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Monoethanolamine Wastewater Treatment via Adsorption Method: A Study on Comparison of Chitosan, Activated Carbon, Alum and Zeolite

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Abstract: This research was conducted to evaluate the feasible methods to recycle and reuse the monoethanolamine (MEA) in the CO_2 removal unit and at the same time, maintaining the amine concentration level. The adsorption performance of chitosan was compared to activated carbon, alum and zeolite. Amine contaminated waste water contains about 230,000 mg L^{-1} of COD, 69,000 mg L^{-1} of suspended solid, 596 mg L^{-1} of residue oil and 41% of amine concentration. Preliminary results showed that application of chitosan managed to reduce the COD by up to 83%, suspended solid by up to 57 and 95% for residue oil removal at the defined optimum experimental condition (weight of absorbent: 5%, contact time : 1 h, mixing rate: 100 rpm, ambient temperature : 25-30°C and pH 11). For activated carbon, alum and zeolite, the results showed reduction of COD by up to 80, 73 and 70%, suspended solid by up to 49, 43 and 38%, respectively. For residue oil removal, activated carbon was 87%, alum was 64% and zeolite was 46% at the same experiment conditions. In conclusion, chitosan showed the best adsorption performance followed by activated carbon, alum and zeolite.

Key words: Chitosan, amine, COD, suspended solid, residue oil

INTRODUCTION

In petrochemical industry, especially in natural gas processing plant, raw natural gas which contains carbon dioxide needs to be treated to remove the CO_2 prior further processing activities. This CO_2 is considerably as interference in the processing activities and would thwart the product quality. Additionally, the CO_2 recovered from the process, often stored for other applications, for instance it can be used for enhanced oil recovery application or in the chemical and food industries. In other industries, CO_2 also has been removed from the flue gases before releasing to atmosphere through stack. This is done to minimize the greenhouse effect and circuitously generate revenue to the company by selling the recovered CO_2. Technologies to separate CO_2 from flue gases are based on absorption, adsorption, membranes or other physical and biological separation methods. The most commercially used technology is amine based CO_2 absorption systems. The reasons being used widely are the system can be used for dilute systems and low CO_2 concentration, easy to use and can be retrofitted to any plants. Absorption processes are based on thermally regenerable solvents, which have a strong affinity for CO_2. The solvent is regenerated at elevated temperature, thus requires thermal energy for the regeneration (Abu-Zahra *et al*., 2007). Currently, aqueous mono-ethanolamine (MEA) is widely used for removing carbon dioxide and hydrogen sulfide from flue gas streams (Harold *et al*., 2004). It has been used in the Flour Daniel technology's Econamine FG™ and Econamine FG Plus™ (Mariz, 1998) and the ABB Lummus Global technology (Barchas, 1992). MEA is an organic chemical compound which has both primary amine (due to an amino group in its molecule) and a primary alcohol (due to a hydroxyl group). Like other amines, MEA acts as a weak base, toxic, flammable, corrosive, colorless and viscous liquid with an odor similar to ammonia. MEA is produced by reacting ethylene oxide with ammonia (Harold *et al*., 2004).

The conventional MEA flow sheet is shown in Fig. 1. The flue gas containing CO_2 enters the absorber and contacts an aqueous solution of MEA flowing counter currently to the flue gas stream. CO_2, a weak base, reacts exothermically with MEA, a weak acid, to form a water soluble salt. The rich MEA stream exits the absorber at the bottom of the column. It is then preheated in a heat exchanger by the lean MEA stream leaving the stripper and enters the stripper where, with the further addition of heat, the reaction is reversed. The chemical solvent is regenerated in the stripper at elevated temperatures

