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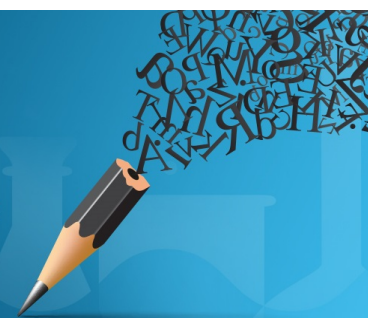
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The Potential of Silica from Rice Husk Ash on Removal of Sulphide in Wastewater

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Abstract. The production of propylene from propane dehydrogenation process in the petrochemical sector regularly produce high concentration of sulphur in the form of sodium sulphide (Na_2S). High concentration of sulphide can lead to corrosion in sewage pipes, massive fish kill and obnoxious odors into the atmosphere. Adsorption technique using low-cost and environmentally friendly adsorbents derived from natural resources such as rice husk ash (RHA) may offer a suitable alternative for in situ removal of contaminants such as sodium sulphide in industrial wastewater. In this work, the use of silica synthesized from RHA was investigated for its potential in removing high concentration of sulphide (S^{2-}) in the form of sodium sulphide from wastewater. Results showed that pure silica with the size around 0.9 to 2.0 µm was successfully synthesized from RHA. Significant reduction of sulphide level was observed after being treated with RHA-based silica calcined with clay compared to other adsorbents such as chemically treated nanoporous zeolite and natural clay itself with more than 90 % removal after 120 minutes of treatment with the value of the pseudo-first-order rate constant, k of 0.1404, 0.14 and 0.1519 for silica compared to zeolite. This suggests that the use of silica derived from RHA has a potential to be used as sulphide remover in industrial wastewater without extensive chemical treatment to improve its removal capacity.

INTRODUCTION

Sulphide (S^{2-}) is an inorganic anion of sulphur which can be derived from sodium sulphide (Na_2S) or hydrogen sulphide (H_2S) in the wastewater effluent from petrochemical sector [1]. High concentration of sodium sulphide produced during propylene production from propane dehydrogenation process has become the most common problem for many petrochemical companies [2]. The excess amount of sulphide can lead to corrosion of sewage pipes as well

as causing wide ranges of health and environmental effects [3]. Conventional methods have been applied by most industrial companies in treating their wastewater effluents such as membrane filtration, chemical precipitation, ion exchange, coagulation, flocculation, oxidation, electrolysis, reverse osmosis and adsorption [4–7]. However, these methods require high maintenance cost, skilled manpower to operate, treating specific contaminants, impracticable and not environmentally friendly. Chemical methods such as oxidation, ion exchange and electrochemical treatments can remove wide range of heavy metals, however, their application is inadequate because of high energy costs and formation of by-products [8,9]. Physical methods such as membrane filtration and reverse osmosis may lead to the fouling of the membrane and production of concentrated sludge during treatment process respectively [10].

