MATEC Web of Conferences **154**, 01020 (2018) https://doi.org/10.1051/matecconf/201815401020
ICET4SD 2017

Removal of calcium and magnesium ions from hard water using modified Amorphophallus *campanulatus* skin as a low cost adsorbent

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Abstract. Low cost adsorbent from *Amorphophallus campanulatus* skin has successfully synthesized to remove calcium and magnesium ions in the syntetic hard water. *A. campanulatus* skin were dried, crushed into powder form and modified by acid modification. A batch experiment with various parameters was used in this research. Various isotherm models were applied to fit the experimental data. Adsorption capacity of Ca and Mg on KB and KM adsorbents in 100 ppm solution respectively 10,85 mg/g, 27,64 mg/g, 1,79 mg/g and 20,1 mg/g. It was found out that the adsorption behavior of hard mineral ions by adsorbents match well with the Dubinin Radushkevich isotherm model. Based on the result, it can be concluded that a acid modified *A. campanulatus* skin is quite potential as a new low cost adsorbent which is expected to be applied to Indonesian groundwater which have high degree of hardness.

1 Introduction

Hard water is water that has high mineral content mainly calcium and magnesium ions. Water hardness causes a variety of problems in either house hold water supply or industrial water systems, such as the buildup of lime-scale that fouls plumbing and promotes galvanic corrosion, and the formation of membrane scaling in seawater desalination. Water softening is a process to remove the water hardness from various water streams and the conventional methods include the lime-soda ash treatment and ion exchange resin [1]. Permanent hardness is usually caused by the presence of calcium and magnesium sulfates in water which become more soluble as temperature rises. Therefore, permanent hardness cannot be removed by boiling. It can be removed by using a water softener which works on the principle of ion exchange in which calcium and magnesium ions are exchanged with sodium or potassium ions, reducing the concentration of hardness minerals to tolerable levels and thus making the water softer and giving it a smoother feeling [2].

Adsorption is the process that can separate objects which neither impossible to be applied nor impracticed by conventional techniques [3]. Zeolite, activated carbon, activated alumina are used as adsorbent. But recently there are researches that concern on making of the novel adsorbent. This novel adsorbent is made not only from unusual sources but also made from the polisaccarides. Polisaccarides which is choosen as adsorbents due to their easily to synthesize, have large adsorption capacity and cheap [4]. Elephant foot yam contains polisaccarides that not explore before. So this project focused on evaluation of the characteristics of the acid modification of the elephant foot yam skin adsorbents and their ability to adsorp both ion Ca^{2+} and Mg^{2+} in aqueous solution.

2 Material and methods

The main materials of this subject are *A. campanulatus* skin, pure distilled water, Merck's hydrochloric acid and Merck's sodium hydroxide. The selected fresh foot yam tubers is obtain from the farmers at Ngawi, East Java, Indonesia which has the itchy yellowish tuber.

2.1 Pretreatment of *A. campanulatus* skin

A. campanulatus fresh tuber firstly cleaned then peeled the skin. The skin then dried in the oven at 50°C for 24 hours. The dried skin then grinded and sieved on 200 mesh sieve after that the sieved skin has been stored into a sterile plastic bag

2.2 Modification of A. campanulatus skin

Sieved *A. campanulatus* skin then modified with acid to improve its adsorption ability. Five hundred grams of sieved *A. campanulatus* skin then dissolved into 2 litres of HCl solution for 3 hours. This acid mixture the neutralized with NaOH solution until pH 7 was reached. The neutral mixture then separated with filter paper. The distilate was dried in oven at 60°C for 1-2 days. The modified skin then stored into a sterile plastic bag.

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 https://doi.org/10.1051/matecconf/201815401020

2.3 Characterization of the adsorbents

There are two characterization of this project. They are suface morphology characterization and chemical bonding characterization. The adsorbents surface morphology was visualized by FEI Inspect S50 Scanning Electron Microscope (SEM). The chemical bonding was determined with Thermo Nicolet Avatar 360 Fourier Transform Infrared Spectroscopy (FTIR).

