced in various anthropogenic activities, would cause significant toxicity in the water and biota, and may pose hazards for the environment and human health through gradual bioaccumulation. Advanced techniques such as chemical precipitation, adsorption, ion exchange, reverse osmosis, membrane separation are employed to remove various metal ions observable in high concentration levels in industrial wastewaters. These methods are, in turn, characterized by their relative advantages and disadvantages regarding supply, affordability, ease-of-implementation, waste production etc. Adsorption refers

to the specific method which involves collecting and capturing the gas, liquid or dissolved substances on the surface of an adsorbent. It is a widely used, efficient, effective and popular method for removing metals from water. For years scientists have been using all kinds of clay minerals, zeolites, chitosan, wood, plant, fruit, peel, shells (Bhatnagar *et al.*, 2010), seeds, resins, gel, silica, activated carbon etc. for metal adsorption, with significant levels of success (Internò *et al.*, 2015).

Researchers used various clays in the context of adsorption of metal ions, such as: palygorskite clay from Dwaalboom area of S.Africa for Pb²⁺, Ni²⁺, Cr³⁺, Cu²⁺ metal ions at pH 7 (Potgieter *et al.*, 2009); Ghassoul clay from Morocco for Cd²⁺ and Cu²⁺ at pH<6 (El Ass, 2018); montmorillonite from India's Karnataka region for Cu²⁺ at pH 2.5 (Oubagaranadin and Murthy, 2010); montmorillonite and kaolinite for Fe²⁺ (pH 3), Co²⁺ (pH 5.8), Ni²⁺ (pH 5.7) (Bhattacharyya and Gupta, 2008); Ca-bentonite from Almeria (Spain) and a Na-exchanged bentonite from Milos (Greece) for Cr³⁺ (pH 4), Ni²⁺ (pH 6), Zn²⁺ (pH 6), Cu²⁺ (pH 5) and Cd²⁺ (pH 6) (Alvarez-Ayuso and Garcia-Sanchez, 2003); kaolinite from China's Longyan region for Pb²⁺ (pH 6), Cu²⁺ (pH 6.5), Cd²⁺ (pH 7) and Ni²⁺ (pH 7) (Jiang *et al.*, 2010); Amasya Çeltik clay from Turkey for Pb²⁺ (pH 6), Cr³⁺ (pH 6) (Sarı *et al.*, 2007); Palygorskite clay for Pb²⁺ at pH 5 (Fan *et al.*, 2009), Illite from Tunisia for Pb²⁺ at pH 7 (Eloussaief and Benzina, 2010); smectite from Tunisia for Pb²⁺ at pH 4 (Chaari *et al.*, 2008); illite from Tunisia for Cd²⁺ and Cr³⁺ at pH 3.5 (Ghorbel-Abid *et al.*, 2010). These studies led to significant successes in the removal of metal ions from aqueous solutions. Researchers have also been investigating various processes to make use of waste, by putting them to use, for instance, in water treatment (Kumar, 2006; Sharma *et al.*, 2011; Farhan *et al.*, 2017; Ostovar *et al.*, 2017).

Aluminium (Al) is present in the natural environment as oxides, hydroxides and silicates, combined with other elements, and as complexes with organic matter. In aquatic environments, Al can be observed in aqua- and hydroxo-complexes, as well as in water-soluble complexes of humic and fulvic acids, which, in turn, are decomposition products of organic materials. Aluminium is used in a wide range of applications, thanks to its high

level of electrical and thermal conductivity, amphotericism, lightness, ease of processing and corrosion resistance characteristics (WHO, 1997; Barabasz *et al.*, 2002). Often touted as the metal of the 21st century Al is widely used as a structural material in the construction, automotive, aircraft industries, in the production of metal alloys, in the electricity generation, in kitchen utensils, food packaging, and decoration products. Al compounds are used in drugs and consumer products as antacids and antiperspirants additives. Furthermore, Al is used as a phosphate binder in kidney dialysis processes. The aqueous solution of Al(III) is acidic. Larger amounts of Al change the color of water, and give it a bluish hue. The excessive amount of Al in natural water is often caused by the use of aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$) (alum) as a coagulant in water treatment, mineral-rich soil, or industrial pollution. Aluminium salts are widely used in water treatment to reduce organic matters, colour, turbidity, suspended matter, alg and pathogen microorganism levels (Matilainen *et al.*, 2010). Hence, potable water often contains high aluminium levels of natural origin and/or from the water purification process (Yavuz *et al.*, 2004). The World Health Organisation (WHO) has proposed a guideline value of 0.2 mg L^{-1} . The present drinking water standard limits for aluminium are 0.2 mg L^{-1} (WHO, 2006; EPA, 1990; Singh *et al.*, 2007).

