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The Effect of Solvent and Amine Concentration on the Modification of Silica Sand Waste by Grafting Method as an Adsorbent

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ABSTRACT

Industrial waste is all types of waste materials or residual materials originating from the results of an industrial process. One of the industrial wastes in solid form is silica sand waste from the sandblasting process which has the potential to be used as a source of silica for adsorbents. This experiment is conducted to determine the type of solvent and the best addition volume of APTES in silica modification using amine (APTES). The process used in this experiment is a grafting process, where silica goes through a reflux process with solvents and APTES so that the amine groups attach to the surface of the modified silica. The results of the experiment is analysed using TGA and FTIR, and shows that the most optimal addition volume of APTES is 5 mL with the best types of solvents being ethanol and toluene solvents with the amount of amine loading contained in the modified silica being 1,9430 and 5,2552 mmol γ aminopropyl/gram silica, respectively, but not in water solvents. The results of this study shows a successful APTES grafting of modified silica which can be used as an adsorbent for CO_2 capture.

INTRODUCTION

Silica is a compound with the molecular formula SiO_2 (silicon dioxide), used as an adsorbent obtained from various sources, such as mineral silica, plant silica, and crystal synthesis (Ramadhanty et al., 2021). Sandblasting is the process of cleaning or preparing a metal surface by forcefully firing abrasive material in the form of silica sand onto the surface of the material with the aim of removing dirt in the form of rust due to oxidation between sea water and air (Hendrawan & Aprilian, 2020).

The adsorption method is an effective purification and separation technique because it uses relatively simple equipment and preparation processes (Hastuti et al., 2023). Amine adsorbents can be prepared by three methods, namely: Impregnating, the preparation is easy and produces adsorbents with high adsorption capacity. Grafting, usually carried out by reflux in organic solvents. This adsorbent contains amino functional groups that are chemically bonded to the silica substrate by forming siloxane bridges (Si-O-Si), so it will be more stable compared to adsorbents made by the impregnation method. Coprecipitation of amine compounds with silica during synthesis, in this method, the silica substrate is precipitated simultaneously with the amine to form the adsorbent (Quang et al., 2016).

Grafting is a modification method by reacting hydroxyl groups (silanol groups) found on the surface of mesoporous silica and alkoxy ligands from silane by attaching amine groups to the surface of mesoporous silica (Rahman, 2022). Research conducted by Girimonte et al., 2022, using APTES concentrations with ethanol/water solvents of 10, 20, 40 w/w% using the modified grafting method showed that APTES20 showed the highest potential as an adsorbent in sustainable CO_2 capture in flue gas. Research by Rao et al., 2018 with variable APTS concentrations, namely 30, 40, 50 wt% using grafting method showed that the minimum adsorption capacity and adsorption rate were 2.41 mmol/g and 0.0062 mmol/g obtained from 50% APTS-MCM-41. Research by Santiago et al., 2020, which was a comparison between pure silica and silica grafted with amine, showed that silica modified with amine proved to be more efficient in capturing CO_2 in post-combustion scenarios. Research conducted by Wang & Yang, 2020, using 5 mL of APTES and 50 mL of toluene with SBA-15, showed the result of estimate amine loading of 2,2 mmol/g. Research conducted by Nigar et al., 2016, using 0,65 mL of APTES, showed result of amine loading of 2,05 g/g. Research conducted by Kishor & Ghoshal, 2015, showed that using toluene as solvent and concentration of APTES is 9 mmol/g result in the highest amine loading of 2,67 mmol/g.

This study was conducted with a new approach by comparing the types of solvents (ethanol, water, and toluene) with the volume of APTES used. The solvent used is based on the commonly divided groups of solvent, namely anhydrous such as toluene, and aqueous, such as ethanol and water. While the volume of APTES used is based on the commonly used 5 mL, however there is no direct comparison for lower volume used. Several studies have investigated the differences between amine loading obtained using either anhydrous or aqueous solvents, however there is a lack in corelation with the volume APTES used. The study aims to determine the optimal combination of solvent types and volume of APTES used in making modified silica adsorbents by observing the amount of amine loading that is successfully grafted.

