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Analysis of Composite Adsorber with Graphite Nanofiber Based Nanofluid as Coolant

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Abstract. The use of composite adsorbent with nano particle additives having high surface area can lead to enhanced heat transfer, higher adsorption capacity and faster rate leading to better adsorber performance. The objectives of the present study were to investigate the effectiveness of nanofluid as a cooling fluid of a composite adsorber by carrying out nanofluid characterization and to investigate adsorption-desorption characteristics of a composite adsorbent for ammonia as an adsorbate.

An experimental set up with tube-in-tube type configuration was constructed to monitor the thermal characteristics (heat transfer from and to the adsorber) and ammonia adsorption/ desorption rates. The composite of calcium chloride with activated carbon and expanded graphite nanoparticles was made having different concentrations of $CaCl_2$ ranging from 40 % to 80 % in the composite and expanded natural graphite (ENG) content ranging from 0-3 % by weight. The desorption characteristics were studied at different temperatures from 70° C to 110° C. The cooling fluid with and without graphite nanofibers (GNF) was circulated in the inner tube at different flow rates from 5 LPH to 25 LPH.

From the experimentation on adsorption-desorption characteristics, it was found that the total amount of ammonia adsorbed increased from 133 g for 50:50 composition of $CaCl_2$:AC to 156 g for $CaCl_2$:AC composition of 50:50 with the addition of 3 % ENG nanoparticles. Also the adsorption process time reduced from 22 minutes to 18 minutes. For 50 % $CaCl_2$ in the composite the temperature at which the maximum desorption occurred was 70°C.

So, desorption could occur at lower temperature, which is advantageous as it increases the number of options for heat sources to be used. When nanofluid was used as a cooling fluid of the composite adsorber, the total amount of ammonia adsorbed increased from 79.411 g for basefluid to 90.206 g for 0.4 % graphite nanofiber nanofluid for flow rate of 25 LPH. With the use of composite adsorbent of $CaCl_2$:AC of 50:50 composition and addition of expanded natural graphite (ENG) by 3% and when 0.4 % graphite nanofiber nanofluid was used as a cooling fluid, the maximum ammonia was adsorbed up to the bed length of 600 mm only out of the total bed length of 1 m indicating the possibility of reduction in the size of an adsorber.

Keywords: Nanofluid Heat Transfer, Mass Transfer Zone (MTZ), Chemical adsorption, Composite Adsorbent

INTRODUCTION

As an environment friendly and energy saving technology, the solid-gas chemisorption is used for converting the low- grade thermal energy into the high-grade refrigeration power. As a thermal-driven refrigeration technology, adsorption refrigeration has advantages for the utilization of low-temperature thermal energy (i.e. waste heat and solar energy). Adsorption refrigeration has many benefits including easy control, simple structure, less noise and low maintenance [1, 2] which make it very suitable for fishing boats ice making and vehicles air conditioning. Adsorption working pairs used in adsorption refrigeration includes activated carbon-ammonia, zeolite-water, activated carbon-methanol, $CaCl_2$–NH_3, silica gel-water etc. Many researchers have worked on various working pairs and it has been observed that the chemical adsorption has larger adsorption quantity, compared to the physical adsorption [3]. The chemical adsorption process is one type of exothermic reaction occurred between adsorbents and adsorbate. Hence heat rejected during the adsorption process must be taken out from the system as early as possible to maintain the constant adsorption reaction rate. In this research work, nanofluid is used as a secondary fluid to carry the heat rejected during the adsorption reaction. Heat transfer coefficient of the nanofluid increases consid- erably compared to base fluid. Nanofluids are a new type of fluids prepared by dispersing nanometer-sized materials (fibers, tubes, rods, wires, droplets or sheet) in base fluids or in other words nanofluid consists of metallic or non-metallic nanoparticles (such as copper, silver, iron, alumina, copper oxide, Silicon carbide, carbon nanotubes, etc.) suspended in base fluid (such as water, ethylene glycol, oils, etc.). The nanotubes are expected to be very good thermal conductors along the length. The carbon nanotubes

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have a room-temperature thermal conductivity along its axis of about 3000 W/m.K and the copper transmits 385 W/m.K.

The heat and mass transfer performance are important parameters for adsorption refrig- eration systems because it influences the adsorption and desorption rate and as well as the power density significantly [4]. The thermal conductivity of physical and chemical adsorber is very low hence heat cannot be rejected easily from the system. Heat transfer from the ad- sorber at the time of adsorption reaction is the key indicator of adsorption capacity. As the thermal conductivity of the composite adsorber is very low, heat cannot be rejected out from the system which affects the adsorption quantity. Expanded natural graphite can be used to enhance the thermal conductivity of the composite adsorber significantly. Researchers have investigated the enhancement of thermal conductivity of the adsorber by adding expanded graphite. Eun [5] and Wang et al. [6] manufactured silica gel and activated charcoal com- pound blocks by mixing the adsorbents with expanded natural graphite (ENG) powders, and found that there is increase in thermal conductivity and permeability. Tamainot-Telto and Critoph [7] used activated charcoal and in their work, thermal conductivity increased up to 0.44 W/mK. K. Wang [8] et al. also developed a new type of compound adsorbent mixed by $CaCl_2$ and ENG, which improved the thermal conductivity of granular $CaCl_2$ by about 36 times.

In this work, the adsorption performance of ammonia with calcium chloride and activated carbon by using various concentrations of nanofluid was studied. The purpose of this work was to come up with improved composite adsorber bed with the use of nanofluid as a cooling fluid, so that it can be recommended for use in adsorption systems for better thermal performance. The use of nanofluid as a cooling fluid in composite adsorber bed was not reported in the literature.

MATERIALS AND METHODS

Materials

The $CaCl_2$ was obtained from Merck Life Science Pvt. Ltd. (India). The employed $CaCl_2$ is with >98% purity. The activated charcoal was obtained from Loba Chemie Pvt. Ltd.