Al can find its way into various foodstuffs through the soil and irrigation water. Aluminum gets in the food chain mostly through its introduction in the soil after acid rains, and can be bio-magnified once it found its way into an organism. The connection between Al and Alzheimer's disease is widely known, based on the findings of accumulation of significant amounts of Al complexes in the brain tissue of Alzheimer's patients. Accumulation of Aluminum in brain cells is considered among the causes of neurodegenerative disorders such as Alzheimer's (Mirza *et al.*, 2017) and Parkinson's, and amyotrophic lateral sclerosis (ALS, Lou Gehrig's disease). Long-term use of antacids containing aluminum is also associated with the softening of bones through accumulation, as well as adynamia, and finally anemia, through its inhibiting effect on hemoglobin synthesis (Yokel, 2000; Bharathi *et al.*, 2008). Chemical precipitation, reverse osmosis, electrodialysis, cation exchange (Srinivasan *et al.*, 1999) and adsorption (Abdel-Ghani *et al.*, 2015) methods are efficient in Al^{3+} removal from water (Ihara *et al.*, 2008; Pascu *et al.*, 2016).

The objective of this study, in turn, is to use adsorbents prepared by treating natural materials such as natural clay and coconut shells with acids, for the removal of aluminum ions, which are found in excessive volumes in water, and which pose significant health hazards.

2. Material and methods

2.1. Preparation of clay and coconut shell adsorbents

The natural clay mineral collected from Sakarya's Yenigün district and the shells of coconuts purchased at supermarkets were crushed and washed multiple times

using pure water, and then dried in oven at a temperature of 105°C overnight. Then, 10-gram samples were taken from the clay and coconut shells, and treated separately in 10% H_2SO_4 , 37% HCl, and 65% HNO_3 . Thereafter, the samples were dried once again in the oven at a temperature of 105°C , for two hours. 6 individual adsorbent samples prepared through these activation procedures were then used in adsorption experiments.

2.2. Adsorption studies

The batch experiments for Al^{3+} adsorption were performed on an orbital shaker at 200 rpm using glass erlenmeyer flasks containing 500 mL of solution and 0.5 g of the adsorbent. Experiments were performed at room temperature ($20 \pm 2^\circ\text{C}$) and at optimal pH values, except those in which the effects of temperature and pH were investigated. Adsorption studies were performed by using 1 g adsorbent (clay and coconut shell) with various initial Al (III) concentrations ranging from 10 to 200 mg L^{-1} . The preliminary experiments revealed that about 30 min was required for the adsorption process to reach equilibrium. Therefore, a contact period of 120 min was finally selected for all equilibrium tests. The working solutions of 10-200 mg L^{-1} Al(III) were prepared by appropriate dilution of the Al stock solution (Merck nr. 119770) right before use. The concentration of the Aluminium ions was determined by a Spectro Arcos ICP (Inductively Coupled Plasma) spectrometer. The pH of the solution was adjusted to desired values with 0.1 N HNO_3 and 0.1 N NaOH.

The adsorbed Al (III) concentration levels were assessed based on the difference between the total initial Al(III) and final Al (III) concentrations. The adsorption capacities of clay and coconut shell adsorbents as milligram per gram of adsorbents (mg g^{-1} sorbent) were calculated by the following equation:

$$q_t = (C_o - C_t)V/W \quad (1)$$

C_o is the initial concentration of Al^{3+} ion (mg L^{-1}), C_t is the Al^{3+} ion concentration after adsorption time t (mg L^{-1}), V is the volume of metal ion solution (mL) and W is the weight of adsorbent (g). The data gathered through the initial concentration experiments were used in calculations in accordance with Langmuir Freundlich, Temkin and Dubinin-Radushkevich isotherms.

3. Results and discussion

3.1. Characterization of clay and coconut shell sorbents

The structure and chemical composition of the clay collected from Sakarya's Yenigün district were analyzed through X-ray diffractometer (XRD) and X-ray fluorescence spectrometer (XRF) instruments. The results of the analyses are provided in Table 1 and Figure 1. XRF chemical analysis of clay revealed it to be unrefined saponite.

Saponite is a member of Smectites clay group, and contains magnesium and/or iron as well as alkalis other than potassium, and certain alkaline earth elements. Saponite is a naturally occurring 2:1 trioctahedral layered

silicate wherein the anionic layer charge originates from the isomorphous substitution of Al(III) for Si(IV) in the tetrahedral sheet. The gallery cations can be readily replaced by a variety of functional cations for potential applications in catalysis and adsorption (Shao and Pinnavaia, 2010).

