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OPTIMIZATION OF THE ELECTROSTATIC COAL ADSORPTION PROCESS FOR SEA-SALT PRODUCTION FROM SEAWATER

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High sulfate content in seawater forms sulfate salts, which become impurities in sea salts. This study investigates the influence of lime juice in the adsorption of sulfate ions in seawater using commercial activated carbon. A full factorial experimental design was employed to optimize the level factors of activated carbon type, adsorbent dosage, and concentration of lime juice in response to the percentage reduction in sulfate concentration. Activated carbon (GCB) and acid-washed activated carbon (GCA) were two types of coconut shells granular activated carbon used for the experiment without further modification. The main effect and interaction effects were analyzed using analysis of variance (ANOVA) and p-values to define the influence of variables affecting sulfate ions adsorption. The adsorption of sulfate ions in seawater was affected by the interaction between the activated carbon type and the dosage, and the concentration of lime juice. The lime juice factor significantly enhanced the performance of activated carbon to adsorb the sulfate ions in seawater, and the factor's contribution was 58.2 %. The optimum sulfate ions reduction from seawater was attained at levels of factors activated carbon GCB, the dosage of 50 mg, and the concentration of lime juice 50 µl. The interaction between lime juice and activated carbon pores are electrostatic. The impurities are attracted by the revealed polarity of the activated carbon pores. High electronegativity of lime juice acid pulls the negatively charged ions of the impurities. The more economical activated carbon, GCB, which performed better in sulfate ion adsorption, provides an alternative for reducing sea salt impurities. Hence, GCB can directly be mixed with the seawater to produce high quality sea-salt. Therefore, this study is suitable to improve sea salt product quality that processed with activated carbon

Keywords: electrostatic coal adsorbent, sea-salt impurities, sulfate adsorption, lime juice, acid-wash

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1. Introduction

The formation of impurities in salt can deforms the quality of a salt product. A salt product quality is defined by the chemical content of the salt. The chemical of a salt product determines its functionality. Edible salts such as sea-salts have to free from heavy metals and toxic ions. The nutritious minerals and ions such as iodine improve the quality of the salt [1]. The presence of important mineral traces and iodine often measured as the basis to set national standard of salt nutrition [2]. Therefore, the control of chemical content of a salt product is critical.

Seawater contains many ionic components that become the source of impurities in sea salt. The primary ions in seawater are chloride, sodium, magnesium, potassium, calcium, and sulfate. The main constituents of sea salt are sodium and chloride ions, while other ions can form salts such as magnesium chloride, calcium sulfate, and magnesium sulfate, which become the salt's impurities [3]. In general, the sulfate content in seawater is the third largest after chloride and sodium [4]. Since sulfate can form sulfate salts, which become seawater salt impurities, reducing the sulfate content in seawater is an alternative to lowering the level of impurities in sea salt. The technology to reduce or remove the impurities is more costly than the production cost of the salt itself [3]. Since removing impurities is usually done after the crystallization process, reducing the ions that form impurities in sea salt from the raw material, the seawater, may become an alternative worth considering.

The use of additive to improve the quality of a salt product is required to ensure certain characteristic. Such as in food grade salt production where the toxicity from heavy-metals ion must be maintained as low as possible. One of the effective adsorbent of toxic compounds is activated carbon. The use of activated carbon has been reported to reduce the plumbum (Pb), cadmium (Cd), magnesium (Mg), and calcium (Ca) by 10.33 mg/kg, 2.055 mg/kg, 0.02 %, and 0.019 % [5]. The evidence indicates the quality of the salt is not linearly dependent to the concentration of activated carbon. Instead, there is an optimum point where the adsorption effectiveness can be maximized. Therefore, the implementation of full factorial design approach to find the optimum mass of the activated carbon adsorbent is relevant to improve sea salt quality.

2. Literature review and problem statement

Seawater contains many ionic components that become the source of impurities in sea salt. The primary ions in seawater are chloride, sodium, magnesium, potassium, calcium, and sulfate. The main constituents of sea salt are sodium and chloride ions, while other ions can form salts such as magnesium chloride, calcium sulfate, and magnesium sulfate, which become the salt's impurities [3]. In general, the sulfate content in seawater is the third largest after chloride and sodium [4]. Since sulfate can form sulfate salts, which become seawater salt impurities, reducing the sulfate content in seawater is an alternative to lowering the level of impurities in sea salt. The technology to reduce or remove the impurities is more costly than the production cost of the salt itself [3]. Since removing impurities is usually done after the crystallization process, reducing the ions that form impurities in sea salt from the raw material, the seawater, may become an alternative worth considering.