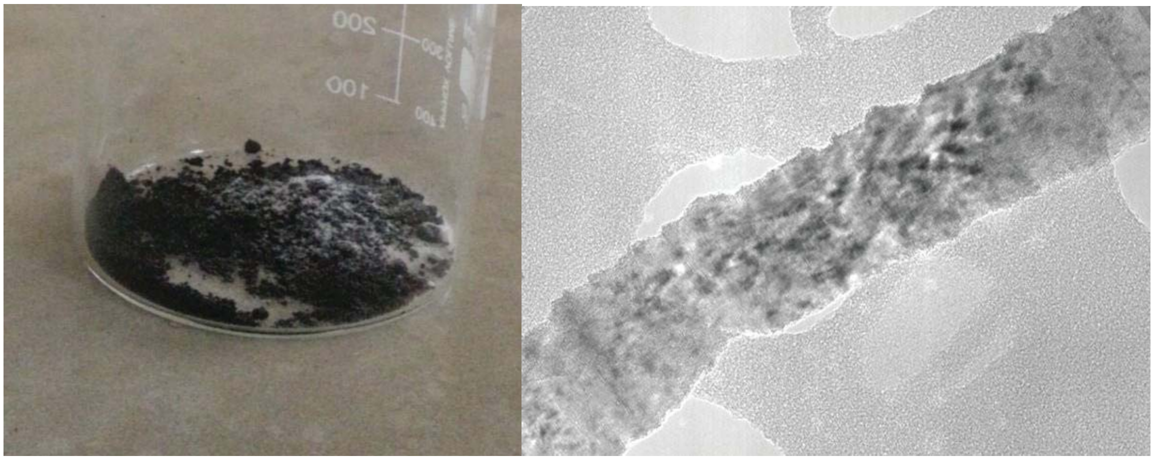
In the present work, graphite nanofiber (GNF) was used as a nanoparticle which was procured from Sigma Aldrich, USA. The nanofibers have an average diameter ranging from 10-200 nm (nanometer) and a length ranging from 10-40 μm (micrometer). Figure 1 shows the electron micrograph of GNF before dispersion into the base fluid.

Preparation of Nanofluid

Generally, graphite nanofibers (GNF) are very cohesive in nature so it is difficult to disperse GNF into liquids such as ethanol, ethylene glycol, water etc. Ultra-sonication method was used to disperse the nanoparticles into the base fluid to obtain the desired result. Nanofluid was prepared using commercial coolant (Water: EG as 80:20) as a base fluid. Two different compositions of nanofluid had been prepared by using 0.2 % and 0.4 % by weight of graphite nano fibers (GNF). Sodium Laurel Sulphate (SLS) was used as dispersing agent. Initially, 200 ml nanofluid was prepared by adding GNF into 200 ml base fluid with 0.1 % SLS. This preparation was kept in an ultrasonicator for 40 minutes to obtain the homogeneous solution of nanofluid.

Preparation of Expanded Natural Graphite

The expandable graphite was added to increase the thermal conductivity of composite adsorbent made up of $CaCl_2$ and activated charcoal. Expanded graphite used in the experiment was having mesh size 80. The expanded natural graphite underwent expansion at a temperature of 400 ℃ for 30 min. Digital muffle furnace was used for heating the expanded natural graphite.



(a) (b)

FIGURE 1. a) Photo of GNF (before dispersion into base fluid) b) Electron micrograph of GNF particle

EXPERIMENTAL WORK

System Design

The test system consists of the adsorption bed, heating elements, magnetic flow pump and rotameter. Figure 2 shows the process flow diagram of composite adsorber test setup. Adsorber bed consists of two concentric tubes made up of stainless steel. The annular gap between the inner tube and the outer tube was filled with composite adsorber material. Nanofluid as a cooling fluid was circulated through inner tube and ammonia was circulated through the annular gap.

In this experiment, 9 heaters each of 3 KW are employed on the outer tube for the heating purpose. PT 100, grade A type temperature sensors (PRT) are used for measurement of temperature having a deviation of 0.5 %. T_1 and T_2 are the two temperature sensors mounted at the inlet and outlet of cooling fluid respectively. Remaining sensors T_3, T_4, T_5, T_6, and T_7 are used to measure the temperature of adsorber bed at different locations. All the temperature sensors are connected to the digital temperature indicators. The cooling system consists of a storage tank, magnetic flow pump, androtameter. Rotameter is used for control of the flow rate of cooling fluid which is flowing through the inner tube. This had ranges from 6.6 LPH to 66 LPH with an error of 0.1%.

During adsorption process, the cooling fluid is pumped from the storage tank to inner tube. Heat loss to the environment can be minimized by adding insulation to the outer tube. The flow rate of the ammonia gas can be measured by using bypass valve. The set up was validated using distilled water before use.

Adsorption and Desorption Process

In this experiment, activated charcoal and $CaCl_2$ is used as composite adsorber which is filled in between the annular gap of the inner tube and the outer tube. Ammonia is used as an adsorbate (refrigerant) which is adsorbed on the surface of the composite adsorbent. The heat liberated during adsorption process is taken by cooling fluid flowing through the inner tube. Nano fluid is used as a cooling fluid.

Adsorption and desorption cycles are performed at various compositions of nanofluids

i. e. 0% (Base fluid), 0.2%, 0.4%. The flow rate of the cooling fluid is also varied with the help of rotameter. Adsorption and desorption cycle is carried out at flow rates of 5 LPH, 10LPH, 15LPH, 20 LPH and 25 LPH for each nanofluid composition.

Measurement of Thermal Conductivity

Activated charcoal and calcium chloride have a very low thermal conductivity which is responsible for several thermal limitations leading to low overall adsorption and desorption kinetics. Hence it is desirable to increase the thermal conductivity of the composite adsor- bent. It is observed that expanded natural graphite (ENG) increases the thermal conduc- tivity of the composite which increases the adsorption and desorption kinetics. The thermal conductivity of composite material with and without expanded graphite was measured ex- perimentally. The thermal conductivity measurement set up was validated using asbestos powder. The thermal conductivity of asbestos was found to be in