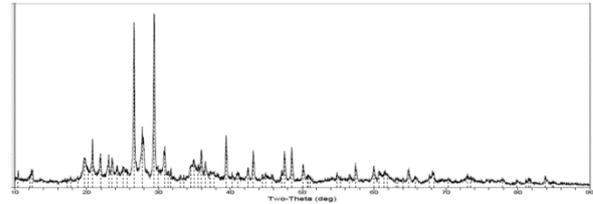


Figure 1. XRD patterns of Saponite clay mineral

Table 1. The chemical composition of the clay mineral

Chemical composition	K.K.	Humidity	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	MnO	SO ₃	SrO
%Amount	8.15	9.1	43.54	17.22	14.03	7.104	5.01	2.63	0.963	0.196	0.851	0.16	0.085	0.057

Humidity: 105 °C

K.K.: 1000 °C

There are various forms of clay in the nature, such as kaolinite, smectite, illite, chlorite, and talc. Given clay's abundance in nature, as well as its affordability and ease of supply, coupled with its high level of specific surface area and replacement capabilities, it is only natural to see many studies in the literature, discussing the use of clay minerals as adsorbents (Silva *et al.*, 2016; Araujo *et al.*, 2013). In order to ascertain the surface characteristics of clay and coconut shell adsorbents, SEM images were taken following activation using H₂SO₄ and adsorption process (See Figure 2a–d).

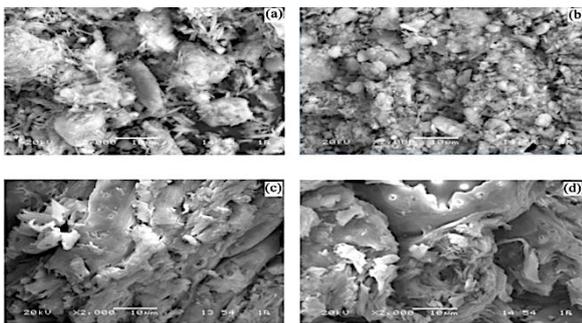


Figure 2. SEM micrographs of NCA (a), after Al³⁺ adsorption NCA (b), CSA (c), after Al adsorption. CSA (d)

3.2. The effect of initial pH, temperature and initial Al³⁺ concentration

In order to determine the most optimal pH value where the best adsorption results were achieved, the experiments were carried out at a temperature of 20°C, at 200 rpm agitation rate for 2 hours, at 4, 5, 6, 7 pH values. Samples taken at the 1st, 5th, 10th, 30th, 60th, 90th and 120th minute of the process were analyzed (See Figure 3 for results).

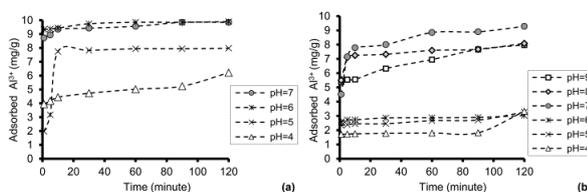


Figure 3. pH influence, Al³⁺ adsorption by NCA (a) and CSA (b)

Figure 3 shows that the pH levels, which ensure the highest level of adsorption are pH 7 for CSA, and pH 6 for NCA. As Aluminum is inclined to transition to a colloidal structure in the pH range 5.5 - 7, its perfect precipitation can be achieved at around pH 8. The pH values used in the experiments, below the range of transition to a complete colloidal structure and sedimentation of Aluminium, are hypothesized to accelerate and increase the efficiency of adsorption.

The temperature analyses were carried out at 20°C, 40°C and 70°C at optimal pH values at 200 rpm agitation rate for 2 hours. The results are provided in Figure 4.

The initial concentration analyses were carried out at 20°C, at 200 rpm agitation rate for 2 hours, at pH6 for clay and pH 7 for coconut shell. The samples taken at 1st, 5th, 10th, 30th, 60th, 90th and 120th minutes were analyzed in ICP (See Figure 5).

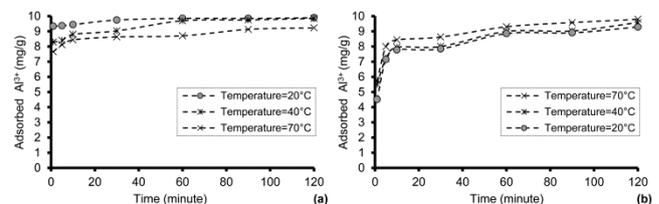


Figure 4. Temperature influence, Al³⁺ adsorption by NCA (a) and CSA (b)