In seawater, the impurities are still in the form of ions, therefore, materials that can attract ions, such as activated carbon, will be used to reduce the sulfate content in seawater. The activated carbon for sulfate reduction can utilize materials that are widely available in the area or modify activated carbon to improve the characteristics of activated carbon suitable for sulfate adsorption [6–8]. Study [6] shows the possibility of sulphate ions removal through the lime interaction with Ferrous ions. The ferrous ions especially that binds to $FeCl_3$ due to the lower electronegativity. However, the use of $FeCl_3$ has the possibilty to change the nutritional content of the salt product. Study [7] utilizes pyrolle monomer bind activated carbon for ions removal. The use of $FeCl_3$ induces pyrolle head to form interchanging positively charged sites. The drawback of using pyrolle is its availability and cost since pyrolle is more expensive than activated carbon. Similar effects occurred as a response to electrocoagulation process as shown by [8]. Even though, electrocoagulation process was required in study [8], which complicates the ion removal process. Thus, the enhancement of activated carbon pores forms polar surfaces that attract ions. This study use two types of activated carbon made from coconut shells from an activated carbon producer without any modifications. Lime juice was added to the seawater solution to enhance the capacity of activated carbon in sulfate adsorption. Lime juice lowers the solution's pH as the adsorption of anions like sulfate ions works well at lower pH [9].

Lime fruits contain several types of acids like ascorbic acid and citric acid [10]. The citric acid content is the primary source of acidity in limes [11]. Citric acid is categorized as polyprotic acids, which are acids that have more than one acidic hydrogen that can react with water to produce the hydronium ion, H_3O^+. Citric acid is a triprotic acid, which means it has three acidic hydrogen atoms, and when it is placed in water, citric acid will ionize and affect the pH of the solution. The coconut shells activated carbon and lime fruits are considerably low cost materials and widely available in tropical countries like Indonesia. Hence, the uses of lime juice enable cleansing in simpler way without requiring additional process.

One of the methods to optimize a process with several factors is factorial experimental design. Factorial designs are most efficient for studying the effects of two or more factors [12]. The interaction of a factor with another factor that affects the change of dependent variable can easily be tracked through full factorial design. Optimum conditions are determined by simultaneously using several factors and different levels of these factors [13]. Therefore, this study applies full factorial design to control lime juice induced activated carbon sulfate ion removal.

3. The aim and objectives of the study

The main aim of this study is to optimize the electrostatic coal adsorption process to obtain the best parameter in order to practically construct a method for the implementation in pure sea-salt production from seawater.

To achieve this aim, the following objectives are accomplished:

– to control the mass ratio of activated carbon and lime juice volume;

– to understand the interaction between activated carbon and lime juice;

– to differentiate the adsorption mechanism of acid-washed and normal activated carbon.

4. Materials and methods

This study analyzed three factors influencing the adsorption of sulfate ions in seawater: the type of activated carbon, the dosage of activated carbon, and the concentration of lime juice. The full factorial design was employed to obtain the optimum level factors for the adsorption of sulfate ions in seawater using activated carbon and lime juice with a full factorial experimental design. The factors combination and the structure of the activated carbon were able to be controlled to obtain a specific adsorption target. The porous surface of activated carbon has the possibility to trap sulfate ions. The sulfate ions were easier to be attached to a clean carbon pore which can be obtained by the lime juice acid wash. Thus, the control of such factors improves the effectiveness of the adsorption process.

Seawater was collected from a beach in Malang, East Java, Indonesia, and stored in a dark and cool storeroom. The activated carbons used were granular activated carbons and were acquired from Java Carbon, Mojokerto, East Java, Indonesia. The granular acid-washed activated carbon (GCA) and granular activated carbon (GCB) produced by the company were used for the experiment without any further treatments. GCA, which is acid-washed activated carbon, has a higher price than CGB to compensate the further treatment. The lime juice was extracted from local lime fruits. The green lime fruits were selected as the acid of the lime fruits decreased with ripening [11].

Characteristics of the activated carbon like size, iodine number (ASTM D4607), moisture (ASTM D2867), ash content (ASTM D2866), bulk density (ASTM D2854), particle size (ASTM D2862), hardness (ASTM D3802), and pH (ASTM D3838) are provided by the manufacturer. Other characterization techniques were used to identify the physical and chemical characteristics of the activated carbon. Surface morphologies of GCA and GCB were observed by Scanning Electron Microscope (SEM), and some elements of concern by Energy Dispersive X-Ray (EDX). The multipoint Brunauer-Emmett-Teller (BET) equation estimated specific surface areas, and the pore diameters were determined according to the Barrett-Joyner-Halenda (BJH) method. Functional groups of GCA and GCB were estimated by Fourier Transform Infrared (FT-IR) spectroscopy.

A preliminary experiment was conducted to obtain the optimum dosages and time to limit the number of factor levels in factorial experiments. Various activated carbon dosages and contact times were used to determine the optimum dosage and adsorption time as the equilibrium adsorption time. Seawater that had been filtered using filter paper Whatman No. 1 to avoid any interference by the deposit was taken as much as 25 ml and put into a 30 ml glass vial. The activated carbon was added to the seawater and then shaken using a rotary shaker at 300 rpm for a determined time at room temperature. After being shaken, the solution was filtered using a 0.45 µm nylon filter. The initial sulfate concentration in seawater was measured from seawater filtered using a 0.45 µm nylon filter. The sulfate concentration was measured based on the National Standardization of Indonesia method (SNI 6989.20_2009) using a UV–V is spectrophotometer (Shimadzu, Japan). The reduction of sulfate was calculated using the (1):

$$\%removal=\frac{C_o-C_t}{C_o}\times 100, \quad (1)$$

C_o – initial sulfate concentration (mg/L);

C_t – sulfate concentration at time t (mg/L).