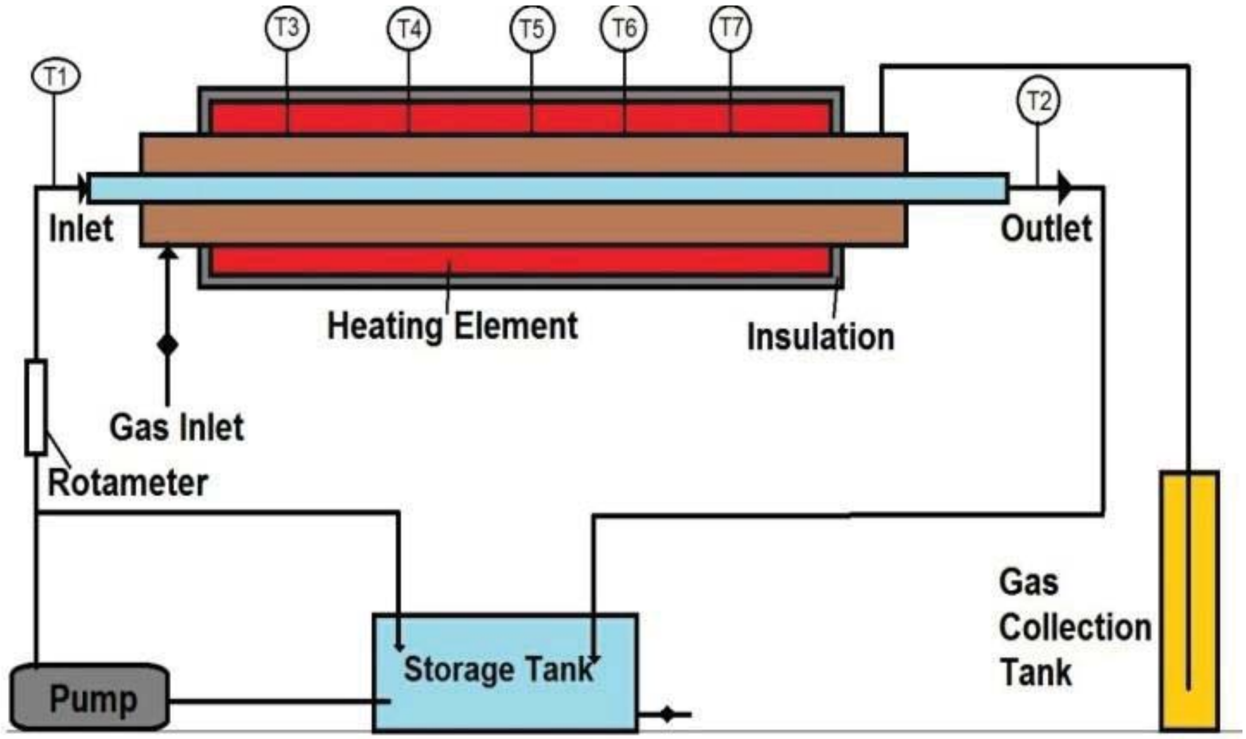


FIGURE 2. Schematic diagram of set up for studying composite adsorber

line with literature value. The apparatus was made up of two thin concentric copper spheres. The composite material was packed in between the two spheres as shown in Fig.3. The inner sphere houses the heating coil. Power supply to the heating coil is given through dimmerstat so that power supply can be varied easily. Voltmeter and ammeter are connected to measure the voltage and current at a particular power supply condition. Thermocouples used to measure the temperatures were Chromel Alumel type. Thermocouples 1 to 3 are fixed on the inner sphere while thermocouples 4 to 6 are fixed on the outer sphere. Temperatures were recorded to claculate the thermal conductivity of the composite material packed between the two concentric spheres. Heat is transferred by conduction through the wall of the hollow sphere formed by the composite material packed in between two thin copper spheres.

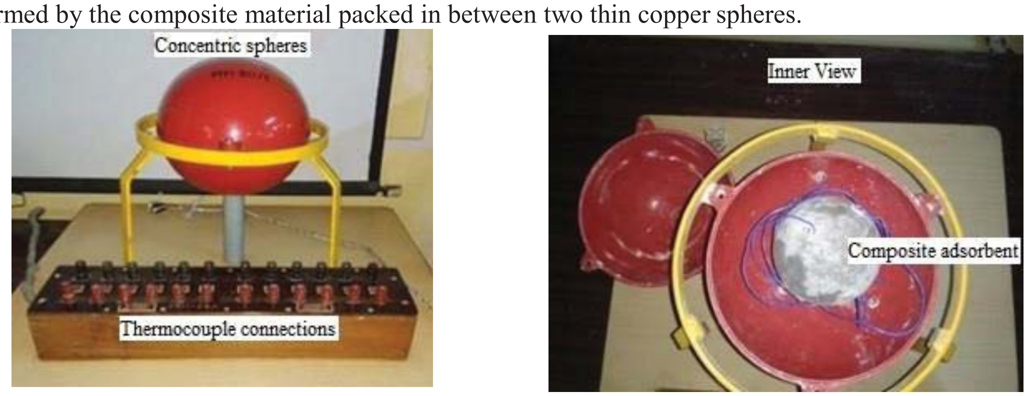


FIGURE 3. Thermal Conductivity Measurement Setup

Thermal conductivity (k) value can be determined as,

$$k=\frac{Q\times(r_o-r_i)}{4\times\pi\times r_o\times r_i\times(T_i-T_o)} \tag{1}$$

Here, r_i is the radius of inner sphere in meter, r_o is the radius of outer sphere in meter, T_i is average temperature of the inner sphere in $^{\circ}$C and T_o is the average temperature of the outer sphere in $^{\circ}$C. Heat input (Q) can be calculated by multiplying current and voltage value measured by ammeter and voltmeter respectively.

RESULTS AND DISCUSSION

Adsorption-desorption performance with NH_3 of composite adsorber AC-$CaCl_2$ having different concentration of $CaCl_2$ ranging from 40% to 80% was investigated. Figure 4 to Figure 8 show the temperature profiles along the length of the tube during ammonia ad- sorption. Adsorption process is exothermic due to the complex formation between $CaCl_2$ and ammonia. The maximum temperature reached indicates the mass transfer zone (MTZ) for composite ad-sorbent of calcium chloride-activated carbon having different concentration of $CaCl_2$. The shift of MTZ from left to right indicates the saturation of adsorption bed with respect to time.

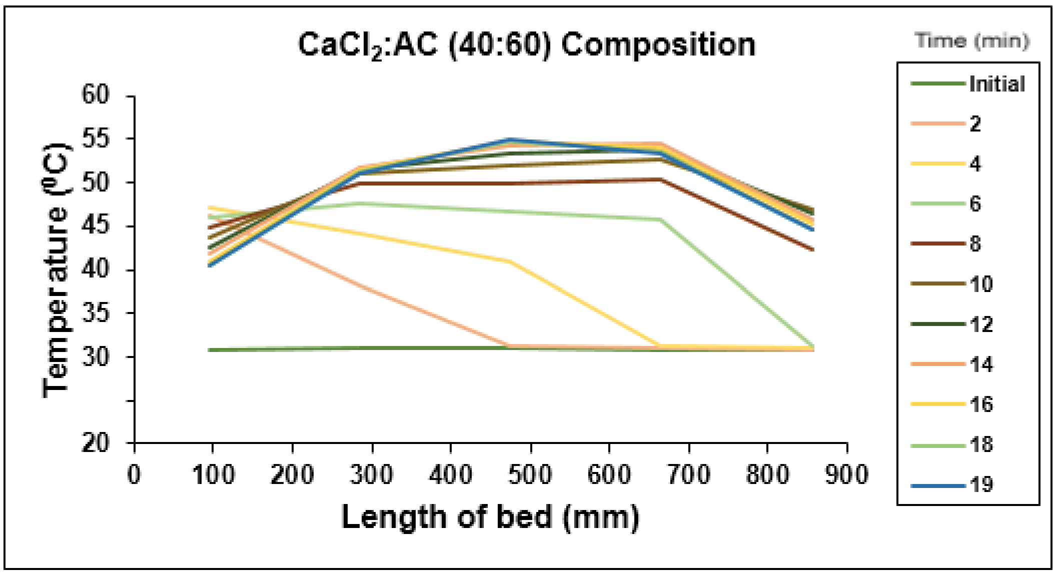


FIGURE 4. T_3 to T_7 $CaCl_2$:AC (40:60) composite (adsorption cycle)