Adsorption has been proved to be a simple and effective technique in treating wastewater effluents as its success basically depends on the efficiency of the adsorbents [11]. Various types of low-cost adsorbents such as zeolites, clays, rice husk, coconut husk and palm press fibers have been developed and applied in wastewater treatment from industrial wastes, agricultural wastes and natural materials [12–14]. Low-cost adsorbents from agricultural wastes can be easily obtained due to its abundance in nature and sometimes only requires a little modification to improve their adsorption capacity [15]. Many adsorbents are known as cation exchanger as they can remove most cationic contaminants presented in wastewater effluents. However, anionic contaminants such as sulphide in the form of S^{2-} are also presence in wastewater effluents which could bring negative impacts to human health and environment. Natural zeolites such as clinoptilolite, mordenite and natrolite have been studied for its potential in treating wastewater [11,16,17]. Natural zeolites are particularly competent for removing undesirable heavy metal ions from industrial wastewater because of its exchangeable ions which are relatively innocuous [4]. However, natural zeolite was less effective in removing anionic contaminant such as phosphate ions (PO_4^{3-}) [18] and diclofenac [19]. Clays can also be considered as an alternative in removing contaminants from wastewater due to its porosity, surface charge, surface functional group and large specific surface area [20]. Clays are composed of phyllosilicate minerals that contain amount of water molecules trapped in the mineral framework [21]. Known as cation exchanger, the surface of clay is predominantly negatively charged, therefore can only capture a little number of anions in solutions [22]. Although there are studies reported about the use of clay to remove sulphur compounds [23-25], no studies were done on the removal of sulphide ion (S^{2-}) by adsorption technique using clays. Altering the surface properties using chemical modification with cationic surfactants were shown to improve the removal of anionic contaminants by zeolite and clay [17,18,26]. However, the use of cationic surfactants especially inorganic salts may increase the potential of heavy metal contamination in the treated water. Rice husk ash (RHA) is a low-cost agricultural waste that has been studied for its potential as adsorbent in wastewater treatment [15]. RHA was able to remove other heavy metals such as arsenic(V), chromium (VI), Nickel (II), Cobalt (II) [27-29] as well as other material-based contaminants such as Acid Orange 7 and Amoxicillin [30]. Interestingly, silica derived from RHA was also found to be a good adsorbent to eliminate inorganic contaminants due to its high porosity and large surface area [5,31]. Sivakumar [32] reported a maximum removal of chromium (VI) with 88.3 % removal at an optimum adsorbent dosage of 15 g of silica derived from RHA. It was also reported that 70 % of Zn^{2+} was successfully removed in 100 minutes of treatment time at pH of 5.56 while Cu^{2+} was removed up to 90 % in 60 minutes at pH of 4.8 after being treated with silica derived from RHA [33]. In this work, we investigated the potential of silica derived from RHA in removing high levels of S^{2-} in the form of sodium sulphide in wastewater and compared it with other natural adsorbents such as natural zeolite and clay. We also compared the removal efficiency with chemical modification method in removing sulphide from wastewater.

MATERIALS AND METHODS

Acid treatment to produce silica was performed on RHA according to the method of Dung et al [34]. 200 g of RHA was added into 1.2 L of 1 N hydrochloric acid (HCl) solution. Afterward, the mixture was continuously stirred for 2 hours at 80℃ by using hot plate and immersed for overnight to remove any metal ions in RHA. Acid treated RHA was filtered, washed with distilled water and dried in an oven at temperature of 70℃ for 1 hour and then desiccated in a furnace at temperature of 700℃ for 2 hours. Particulate size analysis (PSA) (Malvern Zetasizer, United Kingdom) was used to analyse the size ranges of samples from the calcined RHA. The samples underwent sonication through probe sonicator with a dilution level of 0.01 g/20 mL at a range between 0 – 10,000 nm before analysed with PSA. Samples were also observed with a scanning electron microscope (SEM) (Zeiss EVO 50, Germany) for a detailed imaging of the particulate size and morphology. The samples were covered with gold coating (Sputter Coater Leica SDC005, Germany) before being observed under SEM. Fourier transform infrared (FTIR) measurements were also performed at room temperature in the range 4,000–400 cm^{-1} using the FTIR spectrometer (Frontier FT-IR, PerkinElmer, USA). To produce treatment balls, Silica synthesized from RHA in the previous step was mixed with