The preliminary experiments found the optimum activated carbons' dosages were 40 mg for GCA and 50 mg for GCB, and the equilibrium adsorption time was 1 hour. Those dosages and time were used to study the effect of added lime juice concentration on activated carbons in reducing sulfate ions in seawater for GCA and GCB. The dosage of 60 mg was included in the experiment to analyze the effect of increasing the dosage on sulfate ion adsorption when lime juice added. For the adsorption experiment using lime juice, various concentration of lime juice was mixed with aquadest to a volume of 10 ml manually and added to 50 ml seawater. The solution was homogenized using a rotary shaker and then filtered using Whatman No. 1 filter paper. For each concentration, two 25 ml of solutions were put in glass vials and added to activated carbon GCA and GCB. The mixtures were shaken in a rotary shaker at 300 rpm for optimum adsorption time at room temperature. After being shaken, the solution was filtered using a 0.45 µm nylon filter, and the sulfate concentration was measured using a UV–Vis spectrophotometer (Shimadzu, Japan). The reduction of sulfate was calculated using (1) using time t=1 hour.

The factorial experiment was conducted for sulfate adsorption on activated carbon by adding lime juice to seawater. Statistical analysis was conducted using full factorials analysis of variance (ANOVA). ANOVA was done using Minitab version 2020. Some factors influence the adsorption of sulfate by activated carbon, such as the activated carbon type, pore volume, pH, activated carbon dosage, and contact time, initial sulfate ion concentration and the characteristics of carbon surface [9]"ISSN":"15803155", "PMID":"34057501","abstract":"In this paper, the adsorption potential of activated carbon prepared by Ziziphus spina-christi lotus leaf for the removal of sulfate from aqueous solution was investigated. To this end, the effect of different parameters such as pH, contact time, temperature, adsorbent concentration, and initial sulfate ion concentration was investigated. The results indicated that the highest adsorption efficiency 84.5%. In this study, sulfate reduction was determined as the response variable, and the effect of the type of activated carbon, the dosage of activated carbon, and the concentration of lime juice added to seawater was characterized. The parameters were optimized using a full factorial experimental design for studying the individual and interaction effects of all factors used in this study simultaneously. Other factors that affect the adsorption of activated carbon, such as temperature, adsorbate concentration, and stirring speed, are used as control factors.

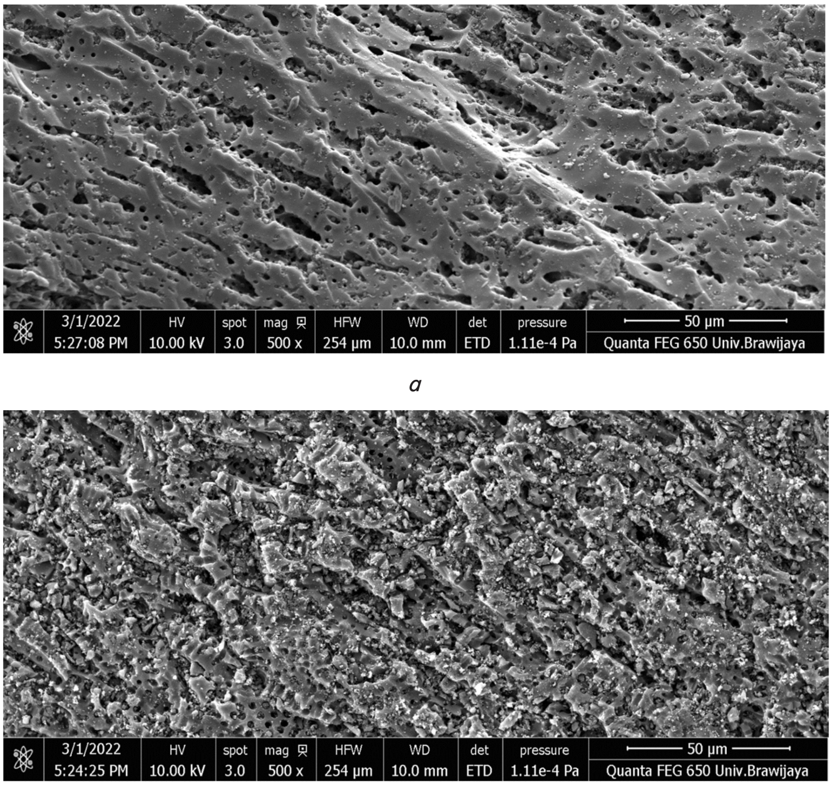
5. Results of the activated carbon adsorption and full factorial design

5. 1. Structural characterizations of the activated carbon

The ash content of GCA is lower than GCB (Table 1), and it is apparent from Fig. 1 that GCA looks cleaner than GCB. GCA is acid-washed activated carbon, and the acid washed reduces ash content [14]. Coconut shell-based activated carbon that gets acid-washed treatment increases the acidic functional groups and lowers the acidity of activated carbons [15]. The manufacturer only specified the pH of acid-washed activated carbon, which is 6.6. The pH of activated carbon produced from coconut shells is normally between nine and eleven. The acidity of activated carbons affects the adsorption process in an aqueous solution. The acidity indicates that the adsorbent has more active sites to interact with anions in an aqueous solution. Based on the acidity, GCA may be preferable in the adsorption of sulfate ions.