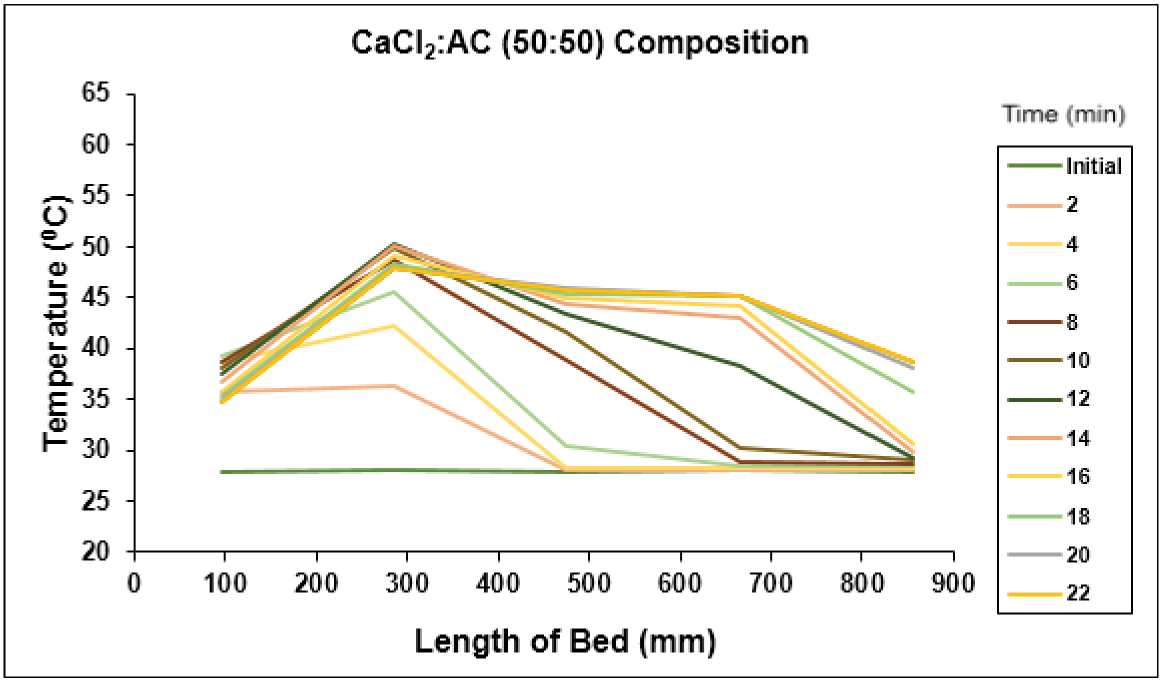


FIGURE 5. T_3 to T_7 $CaCl_2$:AC (50:50) composite (adsorption cycle)

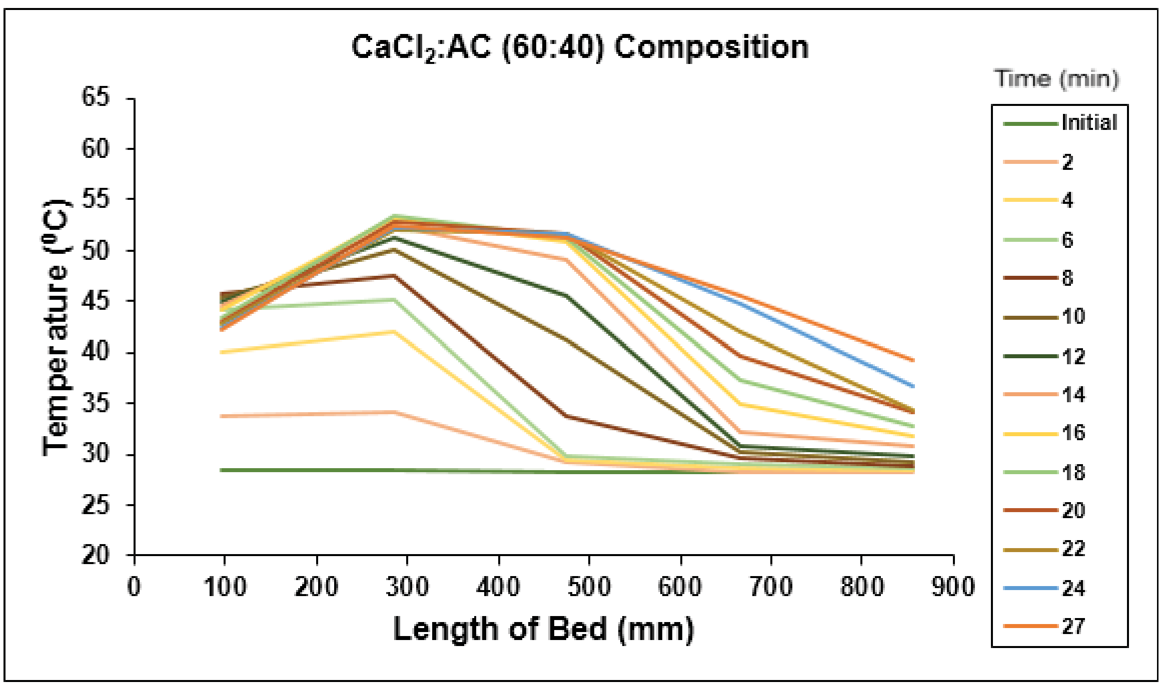


FIGURE 6. T_3 to T_7 $CaCl_2$:AC (60:40) composite (adsorption cycle)

Comparison of these figures indicates that the MTZ shifts to higher length with the increase of $CaCl_2$ in the composite. It is interesting to see that the distribution of the temperature profile along the tube also depends on the composition which suggests that the ammonia flow and reaction proceeds non-uniformly in these composites. This

