Experimental Study of Hydrogen Sulfide Removal from Petroleum Refinery Waste Water Using Agriculture Wastes

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Abstract. Hydrogen sulfide (H_2S) (aq) is one of the most toxic pollutants in petroleum refinery waste water. The removal of H_2S from waste stream is considered as one of the major problems in energy industries. The agricultural wastes considered a source of activated carbons (ACs). The activated carbons obtained from the agricultural wastes were chemically activated using KOH. The prepared ACs were examined in the lab to remove H_2S from wastes water. Moreover, operating factors such as the initial concentration of H_2S (aq), adsorption contact time, dosage, pH of a solution, and agitation speed were tested. The resulted shown that all factors have a significant effect on the removal of H_2S (aq). The initial concentration has a higher impact on removal efficiency. The removal efficiency was more than 96%.

Key word: Hydrogen sulfide, adsorption, activated carbon, waste water.

1 Introduction

The sources of hydrogen sulfide (H_2S) (liquid and gas form), toxicity, and regulations are discussed. The current removal technology such as adsorption equilibrium process was succinctly discussed. The discharged of H_2S is indirectly reliant on human activity. Most chemical plant releases H_2S (aq) as a by-product of sulfide within the range of 58 to 110 million tons of sulfur/year. Whereas it is produced from black sea around 30 to 170 million tons of sulfur/year. Moreover, above 60 million tons per year of toxic H_2S is released from hydro-processing of petroleum, coal and minerals (Startsev et al., 2013). In the Petroleum refinery process a large volume of water is used-up in the process of getting a useful product from crude oil. Typically, water is used in different units for generating the steam with many processes relying on the steam as a separating medium in distillation and hydrodesulphurization units. Figure1 shows a schematic example of the typical water balance in a refinery. This water is used in different units. Mostly, it used for producing steam. Moreover, leakages and spills emanating from equipment during shutdown or start-up of equipment, condensate from steam-stripping operations, and waste water from storage tanks are considered as the major sources of these wastes (EcA, 2010). It is thereafter condensed as aqueous phase and isolated as sour water. As the steam reduces in the existence of hydrocarbons which comprises the hydrocarbons comprising hydrogen sulfide (H_2S) and ammonia (NH_3) are typically absorbed into water that need treatment (EcA, 2010). The pH of sour water is elevated to 12, as a temporary solution, to decrease the odour and corrosion effect until it moved to waste water treatment plant (striping). In addition, waste water in a refinery is created by strippers which use straight steam injection as a stripping medium (EcA, 2010). Table 1 shows the composition of sulfide in selected petroleum refinery

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effluents. Van Hamme et al. (2003) reported that gas streams are first scrubbed with an aqueous washing liquid, with dissolution of the sulfur components into an aqueous phase as seen in Equation (1) and (2).