natural clay to hold the silica material at the ratio of 1:1 by adding deionized water into the mixture of RHA and clay. Commercially available nanoporous zeolite (mordenite type), in the form of powder (NanoMalaysia Berhad) was mixed with deionized water until it can be molded. To produce a combination of zeolite and clay, both materials were mixed at the ratio of 1:1 until it formed a smooth mixture. To produce treatment balls for each material, they were molded into a small ball with the size of approximately ± 0.7 cm diameter. All the treatment balls were then desiccated in a furnace with a temperature of 1000 ℃ for 48 hours before ready to be used. Chemical modification on the surface of adsorbents was performed according to the method of Aprianti et al [35] using $FeCl_3$ as cationic surfactants [17]. The prepared adsorbent balls were immersed into 1 M of iron (III) chloride ($FeCl_3$) solution for 1 hour as to fill in the pores with more cationic charges. The ceramic adsorbents were then washed with sufficient distilled water to wash off excessive surfactants and then dried in an oven at temperature of 150 ℃ for 1 hour before it was ready to be used in the treatment. The concentration tested was 20 ppm, 15 ppm, 10 ppm, 5 ppm and 1 ppm of Na_2S solution. Standard curve was constructed based on these 5 concentrations. The concentration of sulphide ions in the solution was quantified using UV-Visible spectrophotometer based on the US EPA Methylene Blue Method. The adsorption treatment method was carried out by adding 0 g (control), 1 g, 5 g, 10 g, 15 g and 20 g of adsorbent balls into 100 mL of synthetic wastewater. The measurement of concentration of sulphide ions in synthetic wastewater was carried out by following the US EPA Methylene Blue Method containing Sulphide 1 and 2 Reagents. The absorbance of the samples was measured using UV-Visible spectrophotometer at wavelength of 665 nm. Data collected from experiment were analysed for its concentrations (based on standard curve), means, standard errors and clustered columns. One-way ANOVA test was performed for each data by using Sigmaplot software.

RESULTS AND DISCUSSION

Calcination of acid treated RHA with high temperature led to the production of silica. Decreasing in the weight after pre-treatment processes showed that both impurities and large particles were successfully removed during acid treatment process and calcination. Morphological analysis of silica (Fig. 1) observed that the average size distribution of the silica is around 0.9 – 2.0 μm as shown in Table 1. Large clumps of particulate in the sample with a rough patterned texture at the outer epidermis, in which looks like a burnt off chunk of rice husk ash. Both points of Pa 1 and Pa 2 indicates that the particulates are large in size (with diameter of 462.3 μm and 33.09 μm respectively). The clumps which include black clump or unburnt RHA of particulate appear to be similar to RHA observed under SEM on previous work [36]. FTIR analysis showed absorption peaks at 3458.17 cm^{-1}, 1635.89 cm^{-1}, 1095.09 cm^{-1}, 799.72 cm^{-1} and 470.38 cm^{-1}. Broad peak at 3458.17 cm^{-1} is primarily due to the presence of -OH bond stretching such as silanol hydroxyl groups (Si-OH) which happen due to chemically and physically adsorbed water molecules on the surface of silica [37, 38]). The following peak observed at 1635.89 cm^{-1} could be due to the presence of impurities such as sodium and carbonate group (-COOH) [39]. The peak at 1095.09 cm^{-1} represents functional groups of Si-O-Si [40] while 799.72 cm^{-1} and 470.38 cm^{-1} are due to the presence of simple hydroxyl compound and Si-H respectively [41].
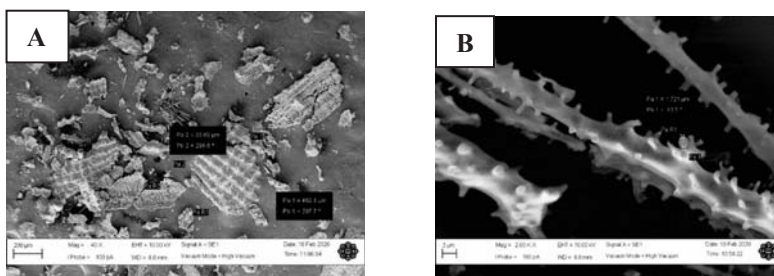

FIGURE 1. The calcined RHA sample observed under SEM.

TABLE 1. Average size distribution of silica extracted from RHA. Data were obtained using Malvern Zetasizer particle size analyzer with water as the dispersant.

