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

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Abstract In this study, experiments were carried out with natural clay in dust form, collected from Sakarya's Yenigün district using coconut shell, used as adsorbent once treated with acids such as HCl, HNO_3 and H_2SO_4, washed, and dried. The adsorbents were then used to carry out simultaneous analyses of the adsorption of Aluminium (Al^{3+}), the presence of which in water may cause problems. The batch of experiments performed at a temperature of 293±2 K, at 200 rpm agitation rate, with an adsorbent level of 1 g/ℓ, produced 98.95% (at pH 6) and 92.83% (at pH 7) maximum Al (III) 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 group clay minerals. The application of Langmuir revealed maximum adsorption capacity of 149.25 mg/g for natural clay adsorbent (NCA), and 120.482 mg/g for coconut shell adsorbent (CSA). Moreover, adsorption kinetics were found compatible with the second order kinetics. The result shows that, clay and coconut shell adsorbents are effective adsorbents to remove Al(III) ion from aqueous solutions with good adsorption rate.

Keywords: adsorption, aluminium, clay, coconut, kinetic

1. Introduction

When wastewater with a high level of metal content, produced through a multitude of anthropogenic activities, is released to the receiving environment, it 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, neutralization, adsorption, ion exchange, reverse osmosis, extraction, 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 method, which involves collecting the gas, liquid or dissolved substances on the surface of an adsorbent. It is a widely used, efficient, effective and popular method used to remove metals from water. For a long time now, the scientists have been using all kinds of clay minerals, zeolites, chitosan, wood, plant, fruit, peel, seeds, resins, gel, silica, activated carbon etc. for metal adsorption, with significant success (Internò et al. 2015).

There are various forms of clay in the nature, such as kaolinite, smectite, illite, chlorite, talc and so on. 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 pieces in the literature, discussing the use of clay minerals as adsorbents (Silva et al., 2016; Araujo et al., 2013).

Researchers used various clays in the context of adsorption of metal ions, such as: palygorskite clay from Dwaalboom area of the Northern Province of South Africa for Pb(II), Ni(II), Cr(III), Cu(II) metal ions at pH 7 (Potgieter, 2009); kaolinite and illite from Tunisia region for Cu(II) at pH5.5 (Eloussaief, 2009); montmorillonite from India's Gulbarga Karnataka region for Cu(II) at pH 2.5 (Oubagaranadin, 2010); montmorillonite and kaolinite for Fe(III) (pH 3), Co(II) (pH 5.8), Ni(II) (pH 5.7) (Bhattacharyya, 2008); Ca-bentonite from the Sierra de Gador deposit, Almeria (Spain) and a Na-exchanged bentonite from the Silver and Baryte Company deposits, Milos (Greece) for Cr(III) (pH 4), Ni(II) (pH 6), Zn(II) (pH 6), Cu(II) (pH 5) and Cd(II) (pH 6) (Alvarez-Ayuso and Garcia-Sanchez, 2003); kaolinite from China's Longyan region for Pb(II) (pH 6), Cu(II) (pH 6.5), Cd(II) (pH 7) and Ni(II) (pH 7) (Jiang, 2010); Amasya Çeltek clay from Turkey for Pb(II) (pH 6), Cr(III) (pH 6) (Sarı, 2007); Palygorskite clay for Pb(II) at pH 5 (Fan, 2009), Illite from Tunisia for Pb(II) at pH 7 (Eloussaief, 2010); smectite from Tunusia' s El Hamma Jebel Aïdoudi region for Pb(II) at pH4 (Chaari, 2008); illite from Tunusia' s Jebel Tejra region for Cd(II) and Cr(III) at pH 3.5 (Ghorbel-Abid, 2010). These studies led to significant successes in removal of metal ions from the aqueous solution. For years, researchers investigate means to make use of waste, by putting them to use, for instance, in water treatment (Kumar, 2006; Sharma, 2011).

