

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

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### Abstract

This paper describes the adsorption of Al<sup>3+</sup> 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<sup>-1</sup>) 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<sup>-1</sup>, produced 98.95% (at pH 6) and 92.83% (at pH 7) maximum Al<sup>3+</sup> 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<sup>-1</sup> for natural clay adsorbent (NCA), and 120.482 mg g<sup>-1</sup> for coconut shell adsorbent (CSA). Moreover, adsorption kinetics were found to be consistent with the second order kinetics (R<sup>2</sup> > 0.95). The result shows that, natural clay and coconut shell adsorbents are effective adsorbents to remove Al<sup>3+</sup> 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 Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup> metal ions at pH 7 (Potgieter *et al.*, 2009); Ghassoul clay from Morocco for Cd<sup>2+</sup> and Cu<sup>2+</sup> at pH<6 (El Ass, 2018); montmorillonite from India's Karnataka region for Cu<sup>2+</sup> at pH 2.5 (Oubagaranadin and Murthy, 2010); montmorillonite and kaolinite for Fe<sup>2+</sup> (pH 3), Co<sup>2+</sup> (pH 5.8), Ni<sup>2+</sup> (pH 5.7) (Bhattacharyya and Gupta, 2008); Ca-bentonite from Almeria (Spain) and a Na-exchanged bentonite from Milos (Greece) for Cr<sup>3+</sup> (pH 4), Ni<sup>2+</sup> (pH 6), Zn<sup>2+</sup> (pH 6), Cu<sup>2+</sup> (pH 5) and Cd<sup>2+</sup> (pH 6) (Alvarez-Ayuso and Garcia-Sanchez, 2003); kaolinite from China's Longyan region for Pb<sup>2+</sup> (pH 6), Cu<sup>2+</sup> (pH 6.5), Cd<sup>2+</sup> (pH 7) and Ni<sup>2+</sup> (pH 7) (Jiang *et al.*, 2010); Amasya Çeltik clay from Turkey for Pb<sup>2+</sup> (pH 6), Cr<sup>3+</sup> (pH 6) (Sarı *et al.*, 2007); Palygorskite clay for Pb<sup>2+</sup> at pH 5 (Fan *et al.*, 2009), Illite from Tunisia for Pb<sup>2+</sup> at pH 7 (Eloussaief and Benzina, 2010); smectite from Tunisia for Pb<sup>2+</sup> at pH 4 (Chaari *et al.*, 2008); illite from Tunisia for Cd<sup>2+</sup> and Cr<sup>3+</sup> 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  $0.2 \text{ mg L}^{-1}$ . The present drinking water standard limits for aluminium are  $0.2 \text{ mg L}^{-1}$  (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  $\text{Al}^{3+}$  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  $105 \text{ }^\circ\text{C}$  overnight. Then, 10-gram samples were taken from the clay and coconut shells, and treated separately in 10%  $\text{H}_2\text{SO}_4$ , 37% HCl, and 65%  $\text{HNO}_3$ . Thereafter, the samples were dried once again in the oven at a temperature of  $105 \text{ }^\circ\text{C}$ , 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  $\text{Al}^{3+}$  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 ( $20 \pm 2 \text{ }^\circ\text{C}$ ) 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  $200 \text{ mg L}^{-1}$ . 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  $\text{mg L}^{-1}$  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  $\text{HNO}_3$  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 ( $\text{mg g}^{-1}$  sorbent) were calculated by the following equation:

$$q_t = (C_0 - C_t)V/W \quad (1)$$

$C_0$  is the initial concentration of  $\text{Al}^{3+}$  ion ( $\text{mg L}^{-1}$ ),  $C_t$  is the  $\text{Al}^{3+}$  ion concentration after adsorption time  $t$  ( $\text{mg L}^{-1}$ ),  $V$  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).

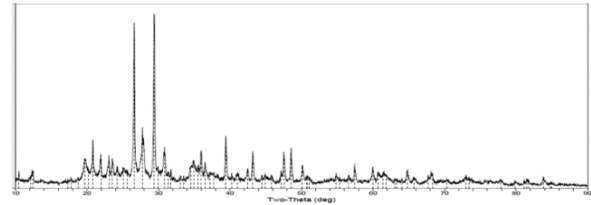


Figure 1. XRD patterns of Saponite clay mineral

Table 1. The chemical composition of the clay mineral

| Chemical composition | K.K. | Humidity | SiO <sub>2</sub> | CaO   | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO  | K <sub>2</sub> O | Na <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | TiO <sub>2</sub> | MnO  | SO <sub>3</sub> | 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 H<sub>2</sub>SO<sub>4</sub> and adsorption process (See Figure 2a–d).