Sample	Average Size (μm)
1	1.674
2	0.9237
3	1.190

TABLE 2. FTIR spectra of extracted RHA powder

Wavelenght (cm^{-1})	Description	References
470.38	Si-H	[41]
799.72	simple hydroxyl compound	[41]
1095.09	Si-O-Si linkage	[40]
1635.89	sodium and carbonate group (-COOH)	[39]
3458.17	silanol hydroxyl groups (Si-OH)	[37, 38]

The removal of S^{2-} from wastewater sample was influenced by the types of adsorbents and their concentrations. Based on Fig. 2 A), only 7 % of S^{2-} was removed from wastewater samples treated with zeolite adsorbent after 120 minutes of treatment time ($p>0.05$). Previous works investigated the removal of anion contaminant, phosphate ion (PO_4^{3-}), from wastewater by using natural zeolite treatment. However, the result showed that natural zeolite was less effective for reducing phosphate ions from wastewater [18]. It proved that the efficiency of natural zeolites was better in removing cations rather than anions. It can also be hypothesized that S^{2-} in wastewater samples can be completely removed by zeolite if the surface area of the adsorbent is modified with cationic surfactant as zeolite has low adsorption capacity for sulphide contaminant. Clay adsorbent was able to remove up to 30 % of S^{2-} in wastewater especially after treated for 120 minutes ($p>0.05$) (Fig. 2 B). It also showed that the adsorption capacity of clay for anion removal is slightly greater than zeolites (7 % removal) even though clay was claimed as cation exchanger [20]. The efficiency of adsorbents including clay minerals for S^{2-} removal may depend on several environmental factors such as pH, ionic strength, surface area, pore volume and pore structure. Therefore, further investigation can be done by looking at various pH levels, increased surface area of the adsorbents, surface modification as well as longer treatment time.
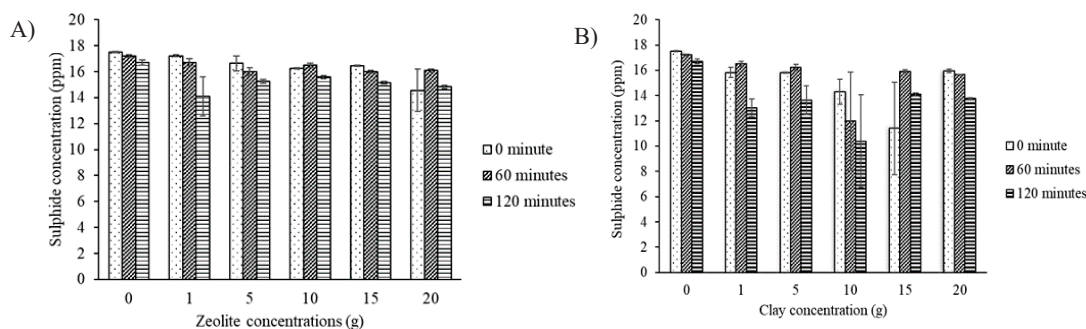

FIGURE 2. A) Removal of S^{2-} by zeolite adsorbent without surfactant. B) Removal of S^{2-} by clay adsorbent without surfactant Results are the mean from 3 sample replicates ± SEM. ANOVA

Silica obtained in this work was also mixed with clay to form balls due to its crystalline and amorphous structure that weakens its adhesion and cohesion strength. Result indicates that the concentration of S^{2-} decreased as the amount of silica balls increased over treatment time (Fig. 3). 94 % removal of S^{2-} was recorded when 20 g of silica balls were tested on 20 ppm of sulphide for 120 minutes. More than 50 % of S^{2-} removal was obtained when 10 g of silica balls was tested for 60 minutes. Adsorbent made from the mixture of silica and clay can reduce and almost completely remove S^{2-} within short treatment time especially when high amount of adsorbent is used in wastewater treatment. Anion contaminants are also able to be reduced and removed by adsorbents which can be made from agricultural wastes with a little modification process involved.
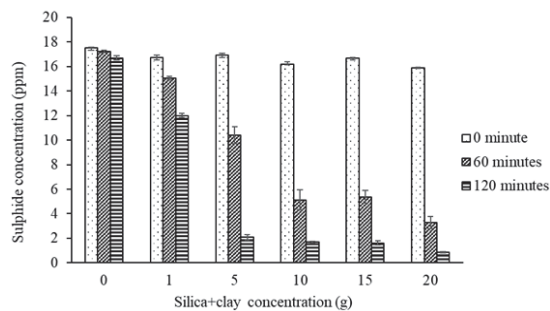
FIGURE 3. Removal of S^{2-} by silica+clay adsorbent without surfactant. Results are the mean from 3 sample replicates $\pm$ SEM. ANOVA.