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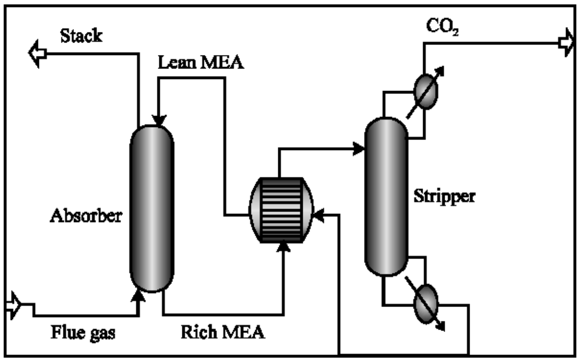

Fig. 1: Basic MEA CO_2 capture process flow sheet

(100-140°C) and a pressure not much higher than atmospheric. Heat is supplied to the reboiler using low-pressure steam to maintain regeneration conditions. This leads to a thermal energy penalty because the solvent has to be heated to provide the required desorption heat for the removal of the chemically bound CO_2 and for the production of steam, which acts as stripping gas. Steam is recovered in the condenser and fed back to the stripper, after which the produced CO_2 gas leaves the condenser. The lean MEA is then recycled back to the absorber (Alie *et al*., 2005). Focusing on the CO_2 absorption process, the heavy hydrocarbon component could be carried over to the absorber with the feed gas which caused sudden foaming in the absorber. The reaction between CO_2 and MEA will produced some salt and increased the amount of suspended solids in absorber also contributed to the foaming problem.

This foaming phenomenon give a number of different problems such as decreased absorption efficiency, increased amine losses, reduced quality of product gas and MEA somehow is not appropriate to feed back into the striper due to properties deterioration and thus give difficulties in optimizing the absorption processes and it has been removed as wastewater.

Once the MEA wastewater enters the Wastewater Treatment Plant (WTP), it will upset the WTP by increasing the loading and significantly increase the COD, oil concentration and suspended solids which complicate the effective treatment of such wastewater. In many occasions, the concentration of amine in the wastewater triggers the COD to exceed the 200,000 ppm level and not possible to be sent to the wastewater treatment plant. The MEA wastewater then has to be stored for disposal and conversely, it costs a lot of money for waste disposal handling, to buy fresh MEA and thus, minimizes the profit margin.

In this study, four types of adsorbents which are chitosan, activated carbon, alum and zeolite based adsorption method were employed and explored in order to examine its feasibility in reducing the COD, suspended solid and oil concentration in the MEA wastewater and at the same time maintaining the level of amine concentration at acceptable limit. Adsorption method is chosen due to its direct application, simple, easy and widely used in wastewater treatment plant. In view of the fact that the MEA wastewater is produced abundantly from petrochemical plants and other processing plants for instance power plant and the lack of researches have been carried out to date, the research needs is significantly important in order to find alternative route methods for treating MEA wastewater which is inexpensive, simple, economically viable and environmental friendly.

Adsorption is the process of accumulating substances that are in solution on a suitable interface. Adsorption is a mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase. The adsorbate is the substance that is being removed from liquid phase at the interface. The adsorbent is the solid, liquid or gas phase onto which the adsorbate accumulates. The adsorption process has not been used extensively in wastewater treatment, but demands for better quality of treated wastewater effluent, including toxicity reduction and has led to an intensive examination (Metcalf and Eddy, 2003). The driving force for adsorption is unsaturated forces at the solid surface which can form bonds with the adsorbate. The forces are typically electrostatic, covalent bonding or van der Waals interactions (reversible).

Stronger interactions involve direct electron transfer between sorbate and the sorbent (irreversible). The strength of this interaction dictates the relative ease or difficulty in removing (desorbing) the adsorbate for adsorbent regeneration and adsorbate recovery. The selective nature of the adsorbent is primarily due to the relative access and strength of the surface interaction for one component in a feed mixture. The solid is the mass-separating agent and the separating mechanism is the partitioning between the fluid and solid phase. An energy separating agent, typically a pressure or temperature change is used to reverse the process and regenerate the sorbent (Richard and Terry, 2004). Adsorption processes are used economically in a wide variety of separations in the chemical process industries. Activated carbon is the most common adsorbent with annual worldwide sales estimated at 380$ million (Richard and Terry, 2004). One common adsorption process is dehydration for the drying of gas stream.