RESEARCH METHODS

Tools and Materials

The tools used in this study includes a stirring rod, beaker glass, cup, funnel, filter paper, condenser, 3-neck flask, oven, volume pipette, spatula, scale, water bath, and heating jacket. The materials used are ethanol 99%, water, toluene 99%, 3-aminopropyltriethoxysilane (APTES), and mesoporous silica.

Variables

The variables used in this study are control variables consisting of mass of mesopore silica is 1 gram, volume of solvent is 50 mL, the duration of reflux is 18 hours, the reflux temperature is in accordance with the boiling point of the solvent used, the oven temperature is 100 ^{o}C, and with the duration of 24 hours. The independent variables used are type of solvent used, namely ethanol, water, and toluene, and the volume of APTES are 1, 2, 3, 4, and 5 mL.

Procedure

Mesoporous silica obtained from the synthesis of sandblasting sand is modified with amine groups using the post-grafting method. One gram of mesoporous silica is refluxs in 50 mL of solvent and APTES at the boiling point of the solvent used for 18 hours. The mesoporous silica that has been modified with the amine group is washed repeatedly using the same type of solvent used, then dried in an oven at 100 °C for 24 hours. The APTES modified silica is analyzed using TGA 600 ^{o}C and 3 samples with a variable volume of APTES of 3 mL are analyzed using FTIR.

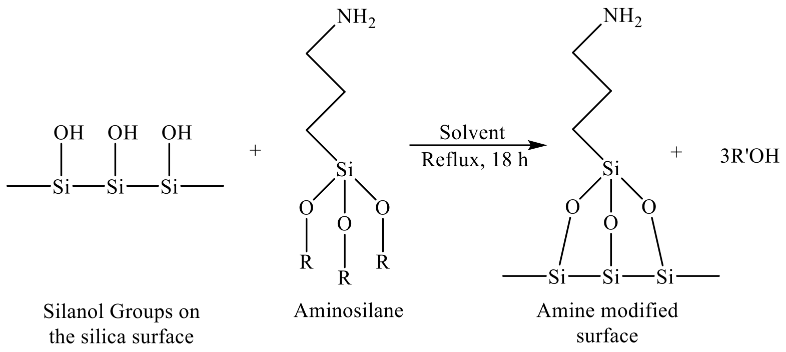

Figure 1. Mesoporous silica grafting scheme using aminosilane (Rahman, 2022)

Amine Loading

In the temperature range of 200 °C and 600 °C all grafted products should be completely decomposed so that the TGA results can serve as a quantitative analysis tool to evaluate the percentage of amine loading grafted on modified silica. It is assumed that the amine groups removed show a molecular weight of about 58,104 g/mol ($CH_2CH_2CH_2NH_2$). The amine loading is evaluated by Eq. (1):

$$\text{Amine loading (mmol } \gamma \text{ aminopropil/g silica)} = \frac{\%\text{mass loss}}{100} \times \frac{1 \text{ mol}}{58{,}104 \text{ g}} \times \frac{1000 \text{ mol}}{1 \text{ mol}} \quad (1)$$

(de O. N. Ribeiro et al., 2019)

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA) of amine modified silica

The following is a graph of TGA result of amine modified silica using ethanol as the solvent.