Based on BET and iodine number, the surface area of GCA is higher than GCB. Based on BJH average pore size, the pore size of the activated carbons is categorized as micropores [16]. From Table 1, GCA has a higher surface area and lower hardness than GCB, but the hardness difference does not seem significant. All of the pores attributes of GCA and GCB only show narrow differences with GCB has more carbon content and reduced oxygen atoms.

The characteristics of GCA and GCB are similar with only few differences. GCB is dirtier due to the higher amount of ash content which is 1.85 % compared to the GCA with only 0.92 % of ashes. The particle size of GCB is also bigger with 99.5 % while GCA only 95.0 %. Another significant difference is shown by the moisture content with 2.20 % of difference which GCB has higher moisture content with 4.50 % while GCA is only 2.30 %. The rest of characteristics show smaller differences.



a

b

Fig. 1. Scanning Electron Microscopy image of: *a* – granular acid-washed activated carbon (GCA); *b* – granular activated carbon (GCB)

Table 1

The characteristics of Activated Carbon

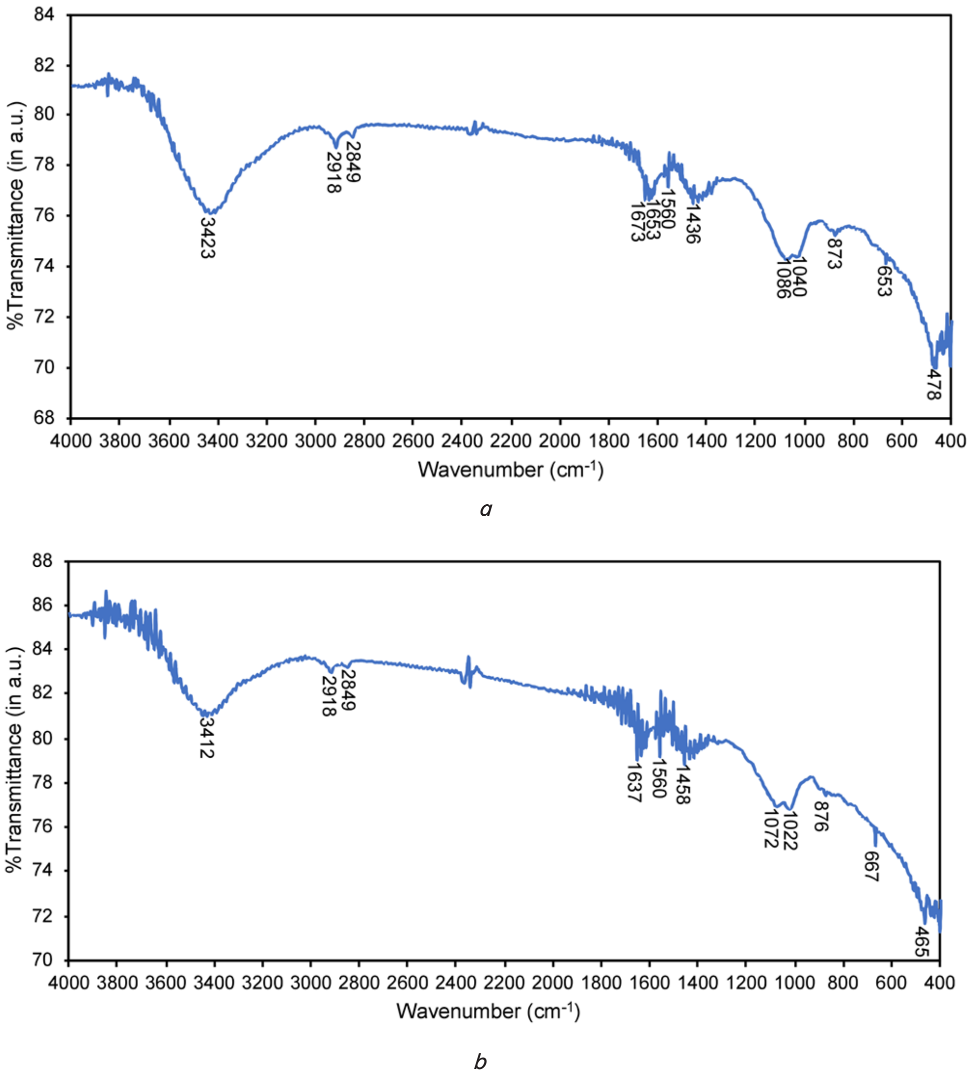
Attributes	GCA	GCB
Size (mesh)	8×30 (0.60–2.36 mm)	8×30 (0.60–2.36 mm)
Iodine (mg/g)	1086	1046
Moisture (%)	2.30	4.50
Ash (%)	0.92	1.85
Bulk Density (g/ml)	0.51	0.51
Particle size (%)	95.0	99.5
Hardness (%)	98.2	98.4
pH	6.60	–
BET Surface area (m^2g^{-1})	817.811	734.490
BJH Average Pore Size (nm)	1.05702	1.06696
BJH Total Pore Volume (cc/g)	0.432223	0.391835
C (at %)	93.60	95.24
O (at %)	4.81	3.22
N (at %)	ND	ND