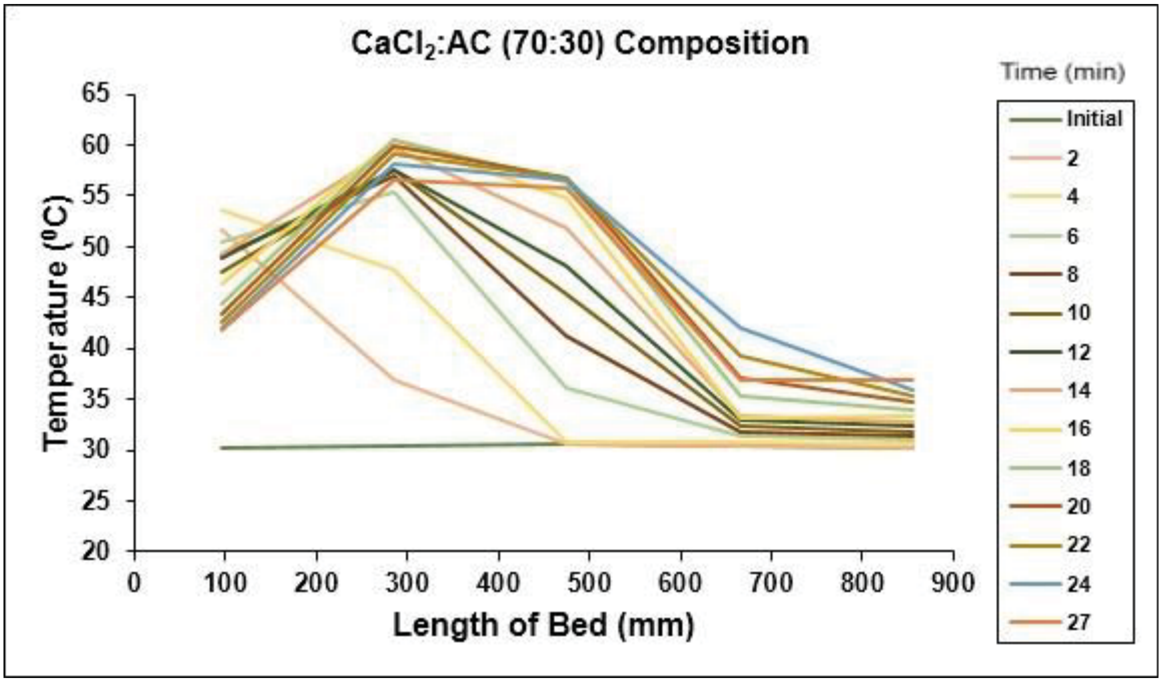


FIGURE 7. T_3 to T_7 $CaCl_2$:AC (70:30) composite (adsorption cycle)

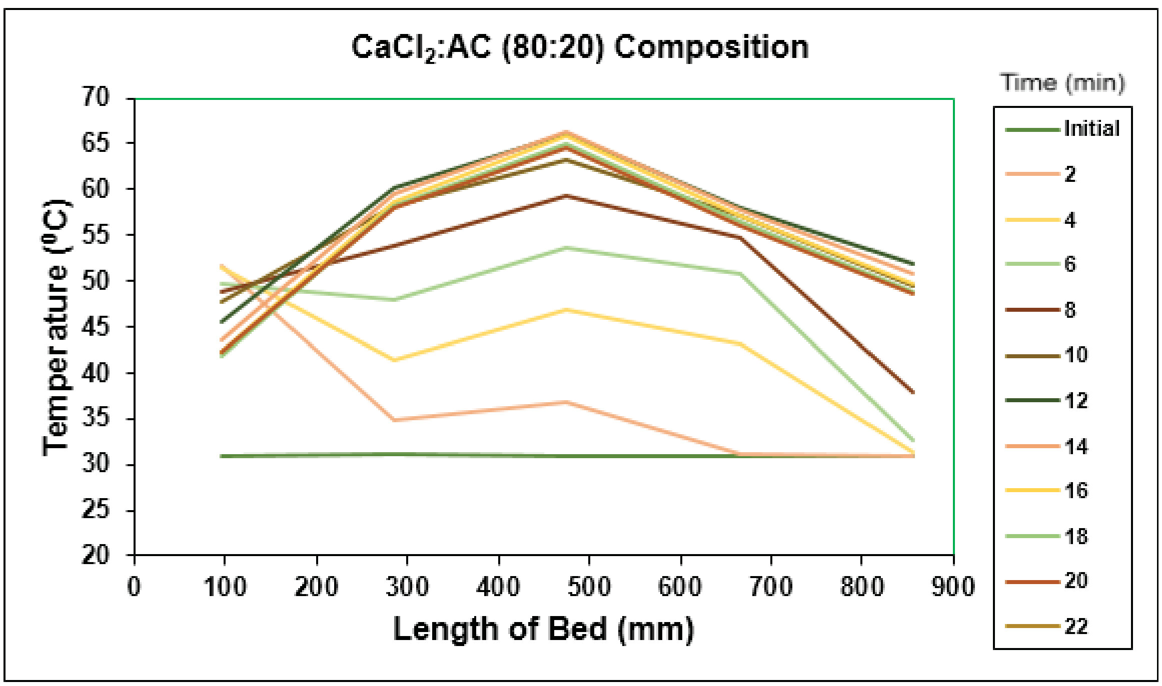


FIGURE 8. T_3 to T_7 $CaCl_2$:AC (80:20) composite (adsorption cycle)

could be associated with the swelling of the salt after complex formation.

Figure 9 shows the amount of ammonia adsorbed for various concentrations of $CaCl_2$ in composite adsorber. It is observed that amount of ammonia adsorbed is 74.1 gm for 40 % $CaCl_2$concentration which increased upto155.24 gm for 80 % $CaCl_2$.

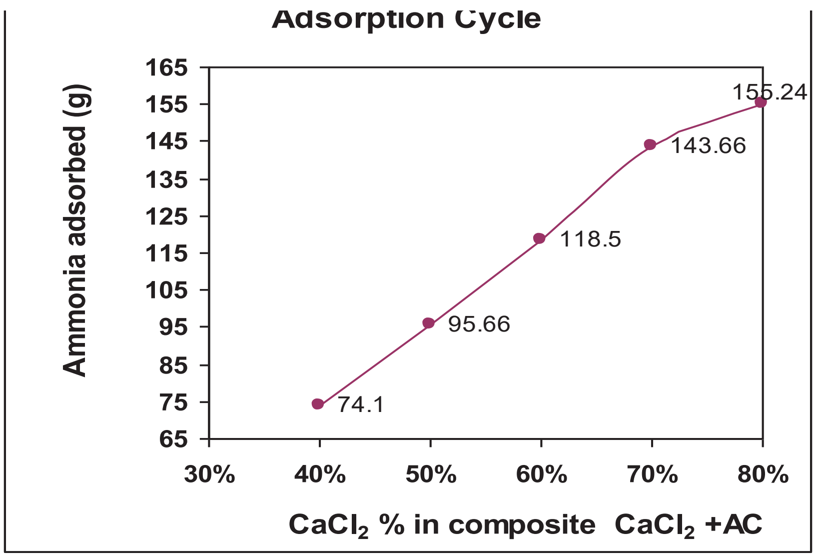


FIGURE 9. Adsorption capacity of various composites of $Cacl_2$ and AC

When expanded natural graphite (ENG) is added into the composite adsorber ranging from 0% to 3%, there is large change in the amount of ammonia adsorbed and also the temperature profile changes. Figure 10 to Figure 12 show the mass transfer zone (MTZ) for composite adsorbent of 50:50 CaCl2:AC composition with 1%, 2% and 3% expanded graphite.