In particular, it is evident that the use of a waste material in removing toxic pollutants from wastewater would bring multiple environmental benefits. Coconut is –more often than not– sold in processed and packaged form. The shells of the fruit consumed at home, on the other hand, are directly disposed in the trash as waste. The utilization of such materials, which often accumulate as waste, is crucial from an environmental perspective. The literature is rich in adsorption analyses regarding metals such as Cr(VI), Co(II), Zn(II), Pb(II), Ni(II), Cr(III) and Cu(II), carried out with Coconut shell as the adsorbent (Bhatnagar, 2010).

Aluminium is a metallic element commonly occurring in nature, the third most abundant in the earth's crust after oxygen and silicon and constitutes about 8% of the Earth's crust (WHO, 1997; Barabasz, 2002).

Aluminium occurs naturally in the environment as oxides, hydroxides and silicates, combined with other elements (such as sodium and fluoride), 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 are in turn, are decomposition products of organic materials.

Aluminum is an environment-friendly element given its hundred percent recycling ability, against a background of commercial use for more than a century. Aluminum is used in a wide range of applications, thanks to its high level of electrical and thermal conductivity, amphoterous, activity softness, lightness, easy processability and corrosion resistance characteristics.

Often touted as the metal of the 21st century, Aluminum metal is widely used as a structural material in the construction, automotive, aircraft industries, in the production of metal alloys, in the electric industry, in kitchen utensils, in food packaging, and in decoration products. Aluminium compounds are used in drugs and consumer products as antacids and antiperspirants additives. Furthermore, Al(III) is used as a phosphate binder in kidney dialysis processes. Aqueous solution of Al(III) is acidic. An excessive amount of Al would change the color of water, and give it a bluish hue. Excessive use of aluminium sulphate ($Al_2(SO_4)_3$ (alum) as a coagulant in water treatment, mineral-rich soil or industrial pollution may be the cause of excessive amount of Al in natural water.

Aluminium salts are widely used in water treatment to reduce organic matters, colour, turbidity, suspended matter, alg and pathogen microorganism levels (Matilainen, 2010). Hence, potable water often contains high aluminium levels of natural origin and/or from the water purification process (Yavuz, 2004).

The World Health Organisation (WHO) has proposed a guideline value of 0.2 mg/ℓ. The present drinking water standard limits for aluminium are 0.2 mg/ℓ (WHO, 2006; EPA, 1990; Singh, 2007). Even though in the olden days Aluminum was thought to be biologically harmless, today its harmful effects on health are under the limelight. Al can be introduced in 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 patients. Accumulation in Aluminum in brain cells is considered among the causes of neurodegenerative disorders such as Alzheimer and Parkinson, amyotrophic lateral sclerosis (ALS, Lou Gehrig's disease). Long-term use of antacids containing aluminum is also associated with 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 methods are efficient in Al removal from water. Denizli and Say prepared magnetic poly(2-hydroxy ethyl methacrylate) (mPHEMA) adsorbent and used for the removal of Al(III) ions from drinking and dialysis water. They found maximum Al(III) adsorption was 722 µmol g^{-1} polymer at pH 5.0 (Denizli and Say, 2001). Singh et al. in their study rice husk carbon (RHC) and commercial granular activated carbon (GAC) used for aluminium removal from drinking water and observed 1.6mg/g maximum adsorption capacity with rice husk char at an optimal pH of 4.2 (Singh et al., 2007).Ihara et al., on the other hand, used membrane filter for separation of aluminum(III) ions from the aqueous solution, and found the method to offer a high level of adsorption (Ihara et al., 2008). They also showed that the membrane they used could be effectively used to remove Al (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 with acids, for the removal of Aluminum ion, which is found in excessive volumes in water, and which poses 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 ^{o}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. Then, the samples were dried once again in the oven at a temperature of 105 ^{o}C, for two hours. 6 individual adsorbent samples prepared through these activation procedures were then used in adsorption experiments, and data was gathered.

2.1. Adsorption studies

The concentration of the aluminium ions was determined by an 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. Adsorption studies were performed by using 1g sorbent (clay and coconut shell) with various initial Al (III) concentrations ranging from 10 to 200 mg L^{-1}. The working solutions 10-200 mg/ℓ Al(III) were prepared by appropriate dilution of the Al stock solution (Merck nr. 119770) immediately prior to their use.