5. 2. Study the interaction between activated carbon and lime juice

Surface area affects the adsorption capacity of activated carbon, but it does not mean that the activated carbon with a higher surface area will have a higher capacity. The capacity also depends on the functional groups of the activated carbon and the molecules or ions to be adsorbed. The functional groups located at the edges of the activated carbon, and the group is much more reactive than the atoms on the inside of the carbon sheet [17]. The group of atoms chemically bonded in various forms of functional groups gives acidic, basic, and neutral properties to the carbon surface [18]. These functional groups can be formed during the carbon activation process and can also be added afterward through a certain treatment process to obtain the desired chemical properties.

The acidic surface is associated with several functional groups, such as carboxyl, lactone, phenol, and lactol [19]. Other functional groups that are also acidic are carboxylic anhydrides, lactones, and phenolic hydroxyls. Functional groups that are acidic at a certain pH are effective for binding cations [20]. The basic activated carbon surface is affected by electrons forming delocalized bonds in the basal planes that attract protons and functional groups that can bind protons [21]. Functional groups that contain basic oxygen are chromene, ketones, and pyrones. The basic nature of the surface can also occur through the addition of nitrogen-containing functional groups on the carbon [18, 22]. Functional groups derived from nitrogen include amide, amine, lactam, pyrole, and pyridine [23]. This functional group can interact with acid molecules through hydrogen bonds, dipole-dipole, covalent bonds, and others [23].

The FTIR can be used to determine the functional groups of activated carbons by identifying the location and peak of shape where the specific chemical bond existed [24]. FTIR spectra of GCA and GCB are shown in Fig. 2. Stretching O–H groups attributed to surface phenolic hydroxyl groups appear in GCA on 3423 cm^{-1} and in GCB on 3412 cm^{-1}. The C=O stretching group that can be assigned to carboxylic groups only appears in GCA at 1673 cm^{-1} vibration. The band of aromatic rings (C=C) in GCA on 1560 and 1653 cm^{-1} and GCB on 1560 and 1637 cm^{-1} (Boehm 2002). The GCA band at 1040 and 873 cm^{-1} and at 1022 and 876 cm^{-1} for GCB indicated chromene and pyrone functional groups.



a

b

Fig. 2. Fourier Transform Infrared spectra of: *a* – granular acid-washed activated carbon (GCA); *b* – granular activated carbon (GCB)

Based on the FTIR identification, both activated carbons contain acid and basic functional groups. Since seawater has various anions and cations, the basic and acid functional groups will react with the ions. The addition of lime juice was directed to enhance the performance of the basic functional groups in adsorbing the sulfate ions.

5. 3. Mass ratio control of sulfate ion reduction

The factors and their levels are presented in Table 2. Each experiment was carried out three times. Due to limited capacity, in one day, an experiment was carried out for one level of activated carbon dosage factor for both types of activated carbon using a lime fruit for all levels of lime juice concentration. The lime fruits were selected from a local market and were green with almost the same weight. Therefore, lime juice can be considered homogeneous for all experiments carried out. The ANOVA was conducted using a three-factor experiment with a completely randomized design. The ANOVA results are presented in Table 3. The model shows an R^2 of 83.51 % (Table 3), which indicates that 83.51 % of the total variations are explained by the model.

Based on ANOVA, the interaction between activated carbon types and the dosages of the carbons was significant. The main effect of the dosage factor was significant, but the main effect of activated carbon type was not significant. In the presence of interaction between dosage and activated carbon factors, it needed to observe the influence of activated carbon factor at fixed levels of dosage factor and the influence of dosage factor at fixed levels of activated carbon types. To further analyze the effect of the interaction, the interaction was plotted (Fig. 3), and a Tukey's test was conducted (Fig. 4).

There were no effect differences in the dosage of 60 mg for both types of activated carbons as well as in the dosage of 40 mg. Although there was no significant difference in those dosages for GCA and GCB, the average sulfate ions reduction in GCA was higher than in GCB. The difference occurred when the dosage was 50 mg. There was a relatively strong activated carbon type effect on sulfate ion reduction at 50 mg. It was reflected in the steep slope at a dosage of 50 mg. There was a significant difference between GCB and GCA, in which GCB showed a greater response in reducing sulfate ions. Since the dosage of 50 mg resulted in the highest sulfate ion reduction for both types of activated carbon, GCB is preferable to use in sulfate ion adsorption in seawater.