It is quite evident from these figures that there is much more uniformity in the ammonia penetration and adsorption. There is increase in the maximum temperature reached after completion of reaction suggesting the increase in the ammount of adsorbed ammonia. It is also possible that the thermal conductivity of the composite would increase with the addition of ENG.

Figure 13 shows the amount of ammonia adsorbed for various concentration of expanded natural graphite at 50 % concentration of $CaCl_2$. From figure 13, it is observed that, amount of ammonia adsorbed is 4.782 gm for 0% of ENG while amount of ammonia adsorbed is 5.492 gm for 3% ENG. Thus, with the addition of ENG the amount of NH_3 adsorbed increases due to increase of porosity as well as surface area. There also possibility of increase in heat transfer coefficient due to the increase of thermal conductivity by the addition of ENG. The thermal conductivity of composite made up of activated charcoal and $CaCl_2$ is low.

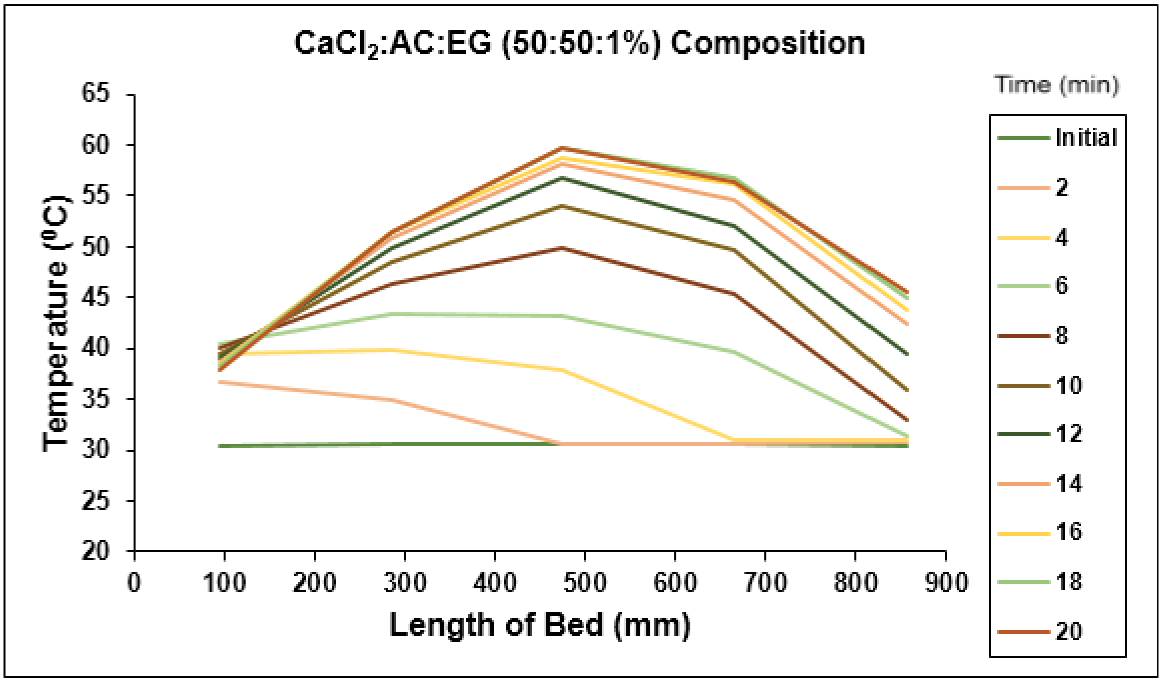


FIGURE 10. T_3 TO T_7 $CaCl_2$:AC:EG (50:50:1%) composite (adsorption cycle)

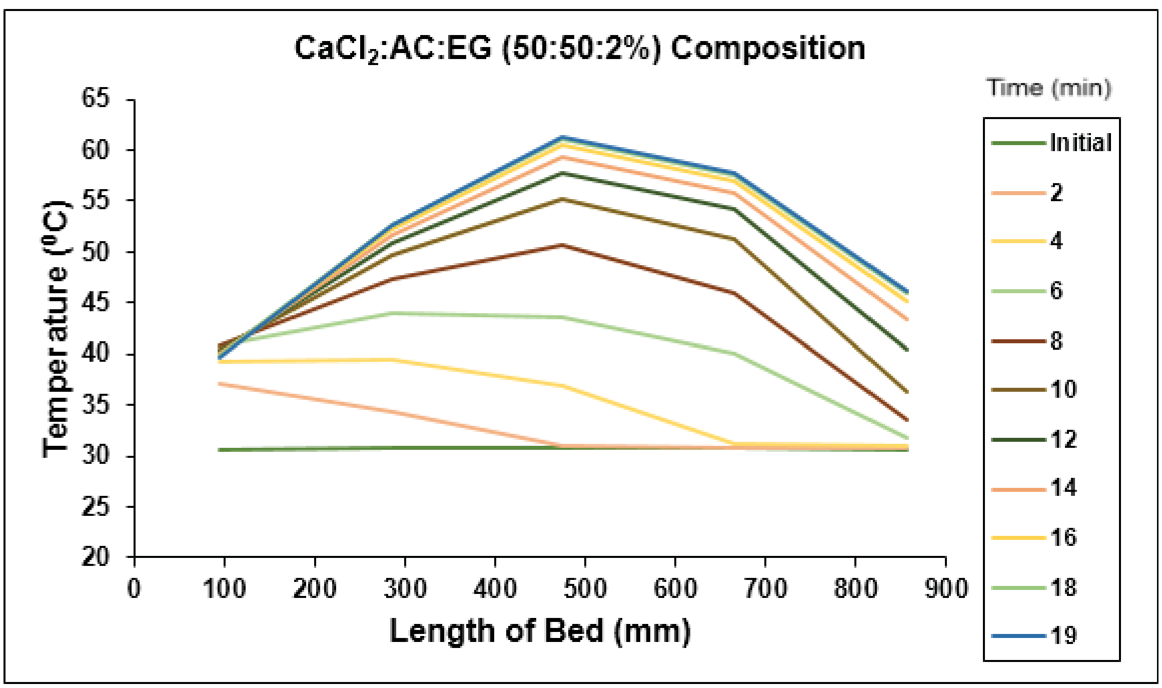


FIGURE 11. T_3 TO T_7 $CaCl_2$:AC:EG (50:50:2%) composite (adsorption cycle)