$$H_2S_{(g)} \leftrightarrow H_2S_{(aq)} \qquad 1$$

$$H_2S_{(aq)} + OH^- \rightarrow HS^- + H_2O \qquad 2$$

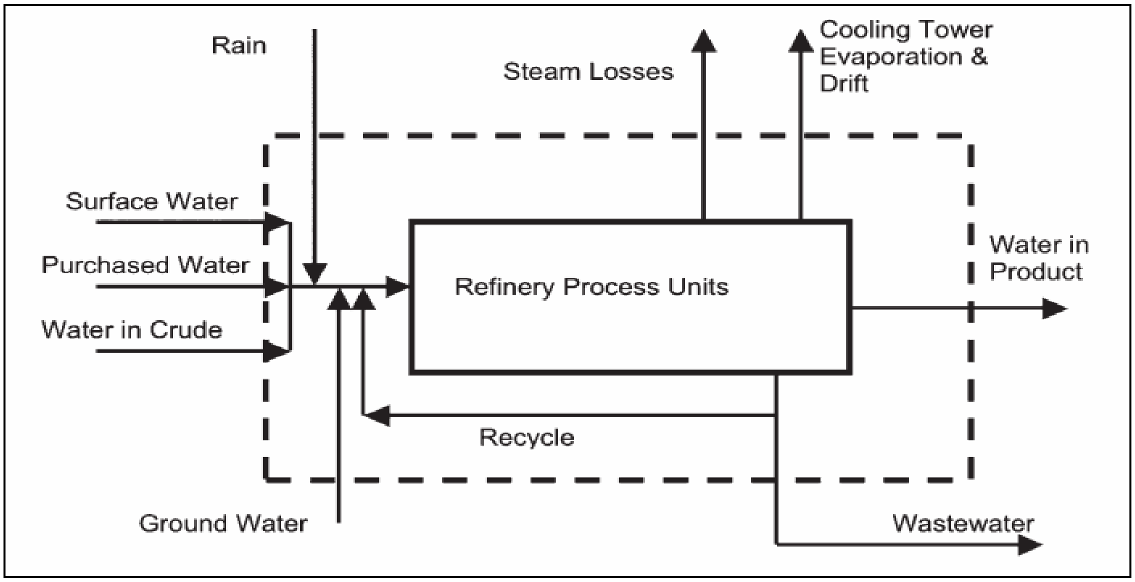

Fig. 1. A schematic example of the typical water balance in a refinery

Source: EcA, (2010).

Hydrogen sulfide (H_2S) is a very hazardous and dangerous material. It causes respiratory problems, safety problems posed by its highly flammable nature as well as economic problems arising from the corrosion of metals (Ozekmekci et al., 2015). Moreover, a part from metal corrosion due to H_2S, concrete surface would be corroded as well due to the gradual formation of sulfuric acid and eventually causes damage on the sewer (Vollertsen et al., 2008). Processing crude oil into useful products such as kerosene and gasoline was achieved by the numerous refinery configurations. During these processes, the petroleum waste water was produced in the units like Hydro-cracking, Hydro-skimmer flare, Hydro-cracker flare, Hydro-skimming, desalter and sour water. They have been reviewed the treatment of petroleum waste water by conventional and new technologies. The pH has a noticeable impact on H_2S forms. H_2S exists in three forms in aqueous systems, such as Hydrogen sulfide (H_2S (aq)), bisulfide ion (HS^-), and sulfide ion (S^{2-}). H_2S is a weak acid. It presents in the reactive molecular form of H_2S (aq) at low the pH value (Jacukowicz et al., 2015) according to the following equations:

$$H_2S_{(aq)} \leftrightarrow H^+ + HS^- \qquad 3$$

$$HS^- \leftrightarrow H^+ + S^{2-} \qquad 4$$

It can be seen from Fig that the pH ranging from 8 to 11, the bisulfide (HS) is the prevalent form and it is the most reactive ion in the free radical chain reaction. Below pH 7, H_2S (aq) is prevalent. At pH 7, the reduced sulfur species in aqueous solution is equally separated between the dissolved bisulfide (HS^-) and the hydrogen sulfide (H_2S (aq)). Sulfide (S^{2-}) dominates at pH >11 (Thompson et al., 1995).

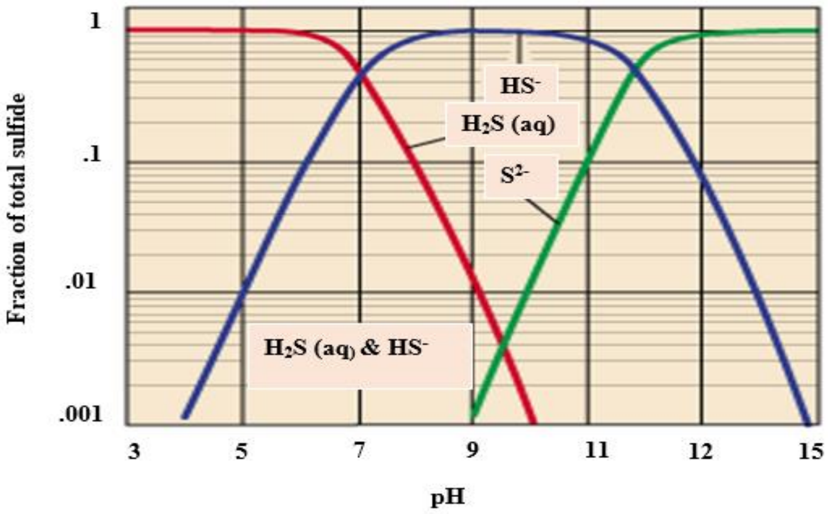

Fig. 2. Distribution of three sulfide species in water

Source: Thompson et al. (1995).