Table 2

Levels of the experimental factors

Factors	Model	Levels						
Activated carbon	Fixed	GCA	GCB	–	–	–	–	–
Dosages (mg)	Fixed	40	50	60	–	–	–	–
Lime juice concentration (µl)	Fixed	20	30	40	50	60	75	100

GCA and GCB had the same pattern with respect to dosages, in which there was an increase in sulfate reduction when the dosage was increased from 40 mg to 50 mg and a decrease in sulfate reduction when the dosage was increased from 50 mg to 60 mg (Fig. 3). It can be related to the physical characteristics of the GCA and GCB, which are not significantly different. In GCA, there was a dosage effect, in which a dosage of 50 mg gives the greatest response to reducing sulfate levels. However, Tukey's test showed no significant differences between the dosages of 50 mg and 40 mg. The significant distinction occurred when the dosage was 60 mg. The pattern was different from the GCB. There was no effect on the type of activated carbon at the dosage level of 40 mg and 60 mg. However, at the 50 mg level, GCB provided a higher reduction in sulfate levels and was significantly different from the other two dosages. Therefore, the lowest dosage, 40 mg, is preferable when GCA is used to adsorb the sulfate ions. However, for GCB, it is a dosage of 50 mg that should be used. GCB provided more sulfate reduction but required more activated carbon.

Table 3

Analysis of variance

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Activated carbon	1	18.29	0.29 %	18.29	18.29	1.69	0.196
Dosage	2	1016.86	16.18 %	1016.86	508.43	47.10	0.000
Lime juice	7	3657.83	58.20 %	3657.83	522.55	48.41	0.000
Activated carbon*Dosage	2	90.78	1.44 %	90.78	45.39	4.20	0.018
Activated carbon*Lime juice	7	106.41	1.69 %	106.41	15.20	1.41	0.211
Dosage*Lime juice	14	172.64	2.75 %	172.64	12.33	1.14	0.332
Activated carbon* Dosage*Lime juice	14	185.66	2.95 %	185.66	13.26	1.23	0.268
Error	96	1036.29	16.49 %	1036.29	10.79	–	–
Total	143	6284.75	100.00 %	–	–	–	–
S=3.28552, R^2=83.51	–	–	–	–	–	–	–

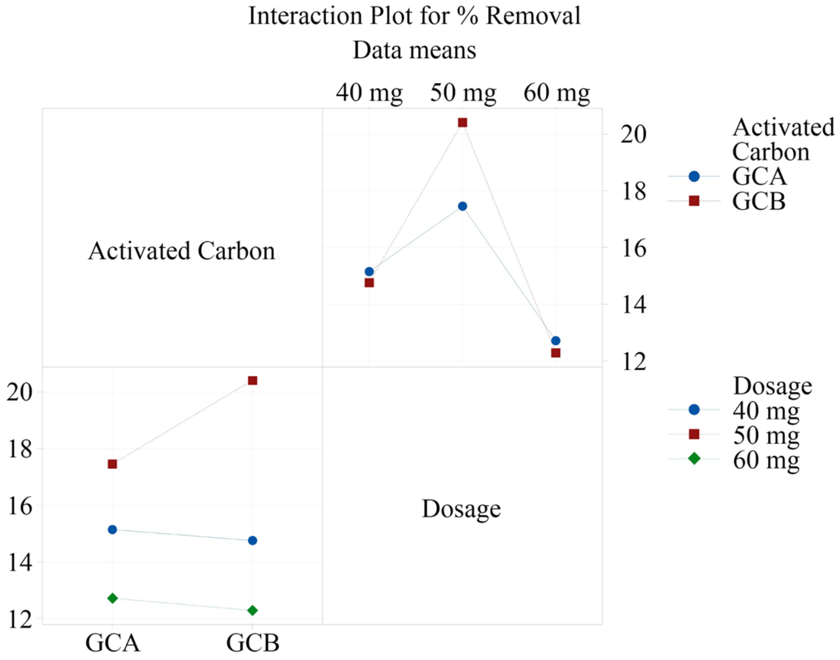


Fig. 3. Activated carbon type and dosage interaction

Activated Carbon*Dosage	N	Mean	Grouping			
GCB 50 mg	24	20.4153	A			
GCA 50 mg	24	17.4570		B		
GCA 40 mg	24	15.1424		B	C	
GCB 40 mg	24	14.7547		B	C	D
GCA 60 mg	24	12.7031			C	D
GCB 60 mg	24	12.2707				D

Fig. 4. Tukey's test of activated carbon and dosage interaction

The highest average of sulfate ion reduction occurred when the lime juice added to the seawater was 30 µl (Fig. 5). That level of lime juice resulted in consistent sulfate ions reduction in seawater for all activated carbon types and dosages (Fig. 6). Although not too significant, GCB showed better performance in reducing sulfate ions. Based on physical and chemical characteristics, GCA preferred ion sulfate adsorption. However, when the activated carbon dosage was 50 mg, GCB showed significant performance in sulfate ion performance. The optimum sulfate ion reduction was on GCB with a dosage of 50 mg and lime juice of 50 µl (Table 4). For GCA, the optimum sulfate ion reduction was lower than GCB. It was at the same dosage as CGB but at a lower lime juice concentration.

The acid-washed treatment of GCA has lower ash content and higher oxygen content than GCB. Therefore, GCA is more acidic and has a more hydrophilic surface. When the dosage of activated carbon was increased from 40 mg to 50 mg, the hydrophilic functional groups also increased. However, when the activated carbon dosage was further increased to 60 mg, the performance of both types of activated carbon decreased. The decrease when the dosage was increased further may be due to the saturation of the adsorbent sites.