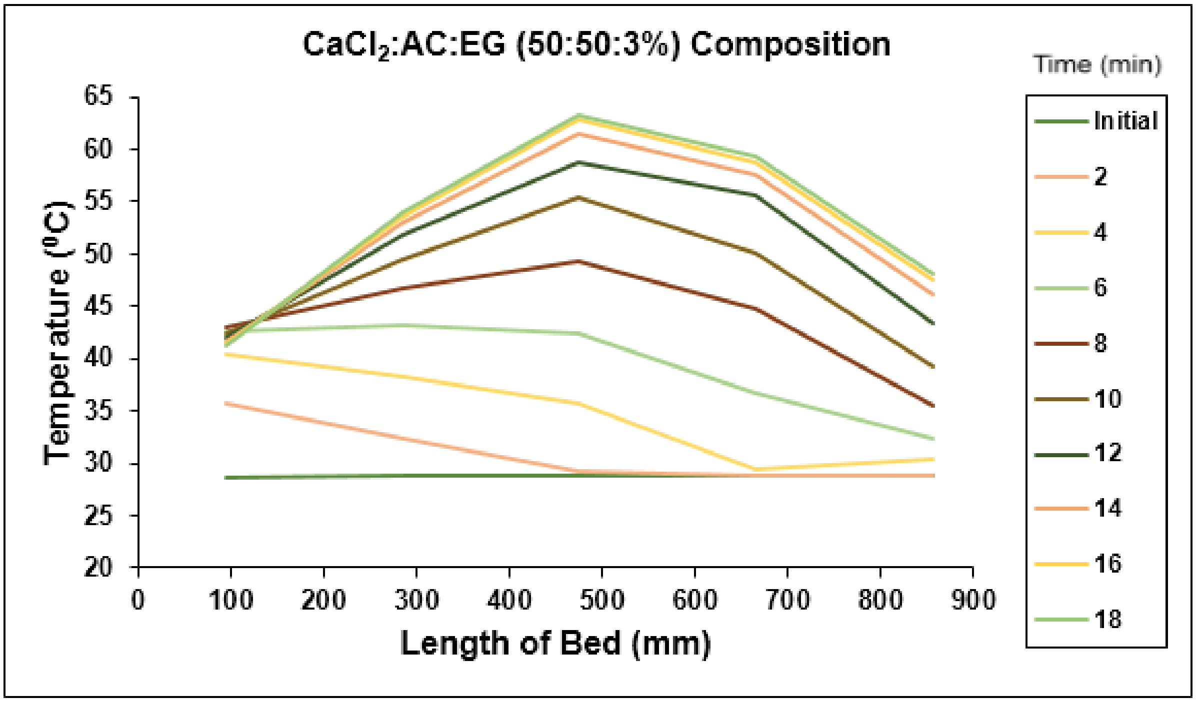


FIGURE 12. T_3 to T_7 $CaCl_2$:AC:EG (50:50:3%) composite (adsorption cycle)

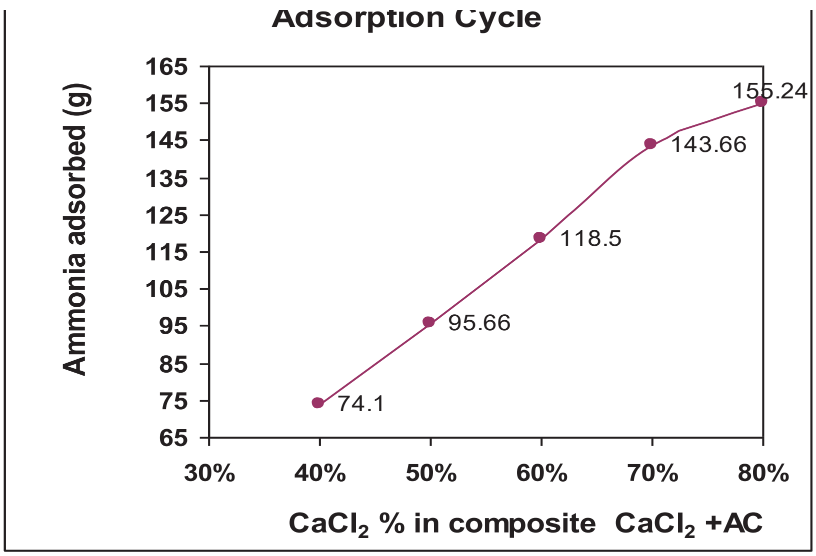


FIGURE 13. Adsorption capacity of various composites Of $CaCl_2$, AC and ENG

Hence expanded natural graphite is added into the composite to increase the thermal conductivity of the composite. Thermal conductivity is measured by adding 1 % ENG and 2 % ENG in activated charcoal and $CaCl_2$ (50:50 compositions). Figure 14 shows the variation of thermal conductivity with heat input. From Figure 15, it is observed that thermal conductivity increases with increase in ENG percentage. Maximum thermal conductivity observed is W/m2K for 2% ENG impregnated in a composite of activated charcoal and $CaCl_2$.Thus, it appears that the heat transfer across the composite also plays a role in decreasing the local heating and improving the ammonia adsorption capacity.

The adsorption performance of the system is investigated at different compositions of nanofluid. Adsorption performance of the system is also investigated at different flow rates of cooling fluid.

The amount of ammonia adsorbed for various flow rates of nanofluid is shown in Figure 15. In adsorption cycle, amount of ammonia adsorbed increases with the flow rate of nanofluid and also with the increase of added GNF in the nanofluid. It thus appears that the heat transfer away from the composite plays important role in the ammonia adsorbed. This can be understood as follows. When the CaCl2 adsorbs ammonia, heat is liberated which increases the local temperature. As the temperature rises, the ammonia adsorbed decreases. However, if the the heat is taken away, the temperature is not high and ammonia continues to get adsorbed. Also, there was increase the heat transfer coefficient of nanofluid with the increase in Reynold's number or flow rate. This again led to the higher ammonia adsorption.