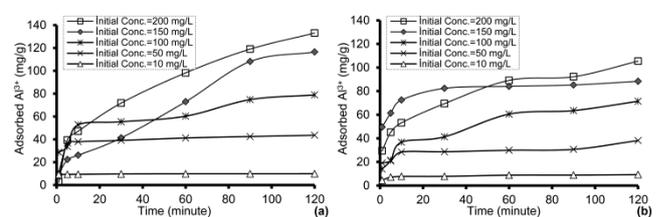


Figure 5. Initial concentration influence in Al³⁺ adsorption onto NCA (a) and CSA (b)

3.3. Adsorption equilibrium isotherms and kinetics

Four isotherm equations were applied for this study: The Langmuir (Equation (1)) (Langmuir, 1918), Freundlich (Equation (2)) (Freundlich, 1906), Temkin (Equation (3))

(Temkin *and* Pyzhev, 1940) and Dubinin-Radushkevich (Equation (4)) (O'Connor *et al.*, 2001) isotherms.

$$q_e = \frac{K_L \cdot C_e}{1 + a_L \cdot C_e} \text{ linearized form as } \frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (2)$$

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

$$q_e = B \ln A + B \ln C_e \text{ and } B = R \cdot T / b \quad (4)$$

$$q_e = q_m e^{(-\beta C_e^2)} \text{ where } \varepsilon = RT \cdot \ln[1 + (1/C_e)] \quad (5)$$

where: q_e : equilibrium capacity in mg g^{-1} ; C_e : the equilibrium concentration in mg L^{-1} ; K_L and a_L are Langmuir constants related to the maximum capacity

(L g^{-1}); K_F (mg g^{-1}) and n (g L^{-1}) are Freundlich constants; A and B are Temkin isotherm constants; q_m is the maximum capacity (mg g^{-1}), β is a D-R constant ($\text{mg}^2 \text{J}^{-2}$), ε : Polanyi potential and $\varepsilon = 1/\sqrt{2\beta}$.

All the parameters calculated from the studied isotherm models along with the correlation coefficients (R^2) are given in Table 2. Al adsorption effected through CSA and NCA adsorbents is found to be best compatible with the Freundlich (See. Figure 6) equation. It is also found to be compatible with Langmuir equation as well. As the surfaces of both adsorbents exhibit significant imperfections, and as adsorption with both adsorbents initially develop very quickly, only to slow down gradually, Freundlich isotherm is considered the best representation of adsorption with both. Temkin isotherm, on the other hand, is a match for adsorption with CSA, while adsorption with NCA does not offer a match. Dubinin-Radushkevich equation is unable to identify any isotherm equilibrium.

Table 2. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm parameters for Al^{3+} adsorption by NCA and CSA

	Langmuir isotherm				Freundlich isotherm			Temkin isotherm			Dubinin-Radush. iso.		
	a_L (L/mg)	K_L (L/g)	Q_0 (mg/g)	R^2	K_F (L/g)	n	R^2	B	A (L/g)	R^2	q_m (mmol/g)	β (mmol ² /j ²)	R^2
NCA	0.09293	13.8696	149.254	0.9389	23.7575	2.4426	0.9885	18.055	8.649	0.8325	85.704	-7.E-08	0.834
CSA	0.05552	6.689	120.482	0.9692	11.8686	1.8362	0.9925	19.214	8.649	0.9233	71.443	-5.E-07	0.854

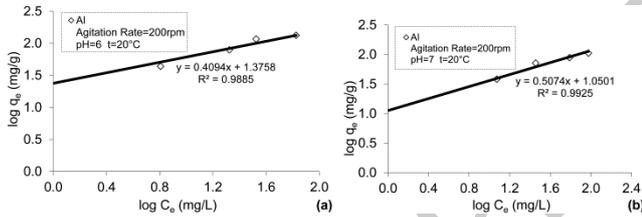


Figure 6. Freundlich isotherm for NCA (a) and CSA (b)

In kinetic studies; Intraparticle diffusion model (Weber and Morris, 1962), Lagergren pseudo-first-order (Lagergren, 1898), Pseudo-second-order (Ho and McKay, 1999) and Elovich (Elovich and Larinov, 1962) models were used to test the experimental data and the associated formulas.

In order to analyze the adsorption kinetics of Al adsorption, Intraparticle diffusion model (Weber and Morris, 1962), Lagergren pseudo-first-order (Lagergren, 1898), Pseudo-second-order (Ho and McKay, 1999) and Elovich (Elovich and Larinov, 1962) kinetic models were applied with the experimental data. The intraparticle diffusion model is expressed as follows:

$$q_t = k_{int} t^{1/2} \quad (6)$$

The pseudo-first order model is represented by the equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

The pseudo first-order model describes adsorption in solid-liquid systems based on the adsorption capacity of solids.