Based on Hard Soft Acid Base (HSAB) concept proposed by [25], the most abundant ions in seawater, such as sodium, magnesium, calcium, chloride, and sulfate, are either hard acids or hard bases, and they will interact with functional groups in activated carbon. Without lime juice added, the adsorption of sulfate ions was low as the ion competes with other anions in seawater for adsorption on the functional groups of the activated carbon [26]. Adding lime juice to the seawater decreased the pH of the solution. The basic sites of activated carbon were likely enhanced.

Table 4

Optimization solution for GCA and GCB

Solution	Activated Carbon	Dosage	Lime Juice	% Removal Fit	Composite Desirability
1	GCB	50 mg	50 µl	24.3432	0.909676
4	GCA	50 mg	30 µl	22.7354	0.856366

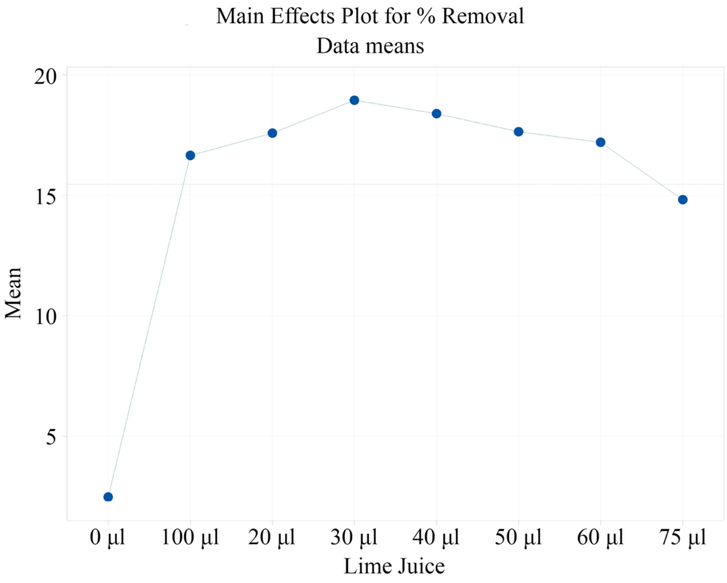


Fig. 5. Main effect plot of lime juice concentration factor

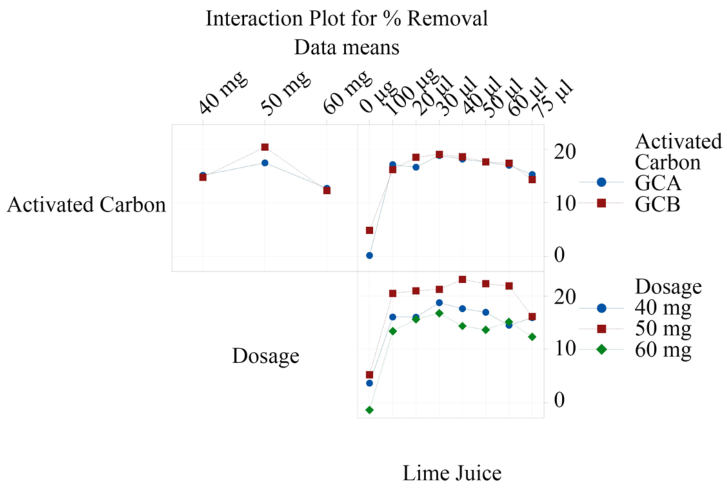


Fig. 6. Interaction of the three factors: activated carbon type, dosage, and lime juice concentration

The effect of the lime juice is aligned with the HSAB concept. The addition of lime juice increases the adsorption rate and without the acid-wash using the lime juice the adsorption rate shows no improvement. However, GCA, which has more oxygen functional groups, shows a lower rate of adsorption of sulfate ions than GCB. Therefore, acid-wash affects the mechanics of the activated carbon adsorption.

6. Discussion of the seawater impurities adsorption result

The hardness level of a carbon-based material defined by its structural thickness. The structural thickness is related to the molecular structure of the carbon. Lower density carbon stacks such as graphene possess higher strength to weight ratio. Meanwhile, higher density stacks such as graphite are harder and tend to brittle [27]. The brittleness of graphite is due to the loose stack binding between each layer of carbon structure. Hence, few layers or a single layer of a carbon structure can easily unattached from the surface. As a result, the adsorption capability is varied across the stacks. The morphology of GCB as shown in Fig. 3, *b* indicates it has more variation adsorption mode than GCA in Fig. 3, *a*.

The surface area of reaction and the stacks of GCA and GCB define the removal capability. The higher surface area of reaction of GCA indicates the capability of the surface to attach more impurities. However, GCB is more effective to remove the impurities even its pore volume is lower and not finer than GCA. Both, GCB and GCA have similar adsorption mechanism due to the insignificant difference in BET and BJH pore characteristics (Table 1). Therefore, the surface structure of GCB favors the chemical interaction with the impurities that contained in the salt crystal.

The interstitial impurity between the salt crystals is accessible by the coarse GCB surface. The smooth GCA surface relies on pores to interact with the impurities around the crystal. Meanwhile, coarse GCB also has slits and non-uniform pores (Fig. 3, *b*). Non-uniform pores orientations of GCB are multidirectional while CGA pores are only capable to provide chemical attack in a single direction. Therefore, shear electrostatic force exerted by the outer surface of GCB able to release the interstitial impurities in the salt crystal.