Table 1 Guidelines for Occupational Exposure to H_2S (g)

[H_2S] (ppm)	Agency	Duration
0.1	AIHA	1 hour
10	OSHA	8hr/day, 40hr/week
10	ACGIH	TLV-TWA 8hr/day, 40hr/week
15	ACGIH	TVL-STEL
20	OSHA	Ceiling
27	EPA	1 hour
30	AIHA	1 hour
32	EPA	30 minutes
37	EPA	4 hours
41	EPA	10 minutes
50	OSHA	10 minutes ceiling
50	EPA	1 hour
76	EPA	30 minutes
100	AIHA	1 hour

2 Experimental

2.1 Preparation of adsorbent

The agricultural waste residue (Coconut shell (CNS), palm kernel shell (PKS) and wood sawdust (WSD) used in this study were collected from a commercial farm located close to University Malaysia Pahang (UMP), Gambang, Pahang, Malaysia. The collected agricultural waste was prepared in our previous study (Habeeb O.A, 2017). Adsorbents characterizations were conducted in our previous work (Habeeb, O. A., 2019).

2.3 Batch equilibrium studies

Experiments for the adsorption of H_2S were conducted in the batch mode. All adsorbents were intensively examined for investigating its ability to adsorb dissolved hydrogen sulfide from synthetic wastewater. Initially, the H_2S concentration was measured. A sample of 0.1 g of an adsorbent was used in each run after degassing at 105 °C for 24 h in an oven. Batch adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.1 g adsorbent and 100 mL of H_2S solutions at various initial concentrations (100, 200, 300, 400, and 500 mg L^{-1}).

3 Results and Discussion

3.1 Batch Adsorption Studies

The adsorption experiments were conducted in a batch mode. The details of batch adsorption process were explained. Subsequently, the initial and final concentrations were measured after the suspensions were filtered. The adsorption studies using One Factor At Time (OFAT) were conducted. Parameters such as initial concentrations of H_2S (aq) (mg/L), adsorption contact time (h), dosage (g), pH of solution and agitation speed (rpm) were determined.

3.2 Effect of Initial H_2S (aq) Concentration

Initial H_2S (aq) concentration is an important factor that affects the RE of H_2S (aq). It is related to the amount of mass transfer between adsorbent and adsorbate (Ouasif et al., 2013). Figure 3 shows the impact of initial concentration on % RE of H_2S (aq) by using ACs adsorbents. Low H_2S (aq) concentration (i.e. 200-600 mg/L) results in higher RE of because the number of active sites on an adsorbent surface is analogous to the number of H_2S (aq) ions in the solution. The higher RE is observed in concentration of 200 mg/L with value of 95.3 %, 89 %, and 75% for ACPKS, ACCNS and ACWSD adsorbents respectively. However, at high H_2S (aq) concentration (i.e. 800-1000 mg/L), the availability of active sites is lesser than the H_2S ions. Therefore, RE decreases as the initial H_2S (aq) concentration increases. The lower % RE of H_2S (aq) was observed in concentration of 1000 mg/L with values of 70 %, 50 %, and 35 % for ACPKS, ACCNS and ACWSD adsorbents respectively. As recommended by DOE for industrial effluent, these values are not environmentally acceptable and need more purification before discharge it to the environment. It is observed that ACPKS gives higher RE at all initial H_2S (aq) concentrations. The effect of initial concentration for all ACs have a negative effect as concentration increased the RE% was decreased.