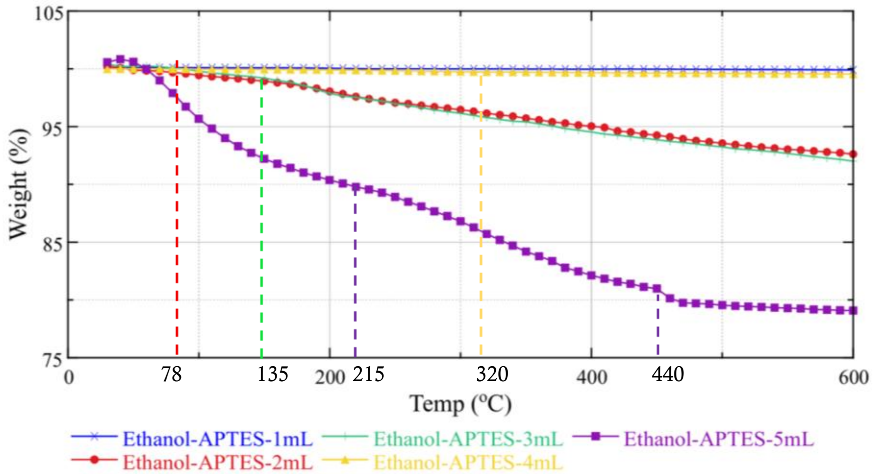

Figure 2. Graph of TGA result of amine modified silica with ethanol solvent

According to Figure 2, there is no significant mass loss for modified silica with ethanol solvent with the addition of APTES-1 mL, which is caused by the absence of decomposable organic components. This can occur due to the sample drying process or an insufficient analysis temperature range. With the addition of APTES-2 mL, there is a first mass loss from room temperature to 78 °C, which is caused by the desorption of ethanol contained in the modified silica. Then there is a second mass loss at which is related to the decomposition of organic species, such as alkyl groups, in the modified silica (Peixoto et al., 2016).

With the addition of APTES-3 mL there is a first mass loss from room temperature to 135 °C, which is caused by the decomposition of extra aminopropyl groups. With the addition of APTES-4 mL there is a first mass loss from room temperature to 320 °C, which is caused by the decomposition of NH_2. With the addition of APTES-5 mL, there is a first mass loss from room temperature to 215 °C, which is caused by the decomposition of NH_2. Then there is a second mass loss at 215-440 °C, which is caused by the decomposition of oxyethyl. There is a third mass loss at 440-600 °C, which is related to the decomposition of organic species, such as alkyl oxy and alkyl groups, in modified silica (Tao et al., 2016). A sharp weight decrease of APTES-5 mL is observed at temperature of about 440 °C, the same decrease in weight is also has been reported by de O. N. Ribeiro et al., 2019.

The following is a graph of TGA result of amine modified silica using water as the solvent.

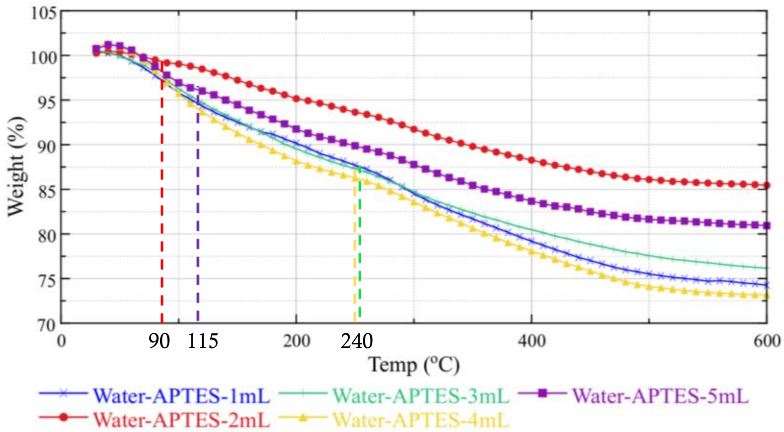

Figure 3. Graph of TGA result of amine modified silica with water solvent

According to Figure 3, In the production of modified silica using water as the solvent with the addition of APTES-1 mL, there is a significant mass loss from room temperature to 600 °C, which indicates the absence of water desorption. With the addition of APTES-2 mL, there is first a mass loss from room temperature to 90 °C, which is caused by water desorption (Yang et al., 2012).