Chitosan, activated carbon, alum and zeolite are four types of adsorbents, which have been used in many applications, ranging from food and separation technology to wastewater treatment. Chitosan is one of the natural products that are potentially can be used as adsorbents. Chitosan is cationic biodegradable biopolymer produced by the extensive deacetylation process of chitin obtained from shrimp shell wastes. Moreover, chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is produced commercially by deacetylation of chitin, which is the structural element in exoskeleton of crustaceans (origin from crabs, shrimp, etc.) (Shahidi and Synowiecki, 1991). Chitosan, poly (D-glucosamine) a natural deacetylated marine polymer has been used in a variety of practical fields including wastewater management, pharmacology, biochemistry and biomedical (Majeti, 2000). Chitosan has excellent properties such as biodegradability, hydrophilicity, insoluble in water, biocompability, adsorption property, flocculating ability, polyelectrolisity, antibacterial property and its capacity of regeneration in a number of applications (Feng *et al*., 2000). Its largest use is as non-toxic adsorbents in the treatment of organic polluted wastewaters and as a chelating agent for toxic (heavy and reactive) metals (An *et al*., 2001).

Activated carbon is used as an adsorbent in many industrial applications as an economic mass separation agent to raise the final product quality. Drinking water, wastewater treatment processes, food and chemical industry processes are typical examples (Sophie and Pendleton, 2001). Activated carbon is the most common adsorbent due to its large surface area per unit mass (300 to 1500 m^2g^{-1}). The surface of activated carbon is non polar or only slightly polar as result of the surface oxide groups and inorganics impurities. Most other commercially available sorbents are polar in nature. This difference has some very useful advantages. Activated carbon does not adsorb water very well. So, it does not require any pretreatment to remove water prior to use and is very useful as a selective sorbent for aqueous system (Richard and Terry, 2004). Despite of its prolific use, activated carbon is still assumed as an expensive material and not much work has been done in order to adsorb residual oil (Ahmad *et al*., 2005).

High surface area per unit mass alumina, either amorphous or crystalline, which has been partially or completely dehydrated, is termed activated alumina. This material is very hydrophilic and is often used for drying or dehydration of gases and liquids. Environmental applications would include water removal from acid gas or organic solvent streams. The surface area per unit mass of this material is usually in the range of 200-400 m^2g^{-1} (Richard and Terry, 2004). The most significant usage of alum is usually overdosed in order to ensure adsorption efficiency.

Zeolites are nanoporous oxide crystalline structures, typically aluminosilicates. The aluminum in the structure has a negative charge that must be balanced by a cation, M. This ionic structure leads to the hydrophilicity of the zeolite. Zeolites have uniforms pore sizes that typically range from 0.3 to 0.8 nm. Zeolites can selectively adsorb or reject molecules based on their size, shape, or sorption strength. The molecular sieving effect is a common term associated with zeolites and refers to selectivity based on size or shape exclusion. Zeolites can also provide separations based on competitive sorption. This situation can lead to reverse selectivity where a larger molecule can be selectively sorbed and separated from a smaller molecule. For example, most zeolites are polar adsorbents and will preferentially adsorb polar species (water) over non polar species (organics) of comparable size (Richard and Terry, 2004).

The potential of using chitosan as alternative adsorbent for the treatment of MEA wastewater is becoming a research interest field in the near future. It has been proven that this adsorbent has capability to adsorb metal ions, oil and grease and improve wastewater quality (Ahmad *et al*., 2006). The literature on the interaction of chitosan with those contaminations has been discussed elsewhere (Guibal, 2004; Evans *et al*., 2002). Due to chemisoption and structure properties of chitosan, the adsorbent is believed capable to treat MEA wastewater tremendously. From the literatures point of view, researches on treatment of MEA wastewater from petrochemical plant are insufficiently conducted. The physical treatment methods would be the interesting research field due to simple, easy, shorter time and economically viable to be commercialized. Due to this, chitosan is believed to be the best natural adsorbent to reduce COD, suspended solid and remove oil from MEA wastewater rather than activated carbon, alum and zeolite.