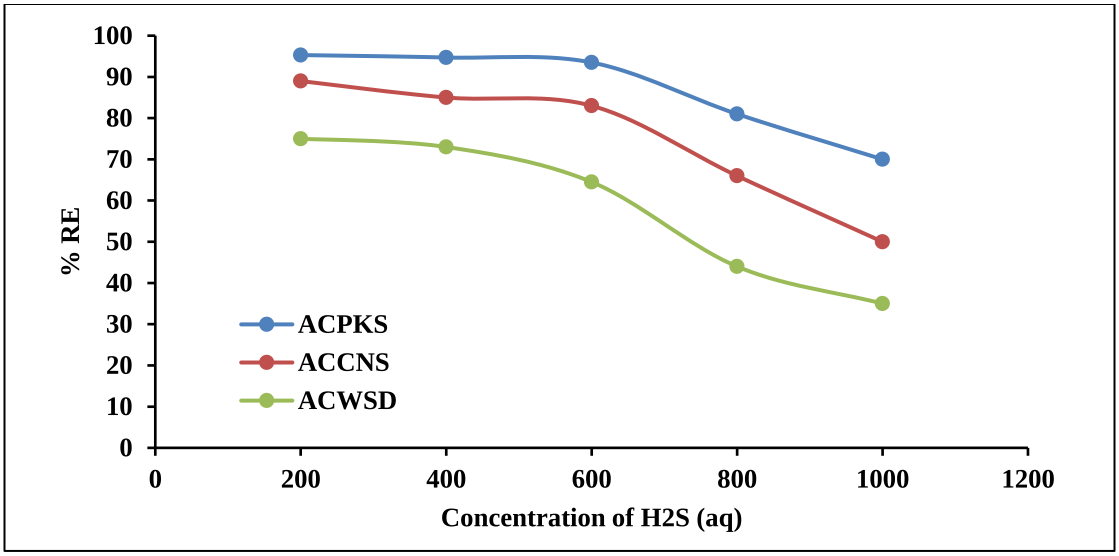

Fig. 3. Effect of initial concentartion of H_2S (aq)on % RE

3.3 Effect of Adsorption Contact Time

The influence of adsorption contact time (using ACs) on the RE of H_2S (aq) was presented in Figure 4. From the result obtained, it is clearly evident that ACPKS gave the highest RE than other adsorbents with ACPKS requiring a lower contact time at ~ 9 h in order to reach the equilibrium state, while ACCNS and ACWSD required 11 h to reach the equilibrium state as succinctly illustrated in Figure 4. In fact, the adsorption process was executed for more than 17 h in order to ensure that complete equilibrium was achieved. All ACs adsorbents revealed that the amount of sorption increased with the increasing adsorption contact time. At the beginning of adsorption process, the adsorbent possessed a larger number of empty active sites. The available number of active sites decreased and the molecule diffusion resistance increased as adsorption was taking place; therefore, the % RE of H_2S (aq) decreases. Hence, the contact time affects the adsorption process significantly. In general, the adsorption of H_2S (aq) ions on the surface of ACs occurred in two stages. In the first stage, adsorption rate was more rapid due to the abundance of vacant active sites on the mesopores surface of the adsorbent. In the second stage, however, the uptake rate decreased due to the required sufficient time to diffuse of H_2S (aq) ions inside the microporous structure.

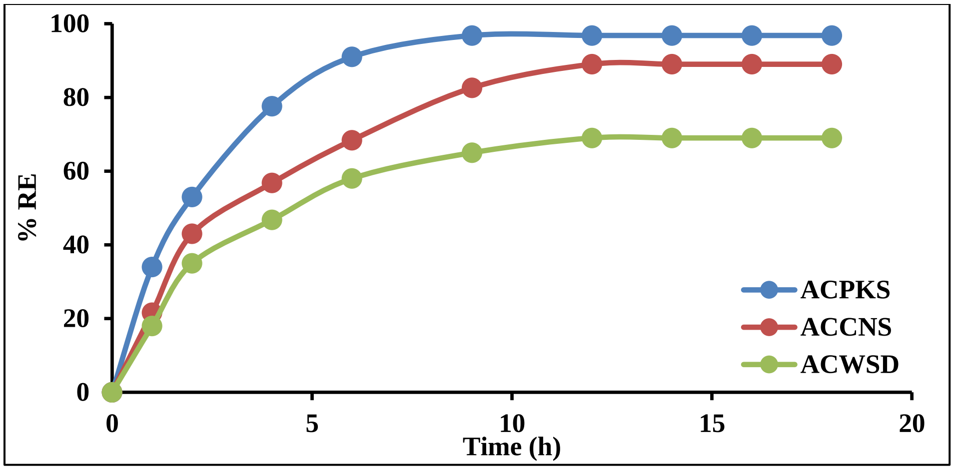

Fig. 4. Effect of adsorption contact time on % RE

3.4 Effect of Adsorbent Dosage

Figure 5 shows the effect of adsorbent dosage on RE of 500 mg/L of H_2S (aq). In general, RE increased as the amount of ACs increases. In fact, as the mount of adsorbents increased, the number of active sites also increases. Therefore, the RE for the H_2S (aq) was greatly enhanced. The effect of the amount of adsorbents (dosage) was not significant compared with effect of contact time and initial concentration as clearly seen in Figure 5.