2.4 Determination adsorption properties of adsorbent

Isotherm adsorption was determined by mixing 1.5 g of sample adsorbents (KB and KM) with 25 mL differential concentration of Ca and Mg artificial hard water (100, 200, 300, 400, 500 [ppm]). Mixture then mixed well for about 30 minutes. After the mixing the adsorbent separated from the filtrate by the Whatmann 40 ashless filter paper, the final concentration of the mixture then analized using Perkin Elmer PinAAcle 900T Atomic Absoprtion Spectrofotometer (AAS). Experimental data then fitted with Langmuir, Freundlich, Temkin and Dubinin Radushkevich isotherm model and studied which the appropriate model(s).

3 Result and discussion

3.1 Effect of acid modification

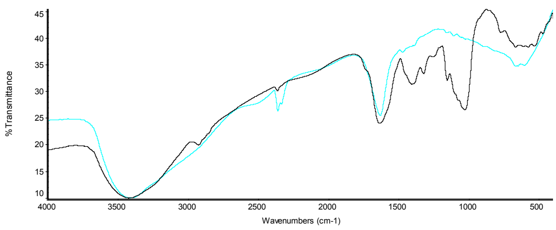

Figure 0.1 FTIR Spectrums of KB and KM

Figure 3.1 represented FTIR spectra of the chemical bonding that occurred in the adsorbent KB and KM. The black line represented KB spectrum and the light blue line represented KM spectrum. Spectra of KB and KM showed the –OH bonds on wavelength around 3.400/cm, the C=O bonds on wavelength around 1.800/cm, the C-O bonds on wavelength 1.000/cm. After the modification, both KB and KM's -OH bonds was tend to be more symmetrical. It can be said that the process of modification with hydrochloric acid may alter-OH bond.

3.2 Characterization of the adsorbents

SEM photograph showed in Figure 3.2 below with 5.000x magnification of KB and 500x magnification of KM. Figure KB that represent the pure dried *A. campanulatus* skin and figure KM represent the modified dried *A. campanulatus* skin. It showed that KM has larger pore than KB due to the diference of magnification. SEM showed that the pore diameter of KB is 412,6 nm and the pore diameter of KM is 64,69 μm. Modification process influences the morpfology and chemical bonding of adsorbents. Based on those characteristic, the KM sample assessed to have a better adsorption ability.

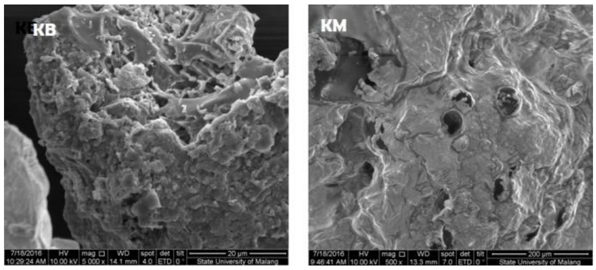

Figure 0.2 SEM Graphs of KB and KM

3.3 Effect of initial concentration

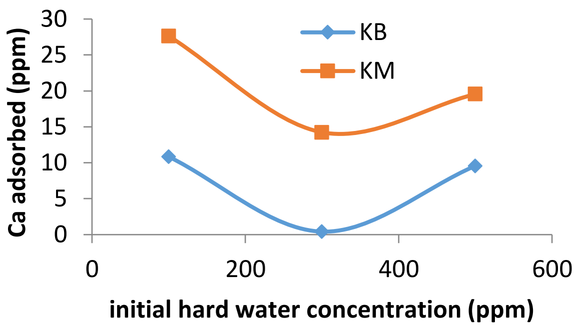

Figure 0.3 Calcium adsorption capacity on KB and KM in various concentration

The relationship between the initial Ca and Mg concentration and the adsorption capacities on KB and KM was studied. As shown in Figure 3.3 above, the adsorption capacities of KB and also KM for Ca was correlated with the initial Ca ion concentration because the process was depend on the concentration. When the concentration rose from 100 ppm to 500 ppm, the adsorption capacities of KB and KM increased from 10.85 to 27.64 mg/g in 100 pmm solution, 0.42 to 14.24 mg/g in 300 ppm solution and 9.57 to 19.56 mg/g in 500 ppm solution. Figure 3.4 below represents the correlation between Mg initial concentration and Mg adsorbed both on KB and KM surface. When the concentration rose from 100 ppm to 500 ppm, the adsorption capacities of KB and KM increased from 1.79 to 20.1 mg/g in 100 pmm solution, 11.33 to 33.66 mg/g in 300 ppm solution and 10.92 to 21.84 mg/g in 500 ppm solution.