The adsorbed Al (III) concentrations were obtained from the difference between total initial Al (III) and final Al (III) concentrations. The adsorption capacities of clay and coconut shell sorbents as milligram per gram of sorbents (mg/g 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 concentrations after adsorption time t (mg L^{-1}), V is the volume of metal ion solution (mL) and W is the weight of sorbent (g).

Four isotherm equations have been applied for this study: The Langmuir (Langmuir, 1918), Freundlich (Freundlich, 1906), Temkin (Temkin et al., 1940) and Dubinin-Radushkevich (O'Connor et al., 2001) isotherms. 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 their formulas.

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 Table1 and Fig. 1.

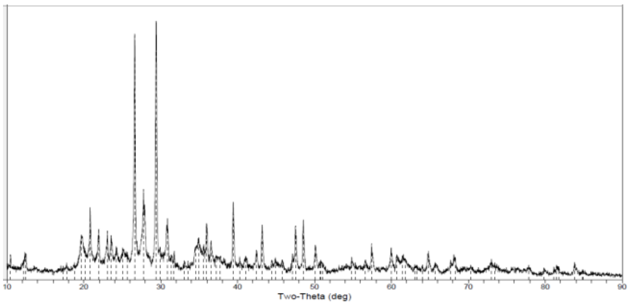

Fig. 1. XRD patterns of Saponite clay mineral

Table 1. The chemical composition of the clay mineral

Chemical composition	K.K.	Humidity	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P2O5	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

XRF chemical analysis of clay revealed 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, 2010).

In order to ascertain the surface characteristics of clay and coconut shell sorbents, SEM images were taken following activation using H2SO4 and adsorption process (See Fig. 2 a, b, c, d).

3.2. Effect of initial pH, temperature and initial Al^{3+} 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 1th, 5th, 10th, 30th, 60th, 90th and 120th minute of the process were analyzed (See Fig. 3 for results).

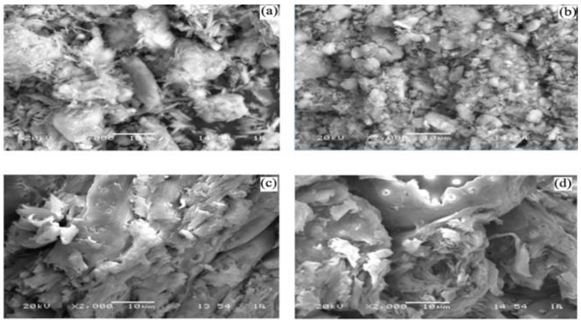

Fig. 2. SEM micrographs of NCA (a), after Al adsorption NCA (b), CSA (c), after Al adsorp. CSA (d)

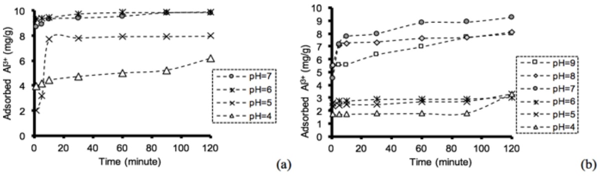

Fig. 3. pH influence, Al ads. by NCA (a) and CSA (b)

Fig. 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 around pH 8. The pH values used in the experiments, below the range of transition to a complete colloidal structure and sedimentation of Aluminum, are hypothesized to accelerate and increase efficiency of adsorption.

The temperature analyses were carried out at 293, 313 K and 343 K at optimal pH values at 200 rpm agitation rate for 2 hours. The results are provided in Fig. 4.