Then there is a second mass loss at 90-600 °C, which is related to the decomposition of organic species, such as alkyl groups. With the addition of APTES-3 mL and APTES-4 mL there is a first mass loss from room temperature to about 240 °C, which is caused by the decomposition of NH_2. Then there is a second mass loss at 240-600 °C, which is related to the decomposition of organic species, such as alkyl groups (Yue et al., 2015).

When APTES-5 mL is added, there is a first mass loss from room temperature to 115 °C, which is caused by water desorption followed by a second mass loss that occurs at 115-600 °C. The relatively large mass difference can be caused by the degradation of organic groups that do not interact with the silica surface (Wamba et al., 2018).

The following is a graph of TGA result of amine modified silica using toluene as the solvent.

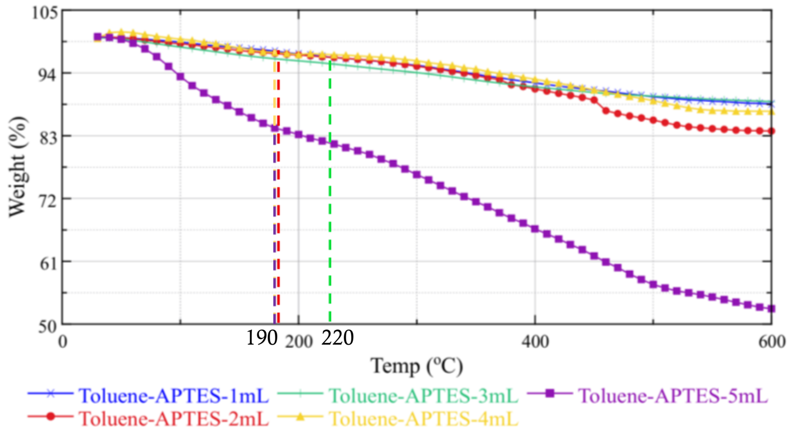

Figure 4. Graph of TGA result of APTES modified silica with toluene solvent

According to Figure 4, In the production of modified silica using toluene as the solvent with the addition of APTES-1 mL there is a mass loss from room temperature to 600 °C. With the addition of APTES-2 mL, APTES-4 mL, and APTES-5 mL there is a first mass loss from room temperature to 190 °C, where there is an endothermic phenomenon and the melting point of the amine modified material occurs at 180 °C. With the addition of APTES-3 mL there is a first mass loss from room temperature to 220 °C, which is caused by the decomposition of NH_2. This relatively large mass difference can be caused by the degradation of organic groups that do not interact with the silica surface (Wamba et al., 2018).

Based on the analysis results, it can be concluded that the greater the difference in mass changes as the temperature increases, the higher the number of APTES successfully grafted in the silica modification process. In the sample using ethanol solvent, the modified silica successfully grafted with the most APTES are samples with the addition of APTES-5 mL, APTES-2 mL, and APTES-3 mL. In the sample using water solvent, the modified silica successfully grafted with the most APTES are samples with the addition of APTES-1 mL, APTES-3 mL, and APTES-4 mL. The toluene solvent sample with the addition of APTES-5 mL is the sample with the greatest grafting results among the other samples. This is in accordance with the theory of Rahman, 2022 that the greater the mass loss and the greater the amount of amine used in the amine grafting process, the higher the amount of amine that can attach to the modified silica.

The calculation of amine loading on amine modified silica

The following is a table of amine loading data on silica that has undergone a grafting process using APTES.