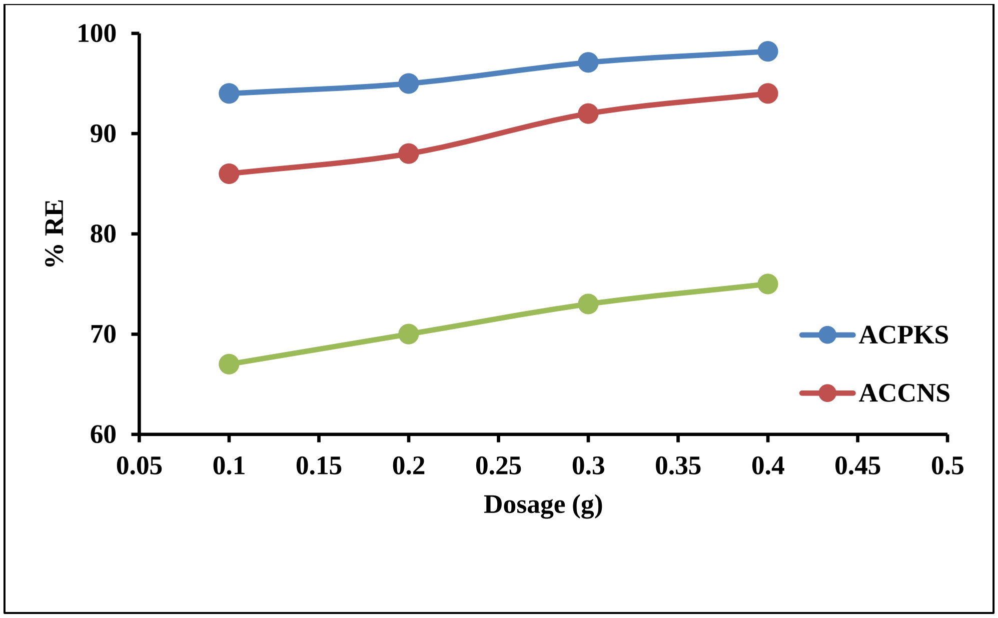

Fig. 5. Effect of amount of adsorbent on % RE

3.4 Effect of Initial Solution pH

Removal efficiency of 500 mg/L of H_2S (aq) can be affected by several factors such as competitive effects of hydrogen ions with dissolved H_2S (aq) ions. The changes in the ionic forms for the functional groups on the adsorbent surface and speciation form of H_2S (aq) in solution. Therefore, it is necessary to investigate the effect of pH while keeping other variables constant. The effect of initial pH on RE is shown in Figure 6 with ACPKS exhibiting higher RE of H_2S (aq). Hence, as the initial solution pH increases, the RE increases until pH 7 was attained. However, RE experienced a decrease thereafter which is due to the fact that the concentration of hydrogen ions (H^+) was very high at a very low pH which could result in it competing with H_2S (aq) ions for any available active sites. Thus, as the initial solution pH increases, the number of hydrogen ions (H^+) decreases also. Therefore, the competition between ions (H^+) and dissolved H_2S (aq) ions on the available active sites experienced a decrease.

The state of hydrogen sulfide becomes unstable which could easily be converted to either liquid or gaseous form, as illustrated in Equation (1). As the pH increases, H_2S (g) was converted to H_2S (aq) and dissociated to ions such as bisulfide (HS^-) and sulfide (S^{2-}) as shown in Equations (2) and (3), respectively. At pH = 7, both H_2S (aq) and HS^- ions are dominant as seen in Figure 2. Thus, RE experienced an increase at this particular pH value. Thereafter, the solution turned to basic (interacts with HS^- and S^{2-} ions). Therefore, RE decrease was due to the basic ACs surfaces as reported by Kalapala, s(2014). As a result, pH 7 gave higher RE for the H_2S (aq) as shown in **Fig** 6. The pH has a significant effect on ACPKS compared with other adsorbents.