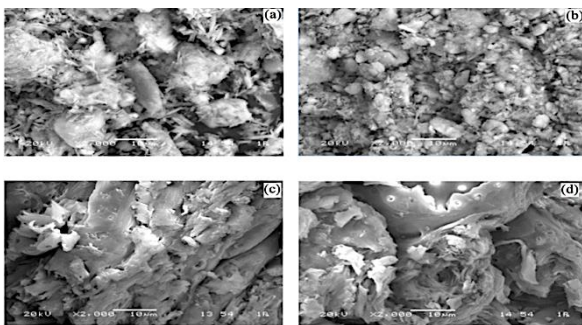


Figure 2. SEM micrographs of NCA (a), after Al<sup>3+</sup> adsorption NCA (b), CSA (c), after Al adsorption. CSA (d)

3.2. The effect of initial pH, temperature and initial Al<sup>3+</sup> 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 1<sup>st</sup>, 5<sup>th</sup>, 10<sup>th</sup>, 30<sup>th</sup>, 60<sup>th</sup>, 90<sup>th</sup> and 120<sup>th</sup> minute of the process were analyzed (See Figure 3 for results).

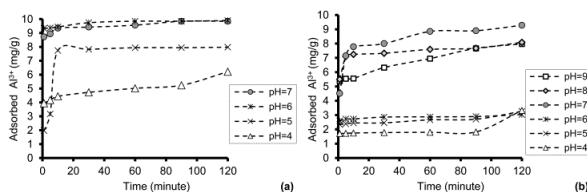


Figure 3. pH influence, Al<sup>3+</sup> adsorption by NCA (a) and CSA (b)

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 1<sup>st</sup>, 5<sup>th</sup>, 10<sup>th</sup>, 30<sup>th</sup>, 60<sup>th</sup>, 90<sup>th</sup> and 120<sup>th</sup> minutes were analyzed in ICP (See Figure 5).

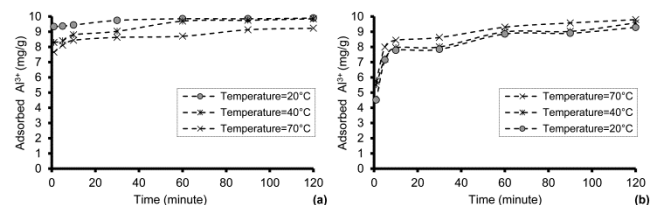


Figure 4. Temperature influence, Al<sup>3+</sup> adsorption by NCA (a) and CSA (b)

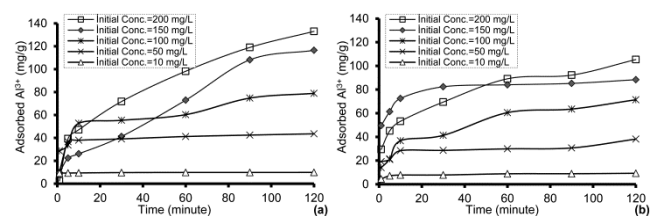


Figure 5. Initial concentration influence in Al<sup>3+</sup> adsorption onto NCA (a) and CSA (b)

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.

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

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

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

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

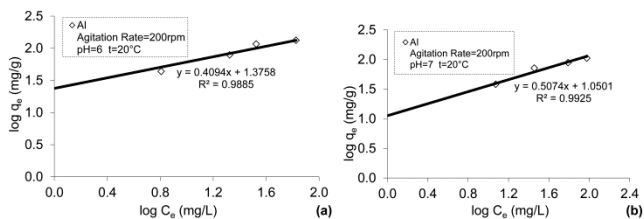
where:  $q_e$ : equilibrium capacity in  $\text{mg g}^{-1}$ ;  $C_e$ : the equilibrium concentration in  $\text{mg L}^{-1}$ ;  $K_L$  and  $a_L$  are Langmuir constants related to the maximum capacity

( $\text{L g}^{-1}$ );  $K_F$  ( $\text{mg g}^{-1}$ ) and  $n$  ( $\text{g L}^{-1}$ ) are Freundlich constants;  $A$  and  $B$  are Temkin isotherm constants;  $q_m$  is the maximum capacity ( $\text{mg g}^{-1}$ ),  $\beta$  is a D-R constant ( $\text{mg}^2 \text{J}^{-2}$ ),  $\varepsilon$ : 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  $\text{Al}^{3+}$  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)       | $\beta$ (mmol <sup>2</sup> /j <sup>2</sup> ) | $R^2$ |
| 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:

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

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:

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

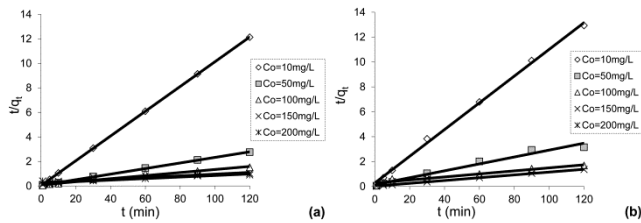
Finally, the Elovich's model is expressed as,

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

Where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_t$  ( $\text{mg g}^{-1}$ ) 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  $t^{1/2}$ .