Previous studies reported that modification of the surface of adsorbents with cationic surfactant will further improve their adsorption capacity and efficiency towards anionic contaminants in wastewater [17,18]. In this study, FeCl$_3$ was selected as cationic surfactant for the surface modification. Fig. 4 A) showed a significant reduction of S^{2-} concentration in wastewater treated with modified zeolite compared to the unmodified ones where S^{2-} was nearly removed within 120 minutes of treatment time (p<0.05). Similar observation can also be seen on modified clays (Fig. 4 B) could be due to the binding capacity of anions with cationic surface of modified zeolite and clay adsorbent as the surface of adsorbents was dominantly occupied with positively charged ions from FeCl$_3$, as observed in previous works [17]. In the absence of surfactant, unmodified adsorbents required a longer treatment time to completely remove S^{2-} from wastewater samples. Modification of the surface of clay adsorbents were found to increase its porosity which led towards higher adsorption capacity, shorten the treatment period and reduce the concentration of S^{2-} in wastewater. The reduction of S^{2-} concentration was greatly influenced by the cationic surfactant on the surface of the adsorbent as it was able to attract and trap the S^{2-} contaminant in the porous surface of adsorbents.
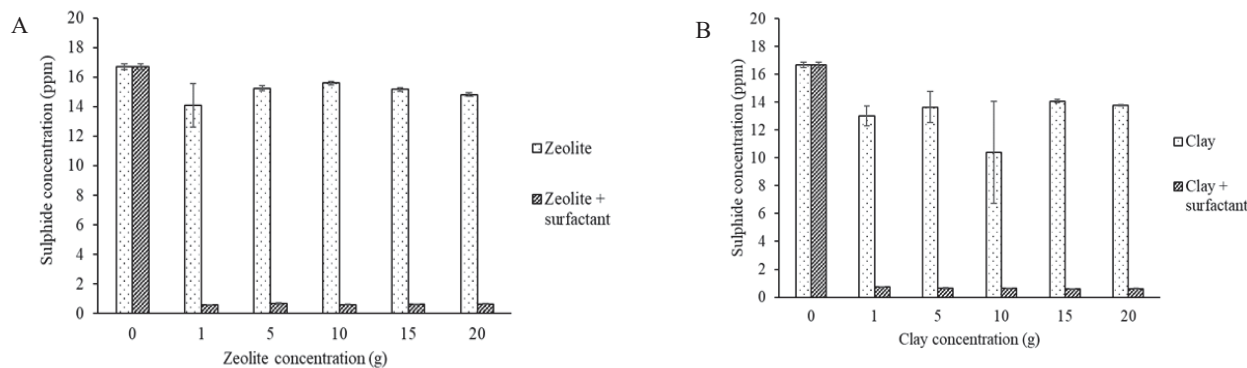

FIGURE 4. A) Removal of S^{2-} by zeolite and modified zeolite. B) Removal of S^{2-} by clay and modified clay. Results are the mean from 3 sample replicates $\pm$ SEM. ANOVA.