This study is to present the performance of chitosan compared to activated carbon, alum and zeolite in treating MEA wastewater and to investigate, which adsorbent projected the highest removal efficiency. In view of the fact that, no work has been done in the literature regarding the treatment of MEA wastewater using these adsorbents like chitosan. Even chitosan performance compared to activated carbon, alum and zeolite has not been explored. Furthermore, not many studies were been done using real effluent, whereby these studies were done using homemade synthetic effluent. The objective of this research was to study a feasible method and investigate the potential and effectiveness of chitosan, activated carbon, alum and zeolite in removing oil, suspended solid and reducing COD from MEA wastewater. The research was also evaluating the potential of recycling the treated MEA wastewater and reuse in the CO_2 removal unit. Jar-test apparatus was employed to evaluate the oil removal performance via adsorption. Thus, the optimum absorbents needed to achieve maximum removal residue oil, suspended solid and COD was determined.

MATERIALS AND METHODS

Experimental materials: Samples of MEA wastewater were collected from Petronas Gas Processing Plant (GPP) in Kerteh, Terengganu. The collected samples were then placed in a thermal resistant plastic container, sealed tight and labeled, before transported to the laboratory. For preservation, samples were refrigerated at about 4°C in order to prevent the wastewater from undergoing biodegradation due to microbial activities. A portion of the samples was analyzed for its characteristic.

Chitosan was supplied by Mathani Chitosan Pvt. Ltd. (India) in off-white flakes form with viscosities and DDA are about 30-3000 mPa.S (at 25°C) and 85-98%, respectively were used for the amine contaminated wastewater treatment. Activated carbon was supplied by Scharlau Chemie S.A (Spain), Zeolite was supplied by Fluka Biochemica with a mesh size less than 45 μm and Alum was supplied by Merck. N-hexane (Merck) was used as the solvent for oil extraction in the residue oil analysis.

Experimental procedure: A conventional jar test apparatus (JLT6 Jar Test, VELP Scientifica) was used in the experiments to treat MEA wastewater with the adsorbents. It was carried out as a batch test, accommodating a series of 6 beakers together with 6 spindle steel paddles. The samples were mix homogeneously before fractionated into the beakers containing 250 mL of suspension each. Prior to the test, the samples were measured for COD, suspended solid and residue oil and amine concentration for representing an initial concentration. After the desired amount of adsorbents was added to the suspension, the beakers were agitated at identical speed (100 rpm) for 1 h. A sample was withdrawn using a pipette from the top inch of supernatant for analysis, representing the final concentration. The pH of samples was also determined.

Analysis: The residue oil content was measured by using the oil and grease method recommended by APHA method (APHA, 1992), with n-hexane being used as the oil-extraction solvent. The residue oil content in the suspension was determined for each sample of MEA wastewater both before and after each experiment. One hundred milliliter of upper aliquots liquid of sample was transferred into a separating funnel. Then, 2.5 mL of 50% sulfuric acid, H_2SO_4 was added to re-active the sample. After that, 30 mL of n-hexane were added into the separating funnel to collect the oil content.

The contents were shaken vigorously for 2 min and 3 mL of 2-propanol were added to expel the existed bubbles. The samples were allowed to separate into layers for 5 min and the aqueous layer was drip drained into second separating funnel. Extraction was repeated twice with two more portions of 30 mL n-hexane. Then, the all the surface layers were collected and 2 scoops of anhydrous sodium sulphate were added to expel the water in the layers. The samples of extracted residual oil with n-hexane were transferred into round bottom flask and the samples were heated to remove n-hexane. The initial weight was measured and the drying and cooling were repeated until the weight becomes constant in every 1 h.