The pseudo-second-order equation based on equilibrium adsorption is described as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Finally, the Elovich's model is expressed as,

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (9)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the values of amount adsorbed per unit mass at equilibrium and at any time (t), respectively. Where k_{int} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intraparticle diffusion rate constant. Values of k_{int} were calculated from the slope of the linear plots of q_t versus $t^{1/2}$.

k_1 (min^{-1}) is the rate constant of the pseudo-first order equation, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the second-order equation. The parameter α is the initial sorption rate constant (mg/g-min) and β is related to the extent of surface coverage and activation energy for chemisorptions (g mg^{-1}).

Tables 3 and 4 summarizing the results obtained from the graphs reveal that adsorption of Al^{3+} metal ions with both adsorbents is a very good match for second order kinetics (See Figure 7). Their correlation factors calculated on the basis of the second order kinetics are 0.99.

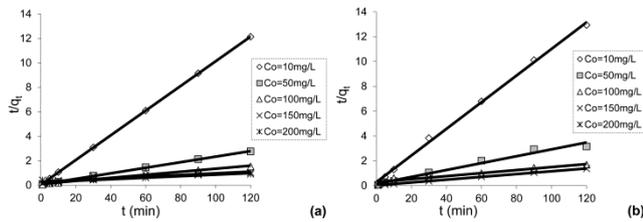


Figure 7. Pseudo Second Order Kinetic for NCA (a) and CSA (b)

Among other kinetics models, intraparticle diffusion model defines adsorption achieved with the adsorbent obtained from clay. As water which, through capillary effect diffuses into the weak Van der Waals bonds of clay, is able to expand the gaps between clay molecules by up to 7 times, the clays are compatible with the intraparticle diffusion model. Elovich equation, on the other hand, offers a partial definition of both adsorption cases.

Table 3. Kinetic parameters and correlation coefficient for the Al^{3+} adsorption on NCA

$Al^{3+} C_0$ (mg/L)	q_e (mg/g)	Intraparticle diffusion model		Pseudo first order kinetic		Pseudo second order kinetic		Elovich model		
		k_{int} (mg/g.dak ^{1/2})	R^2	k_1 (1/dak)	R^2	k_2 (g/mg.dak)	R^2	α (mg/g.dak)	β (g/dak)	R^2
10	9.9	0.063	0.916	0.0322	0.914	0.2968	1	2.825E+28	7.3099	0.907
50	43.59	2.1447	0.512	0.0281	0.769	0.0089	0.9992	1.631E+02	0.1754	0.759
100	78.91	4.7774	0.925	0.0238	0.884	0.0016	0.9806	1.089E+02	0.0967	0.911
150	116.49	11.1030	0.968	0.0257	0.892	0.0002	0.827	1.480E+01	0.0449	0.818
200	133.03	11.2990	0.952	0.0146	0.897	0.0002	0.8751	2.206E+01	0.0406	0.951

Table 4. Kinetic parameters and correlation coefficient for the Al^{3+} ion adsorption on CSA

$Al^{3+} C_0$ (mg/L)	q_e (mg/g)	Intraparticle diffusion model		Pseudo first order kinetic		Pseudo second order kinetic		Elovich model		
		k_{int} (mg/g.dak ^{1/2})	R^2	k_1 (1/dak)	R^2	k_2 (g/mg.dak)	R^2	α (mg/g.dak)	β (g/dak)	R^2
10	9.28	0.3676	0.745	0.0251	0.854	0.0421	0.9984	2.786E+02	1.1215	0.856
50	38.15	0.1528	0.833	0.009	0.664	0.0053	0.9746	7.663E+02	0.3001	0.944
100	71.41	6.4425	0.964	0.0246	0.973	0.0005	0.9502	1.468E+01	0.0754	0.945
150	88.35	3.4483	0.819	0.0267	0.845	0.0054	0.9993	3.939E+03	0.1221	0.640
200	105.36	6.9002	0.973	0.0171	0.941	0.0009	0.967	7.267E+01	0.0680	0.808

3.4. Thermodynamic properties

Thermodynamic parameters can be determined using the equilibrium constant K_c , which depends on temperature. The Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes for Al^{3+} ions adsorption have been determined using Eq. (10).

$$\Delta G^\circ = -RT \cdot \ln K_c \quad \ln K_c = \frac{(T \Delta S^\circ) - \Delta H^\circ}{R} \times \frac{1}{T} \quad K_c = \frac{C_a}{C_e} \quad (10)$$

where, K_c is the equilibrium constant, C_a (mg g⁻¹) and C_e (mg L⁻¹) are the equilibrium of adsorbate and residual concentration in the solution, respectively. R: the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T: temperature in Kelvin (K), ΔH and ΔS parameters can be calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ yields (Van't Hoff), respectively (Yurtsever and Şengil, 2009).