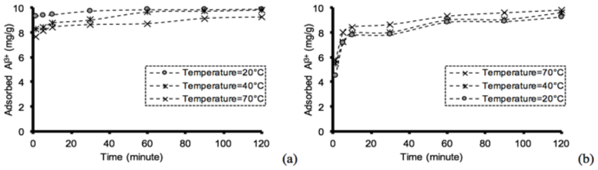

Fig. 4. Temperature influence, Al adsorption by NCA (a) and CSA (b)

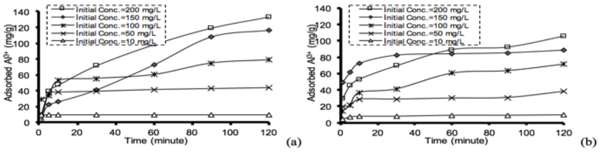

Fig. 5. Initial concentration influence in Al adsorption onto NCA (a) and CSA (b)

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 1th, 5th, 10th, 30th, 60th, 90th and 120th minutes were analyzed in ICP (See Fig. 5).

3.3. Adsorption equilibrium isotherms and kinetics

The data gathered through the initial concentration experiments were used in calculations in accordance with Langmuir Freundlich, Temkin and Dubinin-Radushkevich isotherms. The results of these calculations are provided in Table 2. Al adsorption effected through CSA and NCA adsorbents is found to be best compatible with the Freundlich (See. Fig. 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(III) 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 (mmol²/j²)	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

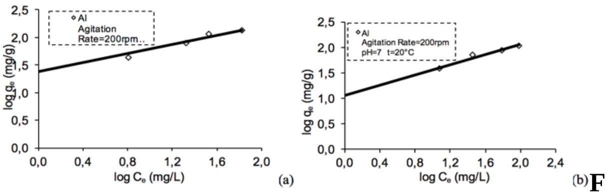

Fig. 6. Freundlich isotherm for NCA (a) and CSA (b)

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

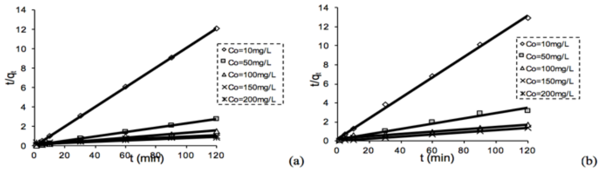

Fig. 7. Pseudo Sec. Ord. Kinetic for NCA(a) and CSA(b)

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 Walls bonds of clay, is able to expand the gaps between clay molecules by up to 7 times, the clays are compatible with the intra-particle 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_o (mg/L)	q_e (mg/g)	Intraparticle diffusion model		Pseudo first order kinetic		Pseudo second order kinetic		Elovich model		
		k_{int} (mg/g.min$^{1/2}$)	R^2	k_1 (1/min)	R^2	k_2 (g/mg.min)	R^2	α (mg/g.min)	β (g/min)	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_o (mg/L)	q_e (mg/g)	Intraparticle diffusion model		Pseudo first order kinetic		Pseudo second order kinetic		Elovich model		
		k_{int} (mg/g.min$^{1/2}$)	R^2	k_1 (1/min)	R^2	k_2 (g/mg.min)	R^2	α (mg/g.min)	β (g/min)	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 analysis was run as well, on the basis of the results of the adsorption experiment carried out at 283, 313, 343 K using clay and coconut shell as adsorbent. Parameters such as the thermodynamic equilibrium constant, Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the adsorption of Al^{3+} ion were calculated, and results are presented in Table 5, 6.

Table 5. Thermodynamic equ. constants in Al ads.

	Temperature, T (K)	283	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. Gibbs free energy, enthalpy and entropy change values in Al adsorption

Al^{3+} adsorption	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (J/mol. K)
Temperature, T (K)	283	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.

5. Conclusions

This study is based on the analysis of the adsorption of Al^{3+} ion to remove it from aqueous solutions, using coconut shell and clay-based adsorbents, which are cheap, natural, and easy to procure. The analyses 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+} ion on the basis of Langmuir isotherm is found to be 120.482 mg/g for CSA, and 149.25 mg/g for NCA. Thermodynamic analyses revealed that adsorption based on CSA was endothermic, whereas adsorption based on CA was exothermic. Adsorption kinetics were, on the other hand, found to match the second order kinetic model.

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