A gravimetric method was used to determine the suspended solid. With the aid of vacuum filtration apparatus, a retained solid on the filter was recorded after heating. The COD test was performed by colorimetric method using Spectrophotometer HACH Model DR/2400 (HACH Company, USA). It measures the amount of oxygen (O_2) required for complete oxidation of organic matter using strong oxidation agent, i.e., dichromate ion ($Cr_2O_7^{2-}$).

The amine concentration was measured by using titration method recommended by APHA method which Taschiro indicator used as amine indicator. The COD, residue oil, suspended solid and amine concentration were determined for each sample of MEA wastewater both before and after experiment. Three replicates of each test were undertaken with the mean value obtained being calculated from the replicates. All tests were performed at an ambient temperature in the range of 26-30°C.

RESULTS AND DISCUSSION

The finding and data gathered from the experimental works were discussed thoroughly and the discussion was encapsulated on the removal efficiency of the adsorbents in term of residue oil, suspended solid and reduction of amine concentration. These parameters evaluation were very crucial in determining the treated MEA could be recycled or else. Whereas, Chemical Oxygen Demand (COD) was also analyzed and this evaluation would provide information to the alternative treatment via wastewater treatment plant if the treated MEA was not possible to be recycled.

Effect on removal of residue oil: The effect of different dosage of adsorbent (wt.%) for different adsorbents compared to chitosan on the removing residue oil of MEA was analyzed by varying the weight of adsorbents with 100 rpm of mixing rate, 1 h of mixing time, 1 h of contact time at 25- 30°C of temperature. The tests were carried out at original pH of the sample, i.e., 11.21. The pH level was maintained as required in the CO_2 removal unit system. Figure 2 shows the removal percentage of residue oil from MEA wastewater using chitosan, activated carbon, alum and zeolite. From Fig. 2, it was observed that at the highest adsorbent dosage (5 wt.%), chitosan show the highest removal rate of residue oil compared to others. Chitosan managed to remove 95% of residue oil while activated carbon was 87%, alum was 64% and zeolite was 46%. It can be concluded that chitosan was far best better than the other adsorbents to remove the residue oil.

Chitosan proved to best adsorbent in removing residue oil in MEA wastewater compared to activated carbon, alum and zeolite. This phenomenon may be explained by the accessibility of hydroxyl groups in chitosan. The deprotonation of the hydroxyl group occurred under alkaline conditions (Sakkayawong *et al*., 2005). The hydroxyl group of the chitosan polymer could adsorb residue oil by covalent bonding. The negative charge from MEA wastewater might be attached to the chitosan surface. The strong alkaline condition aggravates MEA wastewater to break oil droplets. Chitosan provokes physico-chemical effect, apparently serving to demulsify, increase the droplet size and enhance the adsorption of residue oil. More ions particles will be available to form a bond with hydroxyl groups at chitosan surface. Therefore, the electrostatic attraction between residue oils molecules and adsorption site increase and indirectly increase the adsorption of residue oil onto chitosan surface.

However, this is not the case for activated carbon, alum and zeolite. This can be clearly proven by the results. The result shows that activated carbon moderately good removal of residue oil compared to alum and zeolite. Normally, activated carbon is used for separation technology such as color and organics compounds removal in waste and water treatments and so far there is no research done on the removal of residue oil. Besides that, the application of activated carbon is not economically to remove residual oil from MEA wastewater compared to chitosan. Alum and zeolite showed almost a similar trend of poor residual oil adsorption compared to chitosan. The results showed that alum and zeolite were ineffective to remove oil due to their character which is very hydrophilic and is often used for the drying or dehydration of gases and liquid. Most zeolites are polar adsorbents and will preferentially adsorb polar species (i.e., water) over non-polar species (organics) of comparable size (Richard and Terry, 2004). This finding proves that activated carbon, alum and zeolite are poor for residue oil adsorption.