Tabel 1. Table data of amine loading on silica amine using grafting method

Type of solvent	Volume of APTES (mL)	Amine loading (mmol γ aminopropyl/g silica)
Etanol	1	0,0258
50 mL	2	0,9336
	3	1,0094
	4	0,0622
	5	1,9430
Air	1	2,7350
50 mL	2	1,6704
	3	2,3006
	4	2,5819
	5	1,8605
Toluene	1	1,5063
50 mL	2	2,2930
	3	1,2304

	4	1,7077
	5	5,2552

According to table 1, the TGA results and calculations that have been carried out on all samples with the addition of ethanol, water, and toluene as solvents and the addition of APTES of 1, 2, 3, 4, and 5 mL, a conclusion can be drawn on the comparison between the mass loss of the analyzed samples and the amount of amine loading on the modified silica. In ethanol and toluene solvents, the highest amount of amine loading is found in the addition of 5 mL of APTES at 1,9430 and 5,2552 mmol γ aminopropyl/g silica, while in water solvent, the highest amount of amine loading is found in the addition of 1 mL of APTES. The conclusion obtained is that the greater the percentage of mass loss in the TGA process, the higher the value of amine loading contained in the modified silica (Rahman, 2022), and anhydrous solvent such as toluene is the better solvent used for grafting process. The same finding has been reported by de O. N. Ribeiro et al., 2019, where sample with ethanol and toluene as solvent with 5 mL of APTES has the amine loading of 1,2 mmol/g and 2,4 mmol/gram. The higher level of amine loading found in this study is due to the longer reflux time, which gives the amine groups more time to leach on the mesoporous silica.

Fourier Transmission Infra-Red (FTIR) analysis of functional groups in amine modified silica

In the FTIR curve of silica before amine modification, a peak appears at a wavelength of 3743 cm^{-1}, indicating the presence of silanol groups. This peak does not appear in the FTIR analysis results for the amine-modified silica curve with the addition of ethanol, water, and toluene solvents, and an additional 3 mL of amine volume. The following is the curve of unmodified silica according to Rahman et al., 2022.

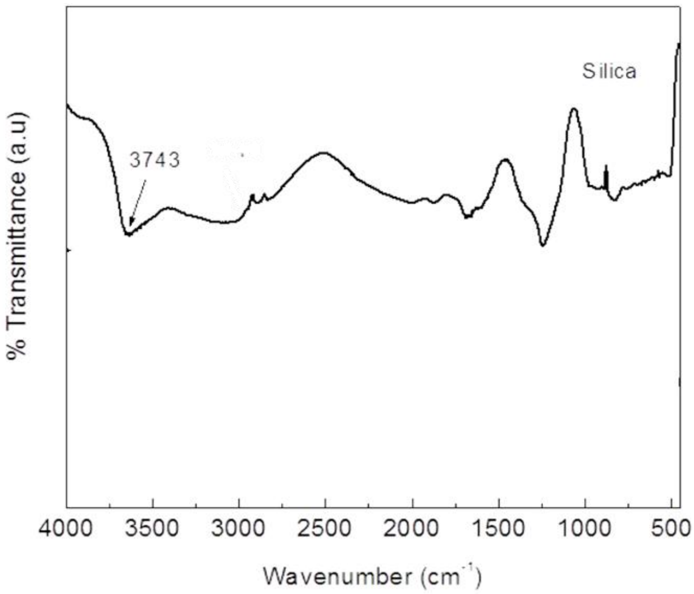

Figure 5. FTIR of mesoporous silica before grafting

The following is a graph showcasing the FTIR result of amine modified silica using ethanol, water, and toluene as solvent.