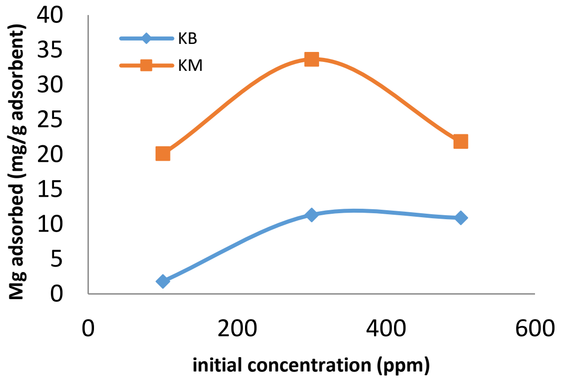

Figure 0.4 Magnesium adsorption capacity on KB and KM in various concentration

3.4 Adsorption isoterm of calcium and magnesium ion into the adsorbents

The adsorption isotherms showed the relations between the concentration of adsorbat and its degree of accumulation of Ca and Mg onto surface of adsorbent at room temperature. Several models of adsorption isotherm have been used to fit to the experimental data. Fitting model used to evaluate isotherm performances for water adsorption. These isotherm models are the Freundlich model, Langmuir model, Temkin model and Dubnin Radushkevich model. Figure 3.5 and Figure 3.6 showed the plot of data isoterm of Ca adsorption onto the KB and KM adsorbents. They showed that the Ca adsorption onto KB and KM are suitable with Dubinin isotherm. Figure 3.7 and Figure 3.8 showed the plot of data isoterm of Mg adsorption onto the KB and KM adsorbents. They showed that the Mg adsorption onto KB and KM are also suitable with Dubinin isotherm.