The performance of silica balls on sulphide removal was further compared with zeolite mixed with clay adsorbent since silica balls were made from the mixture of silica and clay. Silica balls showed higher efficiency in reducing S^{2-} concentration compared with zeolite with more than 50 % after 10 minutes of treatment (p<0.05) (Fig. 5). This might due to their larger surface area, higher porosity and greater adsorption capacity which able to eliminate more ions, and thus become an effective adsorbent in wastewater treatment [5]. The concentration of S^{2-} was gradually reduced as the concentration of silica balls increased. It was also observed that 10, 15 and 20 grams of silica balls were able to remove more than 50 % of 20 ppm S^{2-} levels after 60 minutes of treatment compared to zeolite. The removal of S^{2-} in this work was purely due to silica instead of clay or zeolite. No surface modification treatment using cationic surfactant was conducted on silica further proving its efficiency in removing S^{2-} in wastewater.
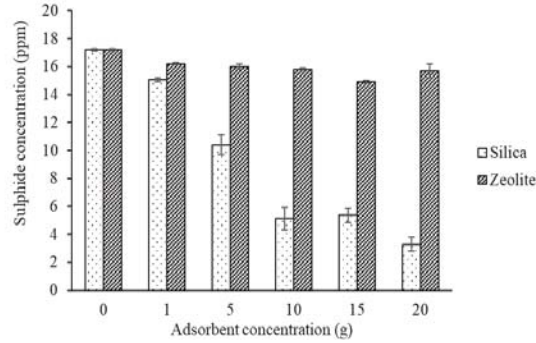
FIGURE 5. Removal of S^{2-} by zeolite and silica in 60 minutes of treatment. Results are the mean from 3 sample replicates ± SEM. ANOVA.

The data obtained were plotted for kinetic analysis to compare the removal rate of S^{2-} between non-treated zeolite and silica after 2 hours of exposure to different concentration of S^{2-}. The Michaelis-Menten-type equation was applied where C, S^{2-} concentration (μ/L); t, time of exposure (minutes); Vm, maximum removal rate (μg S^{2-}/L dry material) and Ks, saturation constant (d^{-1}). Based on the results obtained in Table 3, higher removal rate of S^{2-} (more than 90% removal) was observed after 10 g, 15 g and 20 g of silica balls were exposed to S^{2-} after 120 minutes of treatment with a value of the pseudo-first-order rate constant, k of 0.1404, 0.14 and 0.1519 respectively compared to zeolite balls. In silica derived from RHA, other than having high porosity and large surface area, the presence of rich positively charged ions on its surface had increased its ionic interactions with anionic contaminant such as S^{2-}. However, as the ionic charges of the surface of silica can be highly influenced by pH value, more studies are required to investigate S^{2-} binding to silica from RHA at different pH values. Low adsorption of S^{2-} to zeolite was due to its less efficient binding onto anionic contaminants such phosphate. Surface modification of zeolite with cationic surfactant such as $FeCl_3$ had significantly improved S^{2-} removal as observed in this work.

TABLE 3. Comparison of calculated values of saturation constant k, Log and R squared values between zeolite and silica.

(mg/L)	k (d^{-1})		Log (qe-qt)		R^2 values	
	Zeolite	Silica	Zeolite	Silica	Zeolite	Silica
1	-0.0033	0.04	1.177394	0.885721	0.9938	0.9756
5	0.0207	0.12	1.13115	0.64256	0.8502	0.9956
10	0.0319	0.14	1.037576	0.295187	0.905	0.9507
15	0.039	0.14	0.922075	-0.00876	0.9075	0.9578
20	0.022	0.15	0.965931	-0.39956	0.9654	0.9297

CONCLUSION

Low-cost adsorbents such as RHA offers the possibility for in situ removal of contaminants in industrial wastewater. The ability of silica from RHA for sulphide removal has been studied by comparing the adsorption capacity with other adsorbents such as natural zeolites and clays, which known as cation exchanger. This preliminary result indicates that silica has high potential in removing sulphide from wastewater without being need for further chemical treatment as compared to natural zeolite and clay which offers a greener approach in remediation of industrial wastewater. Further research on other parameters such as pH of wastewater must be investigated to ensure the water is neutral and safe before released into water sources.

ACKNOWLEDGEMENTS

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