Thermodynamic analysis was run as well, on the basis of the results of the adsorption experiment carried out at 293, 313, 343 K using clay and coconut shell as adsorbent. Parameters such as the thermodynamic equilibrium constant, Gibb's free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the adsorption of Al^{3+} ions

were calculated, and results are presented in Tables 5 and 6.

Table 5. Thermodynamic equation constants in Al ads

		Temperature, T (K)			
		293	313	343	R^2
NCA	K_c	94.47	64.59	16.46	0.8689
CSA	K_c	12,95	11,15	47,51	0,612

Table 6. Gibb's free energy, enthalpy and entropy change values in Al adsorption

Temp., T (K)	Al^{3+} ads.			ΔH° (kJ/mol)	ΔS° (J/mol.K)
	293	313	343		
NCA	-10,70159	-10,84660	-7,98728	23009,8264	-46,358864
CSA	-6,02510	-6,27631	-11,01006	-17497,6444	78,3236998

These results suggest that Al^{3+} ion's adsorption on CSA is endothermic, whereas its adsorption on NCA is exothermic.

Many studies showed that agricultural wastes are highly efficient for the removal of metals. Abdel-Ghani *et al.* (2015) studied the removal of Al^{3+} ions from aqueous solution onto rice hull in order to explore their potential use as low-cost activated carbon for effective metal removal from wastewater. Adsorption isotherms were

determined at ~ 20 °C and the experimental data obtained were modelled with the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich isotherms, the pseudo-first order, pseudo-second order and Elovich kinetic equations. On the basis of the experimental results and adsorption models applied in this study, one can reach to the conclusion that equilibrium data were represented well by a Langmuir isotherm equation with maximum Al adsorption capacity of 34.48 mg g^{-1} (pH 5) for Rice Hull Activated Carbon (RHAC). Singh *et al.* (2007) using rice husk carbon (RHC) and commercial granular activated carbon (GAC) for Al^{3+} removal from drinking water, observed 1.6 mg g^{-1} maximum adsorption capacity with rice husk char at an optimal pH of 4.2. Lodeiro *et al.* (2010) studied Aluminium removal from wastewater by refused beach cast seaweed and found maximum adsorption capacity of 22.5 mg g^{-1} at pH 4. Denizli and Say (2001) investigated the adsorption behavior of magnetic poly(2-hydroxy ethyl methacrylate) (mPHEMA) adsorbent in the removal of Al^{3+} ions from drinking and dialysis water. They found maximum Al^{3+} adsorption was $722 \mu\text{mol g}^{-1}$ polymer at pH 5.0. In particular, it is evident that the use of a waste material in removing toxic pollutants from wastewater would bring multiple environmental benefits.

In the present study, natural clay and waste coconut shells were successfully used as a raw material for the preparation of a cost effective adsorbent, which was previously untested in Al^{3+} removal.

4. Conclusions

This study is based on the adsorption studies of Al^{3+} ions to remove it from aqueous solutions, using coconut shell and clay-based adsorbents, which are low cost, natural, and easy to procure materials. The results revealed that the optimal pH value for maximum adsorption was pH ~ 7 for CSA, and pH 6 for NCA. These pH ranges are actually the pH range in which Al assumes a perfect colloidal form. The adsorption equilibriums achieved with both adsorbents match the Freundlich and Langmuir isotherm. Maximum adsorption calculated for Al^{3+} ions on the basis of Langmuir isotherm is found to be $120.482 \text{ mg g}^{-1}$ for CSA, and 149.25 mg g^{-1} for NCA. The maximum Al^{3+} removal efficiencies were 98.95% for NCA at pH 6 and 92.83% for CSA at pH 7. Thermodynamic analyses revealed that adsorption based on CSA was endothermic (ΔS° : 78.32 J/mol.K), whereas adsorption based on NCA was exothermic (ΔS° : -46.35 J/mol.K). Adsorption kinetics were, on the other hand, found to match the second order kinetic model. In this study, the potential use of natural materials such as coconut shells (an agricultural waste) and clay (from Turkey) in the adsorption of Al^{3+} from aqueous solutions were investigated. These materials can be highlighted as promising adsorbents with a noticeable adsorption capacity for the removal of Aluminium ions from aqueous solution even around neutral pH values.