The acid of the lime juice activates the pores of activated carbon. The high electronegativity of nitric acid from the lime juice eliminates the impurities around the pores. The highly electronegative acid exerts strong electrostatic force. The force attracts negatively charge impurities around the pore which clear the pore edges. Consequently, the impurities such as sulfate ions can be removed from the pores. Therefore, the impurities are removed through electrostatic interaction.

The GCA and GCB activated carbon enable effective sulphate ion adsorption. Compared to previous studies on sulphate ion removal, 50mg of GCA and GCB can remove 22 % and 24 % impurities from seawater. GCA and GCB do not require complex activation such as the use of $ZnCl_2$ as done by [6]. The developed GCA and GCB also as effective as polypyrrole modified hardwood-based activated carbon developed by [7] 44.7 mg/g sulfate. The GCA and GCB pores can adsorb negatively charged ion impurities without prior positively charged ion conversion such as Al^{3+} [8]. Therefore, this study results in simpler adsorbent that equally effective with more complex adsorbent.

The BET result shows the character transformation does not directly related to the change in pore characteristic. The higher surface area resulted from the formation of new pores, decreasing the hardness of the activated carbon [28]. The hardness indicates the mechanical strength of the activated carbon, as the pores formed, the carbon walls become thinner, resulting in structural weakness of the carbon. The pore size is suitable to adsorb sulfate ions as the ion radius is much lower than the pore size. GCA has a smaller pore size and higher pore volume than GCB. GCA also has a finer particle size than GCB. Particle size does not affect the adsorption capacity of activated carbons, but the kinetics or speed of adsorption increases as the particle size of activated carbons decreases.

The ANOVA test results provide insights of the adsorbent physical characteristics. The physical adsorption of an adsorbate on activated carbon depends on the activated carbon's pore size and the adsorbate's diameter [29]. The adsorption is also influenced by the concentration of the adsorbate in the solution and the presence of other adsorbate [14]. The pore size of GCA is slightly smaller than GCB (Table 1), but the pore sizes are much smaller than the diameter of sulfate ions [20]. Seawater has several adsorbate ions, such as sodium, potassium, magnesium, calcium, chloride, nitrate, and sulfate. The presence of the other adsorbates can compete with sulfate ions for the adsorption sites. As the diameter of sulfate ions is bigger than the diameter of other ions in seawater, the other ions may not block the access of the smaller pores. However, abundant other ions such as sodium and chloride may block the smaller pores. There is no difference between GCA and GCB based on physical adsorption, as both activated carbons are not significantly different in physical characteristics. The interaction effect of the activated carbon types and the dosages that resulted in the different influences of the dosage of 50 mg should be affected by the third factor, lime juice concentration.

The rise of hydrophilic functional groups lifts up the performance of GCA adsorption. However, higher hydrophilic surface can lead to water adsorption on polar oxygen functional groups that hinder the access of adsorbents to adsorption sites [31]. Hence, the performance of CGA in adsorbing sulfate ions was not as effective as CGB. The decrease when the dosage was increased further may due to the saturation of the adsorbent sites. The decreased pH protonates the functional groups, so more sulfate ions are bound to the functional groups. Therefore, the removal of sulfate ions increased. The basic activated carbon surface is located in the functional groups that can bind protons and electrons, forming delocalized bonds in the basal planes that attract protons. GCB has less oxygen content, so it increases carbon basal planes that attract hydronium ions [21]. The increased H_3O^+ cations from lime juice added to the solution may react with the basal plane on carbon surfaces through cation-π interactions [32]. It causes the surface of the basal planes to be positively charged to attract sulfate ions.

Some limitations are imposed in this study. This study only focuses on the removal of impurities from seawater to produce sea salt. Therefore, the result of this study is not guaranteed to produce food grade seal salt. The implementation of full factorial design in this study also has a limitation. This study only looks into the interaction between dosage of activated carbon and lime juice. Future improvement by taking the activated carbon morphology and pore morphology into the account is required. Therefore, the clear impurities removal mechanism could be seen.

7. Conclusions

1. GCB multidimensional pore structure is the optimum structure to perform sulfate ion reduction. The best sulfate ion reduction from seawater using activated carbon and lime juice was attained at the combination levels of factors activated carbon CGB, the dosage of 50 mg, and the concentration of lime juice 50 µl. The optimum response of sulfate ions reduction of 24,34 % was influenced by the interaction between the activated carbon type and the dosage, and the concentration of lime juice.

2. The interaction between the activated carbon and lime juice is electrostatic. The impurity ions removal is possible due to the acid-wash unveils the activated carbon pores. Highly electronegative acid peels off the positively charged covered pores.

3. The adsorption mechanism of GCA and GCB are utilizing the charge on the pores. The pore polarity that revealed by the acid wash has stronger surface interaction with the impurities. GCA is stronger than GCB due to the freer polar active site that available. Hence, the interaction is free without any interruptions.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

Data will be made available on reasonable request.

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