Effect on removal of suspended solid: Figure 3 demonstrates the suspended solid removal of MEA wastewater. The result shows that the suspended solid were decreased consistently from 1 wt.% of chitosan until 5 wt.% of chitosan. The samples were filtered using ceramic filter (0.45 μm) prior experimental works. With 5 wt.% of chitosan, the suspended solid was reduced up to 57%. The Chitosan shows the lowest suspended solid reading compared to activated carbon, alum and zeolite. At the maximum dosage of adsorbents application, Chitosan managed to remove 57% of suspended solid while activated carbon was 49%, alum was 43% and zeolite was 38%.

The result shows the percentage removal of suspended solid in wastewater towards chitosan, activated carbon, alum and zeolite based adsorption treatment. The suspended solid are removed from 1 wt.%

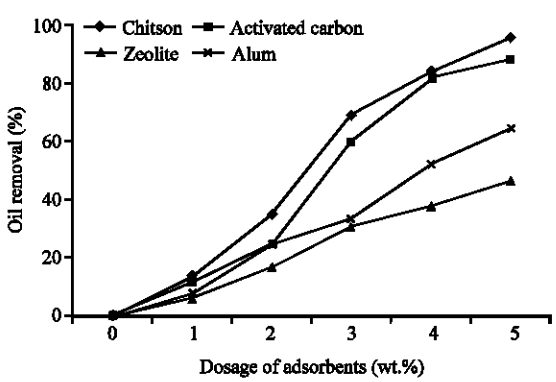

Fig. 2: Percentage of residue oil removed vs. dosage of adsorbents

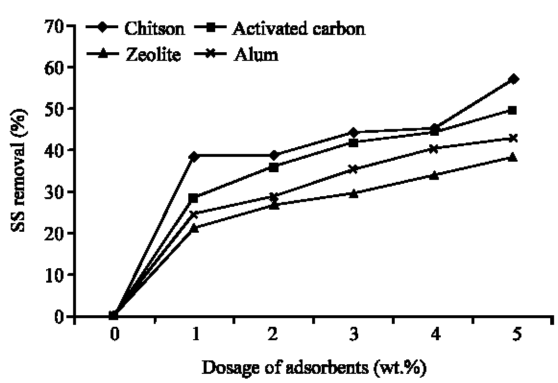

Fig. 3: Percentage of suspended solids removal vs. dosage of adsorbents

to 5 wt.% for all adsorbents but chitosan shows the most effective adsorbent to reduce suspended solid compared to others. It is believed that the small particles and ionic groups in MEA could attach to many hydroxyl groups on the chitosan and electrostatic interaction occurred (Sakkayawong *et al*., 2005). The driving force for adsorption is unsaturated forces at the solid surface which can form bonds with the MEA. Stronger interactions involve direct electron transfer between chitosan and the MEA. The explanation follows the adsorption theory, which mentions the ionic forces, van der Waals forces and covalent linkages involved in the process. Van der Waals forces are weak bonding of physical adsorption.

However, the results also verified that adsorption of suspended solid on chitosan, activated carbon, alum and zeolite was insignificant at strong alkaline condition (pH 11). This is because at this pH condition, chitosan loses its cationic nature (Ahmad *et al*., 2005), whereas activated carbon, alum and zeolite were very unstable. Particularly for alum and zeolite, it was an extreme case, because alum and zeolite charges are very unstable at these alkaline conditions. Furthermore at this pH, the adsorption process itself is very unstable due to the characteristics of MEA wastewater.

Effect on MEA concentration: Figure 4 shows that application of chitosan, activated carbon, alum and zeolite did not significantly affect the level of MEA concentration. At 5 wt.% of chitosan, the MEA concentration is reducing from 41 to 39%. Figure 5 shows that the level of amine concentration (%) was at constant from 1 wt.% of adsorbents to 5 wt.% of adsorbents.

This phenomenon may be explained by the amino groups in chitosan. The amino groups in chitosan are unaffected with amino molecules in MEA due to same groups. Furthermore at alkaline condition, hydroxyl groups in chitosan function as active compound (Sakkayawong *et al*., 2005). Based on the result, it can be assumed there were no chemical reactions or electron transfer between MEA wastewater and adsorbents.