References

- Abdel-Ghani N.T., El-Chaghaby G.A. and Zahran E.M. (2015), Cost Effective Adsorption of Aluminium and Iron from Synthetic and Real Wastewater by Rice Hull Activated Carbon (RHAC). *American Journal of Analytical Chemistry*, **6**(01), 71.
- Alvarez-Ayuso E. and Garcia-Sanchez A. (2003), Removal of heavy metals from waste waters by natural and Na-exchanged bentonites. *Clays and Clay Minerals*, **51**, 475-480.
- Araujo A.L.P.D., Gimenes M.L., Barros M.A.S.D.D. and Silva M.G.C.D. (2013), A kinetic and equilibrium study of zinc removal by Brazilian bentonite clay. *Materials Research*, **16**(1), 128-136.
- Barabasz W., Albinska D., Jaskowska M. and Lipiec J. (2002), Ecotoxicology of aluminium. *Polish Journal of Environmental Studies*, **11**(3), 199-204.
- Bharathi V.P., Govindaraju M., Palanisamy A.P., Sambamurti K. and Rao K.S. (2008), Molecular toxicity of aluminium in relation to neurodegeneration. *Indian Journal of Medical Research*, **128**(4), 545-556.
- Bhatnagar A., Vilar V.J., Botelho C.M. and Boaventura R.A. (2010), Coconut-based biosorbents for water treatment-a review of the recent literature. *Advances in Colloid and Interface Science*, **160**(1), 1-15.
- Bhattacharyya K.G. and Gupta SS. (2008), Kaolinite and montmorillonite as adsorbents for Fe(III), Co(II) and Ni(II) in aqueous medium. *Applied Clay Science*, **41**, 1-9.
- Chaari I., Fakhfakh E., Chakroun S., Bouzid J., Boujelben N., Feki M., Rocha F and Jamoussi F. (2008), Lead removal from aqueous solutions by a Tunisian smectitic clay. *Journal of Hazardous Materials*, **156**, 545-551.
- Denizli A. and Say R. (2001), Preparation of magnetic dye affinity adsorbent and its use in the removal of aluminium ions. *Journal of Biomaterials Science, Polymer Edition*, **12**(10), 1059-1073.
- El Ass K. (2018), Adsorption of cadmium and copper onto natural clay: isotherm, kinetic and thermodynamic studies. *Global Nest Journal*, **20**(2), 198-207.
- Eloussaief M. and Benzina M. (2010), Efficiency of natural and acid-activated clays in the removal of Pb(II) from aqueous solutions. *Journal of Hazardous Materials*, **178**, 753-757.
- Elovich S.Y. and Larinov O.G. (1962), Theory of adsorption from solutions of nonelectrolytes on solid (I) equation adsorption from solutions and the analysis of its simplest form, (II) verification of the equation of adsorption isotherm from solutions. *Izvestiya Akademii Nauk. SSSR Otdeleniya Khimi Nauk*, **2**, 209-216.
- EPA (Environmental Protection Agency) 1990. Environmental Pollution Control Alternatives, EPA/625/4-89/023, Cincinnati, USA.
- Fan Q., Li Z., Zhao H., Jia Z., Xu J. and Wu W. (2009), Adsorption of Pb(II) on palygorskite from aqueous solution: Effects of pH, ionic strength and temperature. *Applied Clay Science*, **45**, 111-116.
- Farhan A.T.A., Ong K.K., Yunus W.W., Jabit M.L., Fitrianto A., Hussin A.G.A. and Teoh C.C. (2017), Isotherm Study of Nickel (II) Adsorption from Aqueous Solution Using Thermally Treated Rice Husk. *Asian Journal of Chemistry*, **29**(3), 589.
- Freundlich H.M.F. (1906), Over the adsorption in solution. *Journal of Physical Chemistry A*, **57**(A), 385-470.