$k_1$  ( $\text{min}^{-1}$ ) 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  $\alpha$  is the initial sorption rate constant ( $\text{mg/g-min}$ ) and  $\beta$  is related to the extent of surface coverage and activation energy for chemisorptions ( $\text{g mg}^{-1}$ ).

Tables 3 and 4 summarizing the results obtained from the graphs reveal that adsorption of  $\text{Al}^{3+}$  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<sup>3+</sup> adsorption on NCA

| Al <sup>3+</sup> C <sub>0</sub> (mg/L) | q <sub>e</sub> (mg/g) | Intraparticle diffusion model               |                | Pseudo first order kinetic |                | Pseudo second order kinetic |                | Elovich model |           |                |
|--|-----------------------|---|----------------|----------------------------|----------------|-----------------------------|----------------|---------------|-----------|----------------|
|  |                       | k <sub>int</sub> (mg/g.dak <sup>1/2</sup> ) | R <sup>2</sup> | k <sub>1</sub> (1/dak)     | R <sup>2</sup> | k <sub>2</sub> (g/mg.dak)   | R <sup>2</sup> | α (mg/g.dak)  | β (g/dak) | R <sup>2</sup> |
| 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<sup>3+</sup> ion adsorption on CSA

| Al <sup>3+</sup> C <sub>0</sub> (mg/L) | q <sub>e</sub> (mg/g) | Intraparticle diffusion model               |                | Pseudo first order kinetic |                | Pseudo second order kinetic |                | Elovich model |           |                |
|--|-----------------------|---|----------------|----------------------------|----------------|-----------------------------|----------------|---------------|-----------|----------------|
|  |                       | k <sub>int</sub> (mg/g.dak <sup>1/2</sup> ) | R <sup>2</sup> | k <sub>1</sub> (1/dak)     | R <sup>2</sup> | k <sub>2</sub> (g/mg.dak)   | R <sup>2</sup> | α (mg/g.dak)  | β (g/dak) | R <sup>2</sup> |
| 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<sub>c</sub>, which depends on temperature. The Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes for Al<sup>3+</sup> ions adsorption have been determined using Eq. (10).

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

where, K<sub>c</sub> is the equilibrium constant, C<sub>a</sub> (mg g<sup>-1</sup>) and C<sub>e</sub> (mg L<sup>-1</sup>) are the equilibrium of adsorbate and residual concentration in the solution, respectively. R: the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T: temperature in Kelvin (K), ΔH and ΔS parameters can be calculated from the slope and intercept of the plot of ln K<sub>c</sub> 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<sup>3+</sup> ions

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

**Table 5.** Thermodynamic equation constants in Al ads

|     | Temperature, T (K) | K <sub>c</sub> |       |       | R <sup>2</sup> |
|-----|--------------------|----------------|-------|-------|----------------|
|     |                    | 293            | 313   | 343   |                |
| NCA | K <sub>c</sub>     | 94.47          | 64.59 | 16.46 | 0.8689         |
| CSA | K <sub>c</sub>     | 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 <sup>3+</sup> ads. ΔG° (kJ/mol) |           |           | 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<sup>3+</sup> 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<sup>3+</sup> 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<sup>-1</sup> (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<sup>3+</sup> removal from drinking water, observed 1.6 mg g<sup>-1</sup> 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<sup>-1</sup> 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<sup>3+</sup> ions from drinking and dialysis water. They found maximum Al<sup>3+</sup> adsorption was 722 μmol g<sup>-1</sup> 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<sup>3+</sup> removal.

#### 4. Conclusions

This study is based on the adsorption studies of Al<sup>3+</sup> 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<sup>3+</sup> ions on the basis of Langmuir isotherm is found to be 120.482 mg g<sup>-1</sup> for CSA, and 149.25 mg g<sup>-1</sup> for NCA. The maximum Al<sup>3+</sup> 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 ( $\Delta S^\circ$ : 78.32 J/mol.K), whereas adsorption based on NCA was exothermic ( $\Delta S^\circ$ : -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<sup>3+</sup> 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.

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