Effect on reduction of Chemical Oxygen Demand (COD): Although, COD is the minor part in this research but it still considered as important part to treat this MEA wastewater. This component was important if the wastewater not possible to reuse in the system, this wastewater will be discharge to wastewater treatment plant based on the wastewater limitation. The result in Fig. 5 shows the COD reducing rate using chitosan, activated carbon, alum and zeolite as adsorbents. The figure appears that the increase of dosage for adsorbents

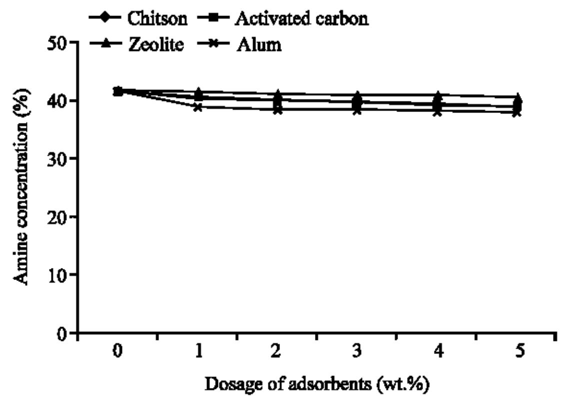

Fig. 4: MEA concentration (MEA) vs. dosage of adsorbents

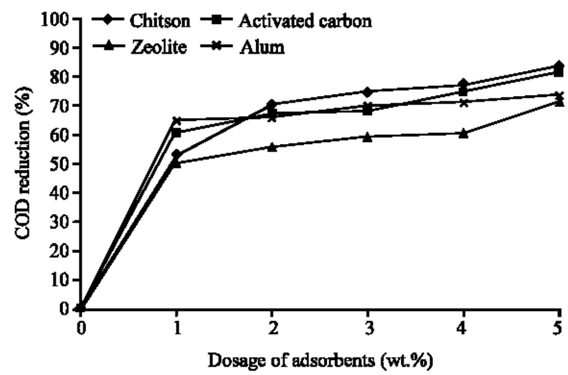

Fig. 5: Percentage of cod reduction vs. dosage of adsorbents

lead to better adsorption performances. Chitosan managed to reduce 83% of COD while activated carbon was 80, alum was 73% and zeolite was 71. It can be concluded that chitosan was far best better than the others adsorbents to reduce COD.

Chitosan contain amine and hydroxyl functional groups, which are very attracted to ions, therefore it possible that negative charge in MEA wastewater could easily bind at chitosan surface by covalent bond and reduced the COD level.

This MEA wastewater contained many types of molecules and ions. Therefore, certain molecules and ions are adsorbed onto these adsorbents surface based on its characteristics. Activated carbon has hydrophobic surface and favors organics over air. Meanwhile alum and zeolites are hydrophilic adsorbents. These characteristics of the adsorbents contributed to the reduction of COD level. From the result shows chitosan is the best adsorbents to reduce COD level compared to activated carbon, alum and zeolites.

CONCLUSION

Chitosan has a potential as an adsorbent to remove residue oil, suspended solid, reducing COD and at the same time maintaining the level of MEA concentration from monoethanolamine (MEA) wastewater. The preliminary result shows that treated MEA wastewater potentially can be recycled and reused in CO_2 removal unit. The chitosan based adsorbent involved both physical and chemical adsorption mechanism under alkaline conditions. The hydroxyl group tended to be the effective functional group for MEA adsorption under alkaline conditions (Sakkayawong *et al*., 2005). In addition, Chitosan is a natural, environment friendly biopolymer, low cost and easily to dispose rather than conventional adsorbents such as activated carbon, alum and zeolites. Further investigation need to be carried out to evaluate the potential of treated MEA wastewater employs in CO_2 removal unit.

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