- Ghorbel-Abid I., Galai K. and Trabelsi-Ayadi M. (2010), Retention of chromium(III) and cadmium(II) from aqueous solution by illitic clay as a low-cost adsorbent. *Desalination*, **256**, 190-195.
- Ho Y.S. and Mckay G. (1999), Pseudo-second order model for sorption processes. *Process Biochemistry*, **34**, 450-465.
- Ihara K., Hasegawa S. and Naito K. (2008), The separation of aluminum (III) ions from the aqueous solution on membrane filter using Alizarin Yellow R. *Talanta*, **75**(4), 944-949.
- Internò G., Lenti V. and Fidelibus C. (2015), Laboratory experiments on diffusion and sorption of heavy metals in a marine clay. *Environmental Earth Sciences*, **73**(8), 4443-4449.
- Jiang M., Jin X., Lu X. and Chen Z. (2010), Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay, *Desalination*, **252**, 33-39.
- Kumar U. (2006), Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review. *Scientific Research and Essays*, **1**(2), 033-037.
- Lagergren S. (1898), About the theory of so-called adsorption of soluble substances. *Kungl. Svenska vetenskapsakademiens handlingar*, **24**, 1-39.
- Langmuir I. (1918), The adsorption of gases on plane surface of glass, mica and platinum. *Journal of the American Chemical Society*, **40**, 1361-1368.
- Lodeiro P., Gudiña Á., Herrero L., Herrero R. and de Vicente M.E.S. (2010), Aluminium removal from wastewater by refused beach cast seaweed. Equilibrium and dynamic studies. *Journal of Hazardous Materials*, **178**(1-3), 861-866.
- Matilainen A., Vepsäläinen M. and Sillanpää M. (2010), Natural organic matter removal by coagulation during drinking water treatment: A review. *Advances in Colloid and Interface Science*, **159**(2), 189-197.
- Mirza A., King A., Troakes C. and Exley C. (2017), Aluminium in brain tissue in familial Alzheimer's disease. *Journal of Trace Elements in Medicine and Biology*, **40**, 30-36.
- O'Connor T.P. and Mueller J. (2001), Modeling competitive adsorption of chlorinated volatile organic compounds with the Dubinin-Radushkevich equation. *Microporous and Mesoporous Materials*, **46**, 341-349.
- Ostovar F., Ansari R. and Moafi H.F. (2017), Preparation and application of silver oxide/sawdust nanocomposite for Chromium (VI) ion removal from aqueous solutions using column system. *Global Nest Journal*, **19**(3), 412-422.
- Oubagaranadin J.U.K. and Murthy Z.V.P. (2010), Isotherm modeling and batch adsorber design for the adsorption of Cu(II) on a clay containing montmorillonite. *Applied Clay Science*, **50**, 409-413.
- Pascu D.E., Pascu (Neagu), Mihaela, Segarceanu M., Melinte (Frunzulica), Carmen E. and Miron A.R. (2016), A Study Regarding Aluminium Adsorption Kinetics from Drinking Water on Two Membranes. *Revista De Chimie*, **67**(7), 1239-1243.
- Potgieter J.H., Potgieter-Vermaak S.S. and Kalibantonga P.D. (2006), Heavy metals removal from solution by palygorskite clay. *Minerals Engineering*, **19**, 463-470.
- Sarı A., Tuzen M. and Soylak M. (2007), Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay. *Journal of Hazardous Materials*, **144**(1-2) 41-46.
- Shao H. and Pinnavaia T.J. (2010), Synthesis and properties of nanoparticle forms saponite clay, cancrinite zeolite and phase mixtures thereof. *Microporous and Mesoporous Materials*, **133**(1), 10-17.
- Sharma P., Kaur H., Sharma M. and Sahore V. (2011), A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste. *Environmental Monitoring and Assessment*, **183**(1-4), 151-195.
- Silva M.P.D., Santos M.D.S.F., Santos M.R.M.C., Júnior S., de Sousa L., Fonseca M.G.D. and Silva Filho E.C.D. (2016), Natural Palygorskite as an Industrial Dye Remover in Single and Binary Systems. *Materials Research*, **19**(6), 1232-1240.
- Singh T.S., Parikh B. and Pant K.K. (2007), Investigation on the sorption of aluminium in drinking water by low-cost adsorbents. *Water SA*, **32**(1) 49-54.
- Srinivasan P.T., Viraraghavan T. and Subramanian K.S. (1999), Aluminium in drinking water: An overview. *Water SA*, **25**(1) 47-55.
- Temkin M.J. and Pyzhev V. (1940), Kinetics of ammonia synthesis on promoted iron catalysts. *Acta Physicochimica URSS*, **12**, 217-222.
- Weber W.J. and Morris J.C. (1962), Advances in water pollution research: removal of biologically resistant pollutants from waste waters by adsorption[C]//International Conference on Water Pollution Symposium, vol. 2. Pergamon, Oxford, pp. 231-266.
- WHO (1997) *Aluminium*. Geneva, World Health Organization, International Programme on Chemical Safety (Environmental Health Criteria 194).
- WHO (2006), *Guidelines for Drinking-Water Quality* (third ed.) World Health Organization, Geneva, Switzerland.
- Yavuz H., Say R., Andaç M., Bayraktar N. and Denizli A. (2004), Performance of dye-affinity beads for aluminium removal in magnetically stabilized fluidized bed. *Biomagnetic Research and Technology*, **2**(1), 5.
- Yokel R.A. (2000), The Toxicology of Aluminum. *Neurotoxicology*, **21**, 813-828.
- Yurtsever M. and Şengil İ.A. (2009), Biosorption of Pb (II) ions by modified quebracho tannin resin. *Journal of Hazardous Materials*, **163**(1), 58-64.