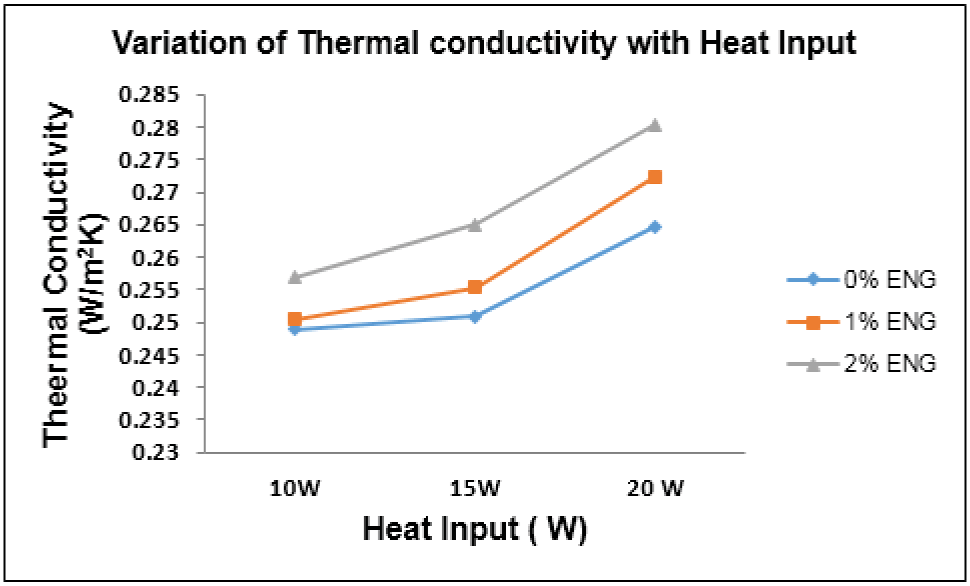


FIGURE 14. Variation of thermal conductivity with heat input

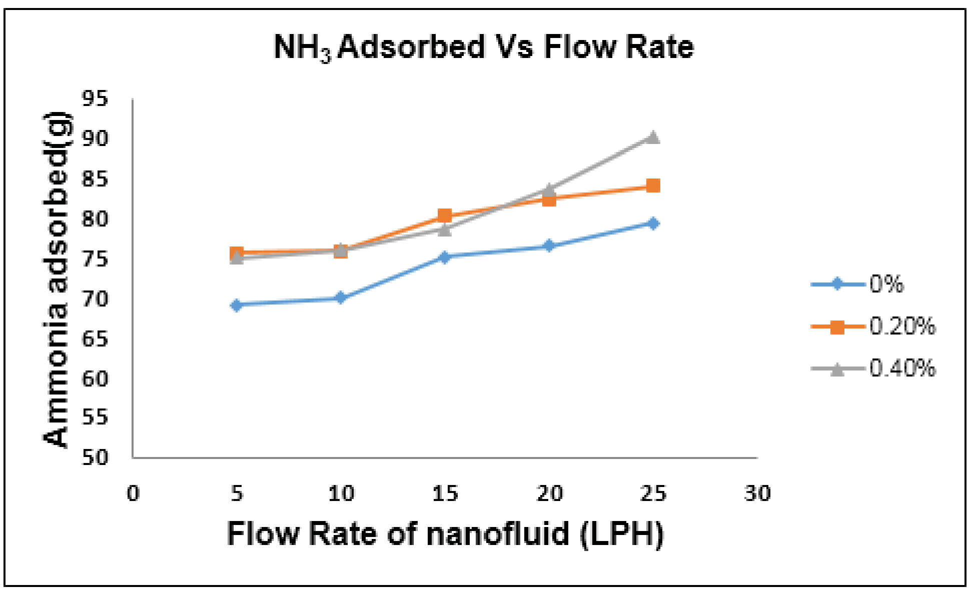


FIGURE 15. Adsorption capacity at various concentrations of GNF in nanofluid and flow rate

CONCLUSIONS

The adsorption performance of $CaCl_2$-NH_3 system was experimentally studied in de- tail using a composite adsorber with different compositions of $CaCl_2$ and activated carbon. Expanded graphite was added to the composite adsorber for enhancing the thermal conductivity and porosity. Nanofluid was used as a heat carrying agent during adsorption process, as adsorption process is an exothermic process. The amount of ammonia adsorbed was measured for different nanofluid composition with different flow rates. The temperature along the length of the tube with adsorber was continuously monitored for all conditions. Conclusions from these studies are;

1) The total amount of ammonia adsorbed was highest i. e. 217 g in case of 80:20 com- position while it was lowest i.e. 103 g for 40:60 among all compositions of calcium chloride- activated carbon composite adsorbent. But the higher composition of $CaCl_2$ had a problem of swelling and agglomeration due to poor heat and mass transfer through the adsorber bed.

2) The amount of ammonia adsorbed on the composite adsorbent of calcium chloride- activated carbon-expanded natural graphite increased with the increase in percentage of expanded natural graphite in the composite as it created more expansion space to adsorption reducing swelling and agglomeration. The total amount of ammonia adsorbed increased from 133 g for 50:50 composition of $CaCl_2$:AC to 156 g for $CaCl_2$:AC composition of 50:50 with the addition of 3 % ENG nanoparticles. The amount of ammonia adsorbed increased as the thermal conductivity of the composite adsorbent increased with the addition of ENG. Also, the rate of ammonia adsorbed increased due to the increase in porosity of the composite with the addition of ENG.

3) After the addition of expanded natural graphite in composite of $CaCl_2$-AC (50:50) the adsorption process time decreased with increase in adsorption amount. For $CaCl_2$-AC (50:50) composition adsorption process time was 22 minutes whereas for 1 % of expanded natural graphite in $CaCl_2$-AC (50:50) composition the adsorption process time was 20 minutes. For 2 % it is 19 minutes and for 3 % it is 18 minutes adsorption process.

4) With the use of composite adsorbent of $CaCl_2$:AC of 50:50 composition and addition of expanded natural graphite (ENG) by 3% and when 0.4 % graphite nanofiber nanofluid was used as a cooling fluid, the maximum ammonia was adsorbed up to the bed length of 600 mm only out of the total bed length of 1 m. This could significantly reduce in the size (in terms of length) of the adsorber bed.

5) Desorption of ammonia was higher at desorption temperature 110°C in case of 80:20 composition of calcium chloride-activated carbon composite adsorbent as swelling and ag- glomeration was dominant. Therefore, it required higher temperature to break the ammo- niate complex formed. Whereas for 50:50 composition, the desorption was higher at 70 °C. Thus, desorption could occur at lower temperature, which is advantageous, as it increases the number of options for heat sources to be used. This clearly suggests that the porosity in the composite plays an important role in adsorption desorption process.

6) Thus, the amount of ammonia adsorbed in the composite is strongly associated with the heat transfer and thermal characteristics of the composite. By the addition of small quantity of nanoparticles either in the composite or in the circulation system, higher quantity and faster rate for ammonia adsorption can be achieved.

7) The adsorption process time decreased with the increase in concentration of expanded natural graphite in the composite. During adsorption, heat dissipation from the composite increased as the thermal conductivity of the composite increased with the addition of ENG. Adsorption rate increased and adsorber bed got saturated faster. Also, the distribution of

ammonia adsorbed along the bed length was uniform giving uniform mass transfer zone across the bed length.

8) The most important finding from these studies is that the thermal conductivity and heat transfer from the composite adsorber play crucial role in the ammonia adsorption desorption process. The addition of ENG to the composite adsorbent and use of nanofluid as a cooling fluid of the adsorber bed can thus improve the quantity of ammonia adsorbed and also the rate of ammonia adsorption desorption.

9) Finally, to summarize, it is recommended to use the composite adsorbent of CaCl2:AC 50:50 with 3 % expanded natural graphite. The cooling fluid of the composite adsorber to be used is 0.4 % GNF nanofluid with the flow rate of 25 LPH. The higher concentrations of nanoparticles in nanofluid are not recommended after taking into account the cost of the graphite nanofibers and increase in the viscosity of nanofluid for higher concentrations. The desorption temperature recommended is 70 ◦C for the composite of CaCl2:AC:ENG.

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