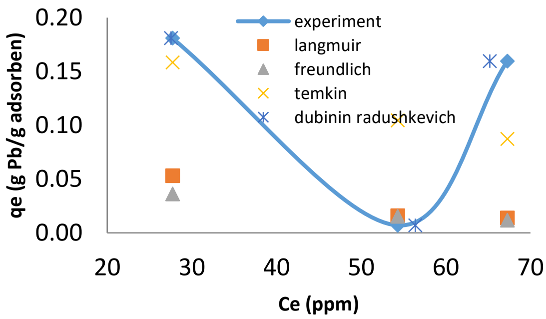

Figure 0.5 Ca onto KB

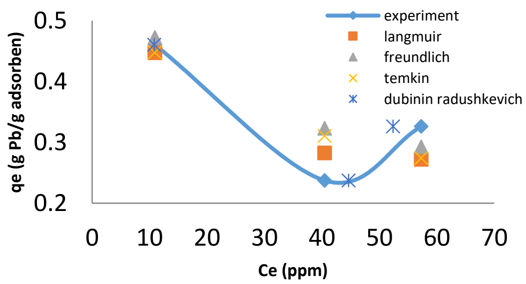

Figure 0.6 Ca onto KM

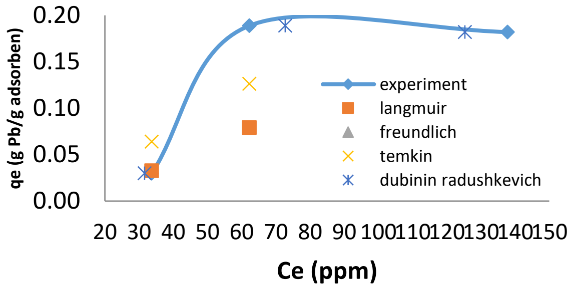

Figure 0.7 Mg Sorption on KB

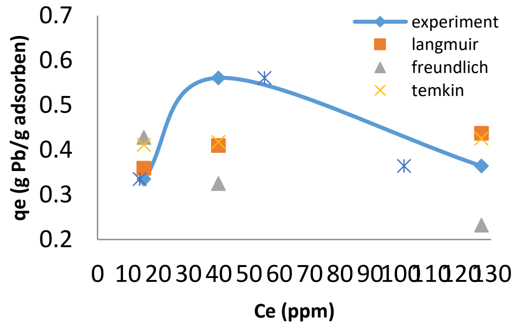

Figure 0.8 Mg Sorption on KM

Table 3.1 showed the details of Ca adsorption isotherm parameters onto KB and KM adsorbents.

Table 0.1 Calcium Isothem Parameters onto KB and KM

	Langmuir			Freundlich		
	K_L	q_0	R^2	K_F	n	R^2
KB	0,044	0,009	0,131	2,418	0,789	0,101
KM	0,207	0,249	0,601	0,946	3,448	0,968
	Temkin			Dubinin Radushkevich		
	A_t	B	R^2	K_{ad}	q_s	R^2
KB	0,005	0,080	0,153	1,674	120,542	0,994
KM	0,001	0,105	0,676	0,902	77,246	0,988

Table 3.2 showed the details of Mg adsorption isotherm parameters onto KB and KM adsorbents.

Table 0.2 Magnesium Isotherm Parameters on KB and KM

	Langmuir			Freundlich		
	K_L	q_0	R^2	K_F	n	R^2
KB	0,006	0,117	0,843	0,040	0,820	0,667
KM	0,254	0,451	0,161	0,946	3,448	0,586
	Temkin			Dubinin Radushkevich		
	A_t	B	R^2	K_{ad}	q_s	R^2
KB	0,055	0,102	0,647	2,512	196,960	0,962
KM	0,005	0,007	0,003	1,448	134,424	0,926

3.5 Comparison of KB and KM with other Ca adsorbent

Table 3 showed the list of adsorption capacity of Ca and Mg by some synthetic adsorbents not only conventional adsorbent but also low cost natural based adsorbent. This study said that the KM has the adsorption ability better than KB for bith ions. Another advantage of KM especially compared to adsorbent conventional is the availability of raw materials for the manufacture of adsorbent abundant sources of biomass, easily regenerated, adsorbent regeneration after use more environmental friendly.

Table 0.3 Mg and Ca adsorption capacity on various adsorbents

Adsorbent	Adsorption Capacity (mg/g)		Initial concentration (mg/L)		Reference
	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	
KB	10.85	1.79	100	100	This study
KM	27.64	20.10	100	100	This study
MPC	85% removed	85% removed	208	147	[5]
Quartz sand	60.00		450		[6]
SDBS-SMB	29.27	29.27	120	120	[7]
Kaolin based geopolimer	76.00	40.00			[8]

4 Conclusion

Novel adsorbent was succesfully synthesized from *Amorphophallus campanulatus* skin modified by hydrochloric acid. The experiment focused on investigation of the effect of modification and the adsorption ability for Ca and Mg ions in aquoeus solution. Modification caused KB more porous and the changed the infrared spectrum of –OH bonding. The adsorption behaviour is dependent on the initial concentration of Ca and Mg ion. Adsorption capacity Ca and Mg on KB and KM in 100 ppm aqueous are 10.85 mg/g, 27.64 mg/g, 1.79 mg/g and 20.1 mg/g. The adsorption follows the Dubinin isotherm. The study also evaluates that the KM has better adsorption ability than KB. So hydrochloric acid modification on the *Amorphophallus campanulatus* skin gave a potential application as another low cost natural based adsorbent.

Authors would say thank to Directorate of Research and Community Service Islamic University of Indonesia for the financial support. We also thank Rudi Syah Putra, head of Integrated Laboratory Islamic University of Indonesia and Abdulloh Fuad, head of Central Laboratory of Mineral & Advanced Materials, Malang State University for their guidance with the experimental element of this research.

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