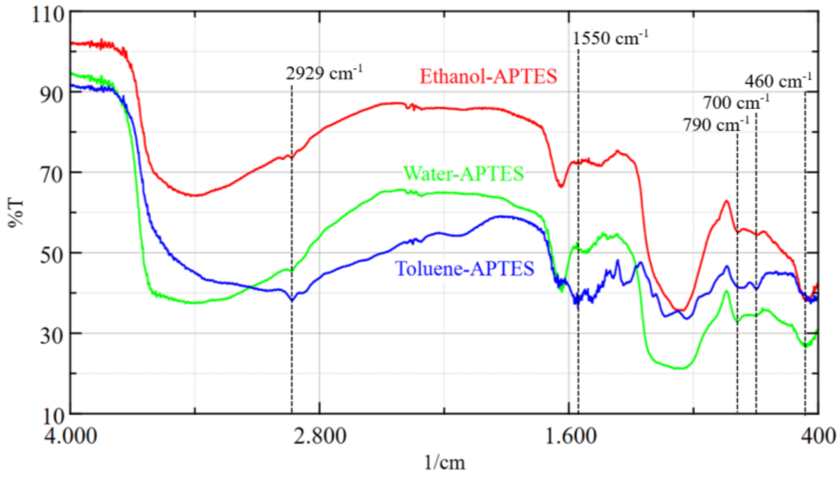

Figure 6. Graph of FTIR test of APTES modified silica

According to figure 6, the FTIR analysis results on amine modified silica with ethanol, water, and toluene solvent, there is a Si-O group where a peak occurs at a wavelength of 460 cm^{-1} (Koshraftar et al., 2021). For ethanol and water solvent, a peak appears at a wavelength of 1051 cm^{-1} indicating the presence of an C-O functional group which usually appears at a wavelength of 1050-1300 cm^{-1}. For ethanol, water, and toluene solvent, peak appears at wavelength of 1500-1550 cm^{-1} indicates the presence of an $-NH_2$ group (Bertuoli et al., 2014). For ethanol and water solvent, peak occurs at 3422 cm^{-1} which usually appears at a wavelength of 3000-3500 cm^{-1} indicates the presence of stretching in the -OH bond (Wamba et al., 2018).

The FTIR analysis results of amine modified silica with water solvent, the presence of a peak at a wavelength of 790 cm^{-1} indicates the presence of Si-O deformation stretching. The peak at a wavelength of 1633 cm^{-1} indicates the presence of asymmetric -OH in water molecules.

The FTIR analysis results of amine modified silica with toluene solvent. Peaks appear at wavelengths of 700 and 933 cm^{-1} indicating the presence of C-H functional groups that usually appear at wavelengths of 675-995 cm^{-1}. There is a peak at a wavelength of 1180-1360 cm^{-1} indicating the C-N amine group. There is a peak at a wavelength of 1610-1680 cm^{-1} indicating the C=C group of alkenes. Peaks at wavelengths of 2885, 2929 cm^{-1} indicate the presence of the C-H functional group (Wamba et al., 2018).

In the FTIR analysis results of amine modified silica, the wave peaks formed between 675-995 cm-1, 1317-2946 cm^{-1} can indicate that Si-OH in silica has been used by the reaction with grafted APTES. The peak at a wavelength of 970 cm^{-1} is not seen in the analysis results due to the release of H bonds between Si-OH on the silicon wall so that bonds are formed between Si-OH and N caused by increased amine loading on modified silica (Zhang et al., 2019). This finding is also has been reported by de O. N. Ribeiro et al., 2019. The peak at a wavelength of 3743 cm^{-1} indicates the presence of silanol groups that appear on the curve of unmodified silica, do not appear on the curve of amine modified silica on the addition of ethanol, water, and toluene solvents, which indicates success in grafting amine groups on modified silica (Rahman, 2022).

CONCLUSION

From the results of the experiments that have been carried out, it can be concluded that the type of solvent, including ethanol, water, and toluene, the solvent with the highest level of efficiency in modifying silica sand adsorbents is the toluene solvent type. In the calculation results, the amount of amine loading grafted on amine-modified silica is the highest when adding toluene solvent.

In the experimental results, the highest amount of amine loading grafted onto amine-modified silica was at the addition of 5 mL of amine volume, namely at the addition of ethanol and toluene solvents, namely 1,9430 and 5,2552 mmol γ aminopropyl/gram of silica, but not in water solvent. This indicates that the more amine loading successfully attached to silica sand, the higher the efficiency level of silica sand adsorbent modification. The results of this study can be used as an additional basis for the use of modified silica as an adsorbent that can be used in CO_2 capture, especially in the selection of solvents and volume of APTES.

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