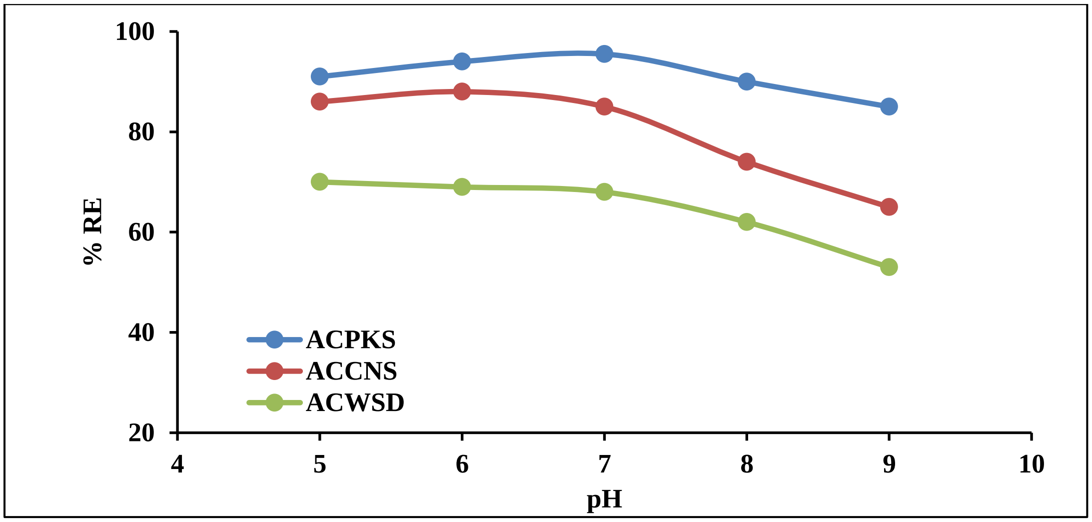

Fig. 6. Effect of initial solution pH on % RE

3.5 Effect of Agitation Speed

Figure 7 shows the influence of agitation speed on RE of 500 mg/L of H_2S (aq) using various ACs adsorbents. For all the ACs, RE increased with respect to the agitation speed. The highest RE was attained at the agitation speed of 150 rpm, which is attributed to the increased solute (dissolved H_2S (aq)) transport from the bulk solution to the ACs active sites. The agitation speed of more than 150 rpm might transform H_2S (aq) from adsorbent surface to the solution. Therefore, the agitation speed of 150 rpm is more suitable.

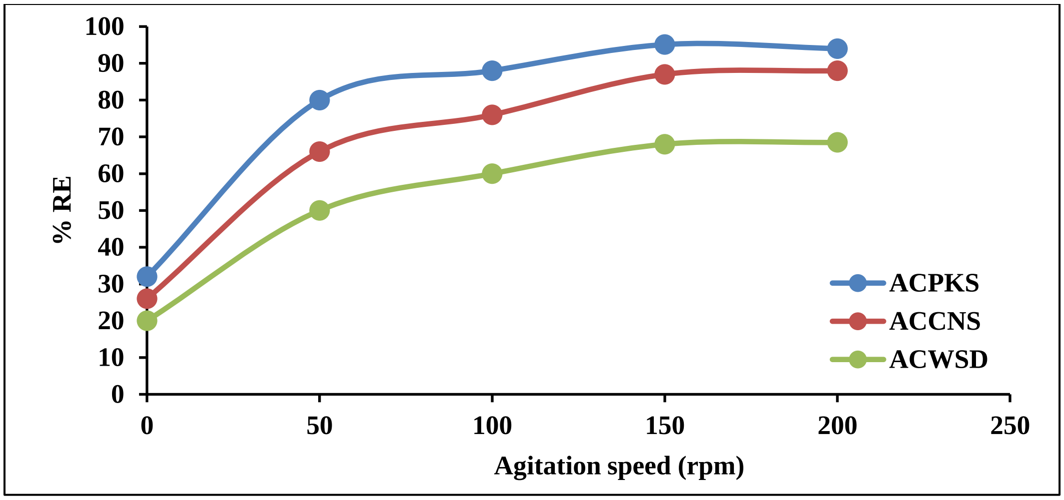

Fig. 7. Effect of agitation speed on % RE

4 Conclusion

The preparation and adsorption studies are conducted to investigate the effect of factors and conditions on the adsorption process. Activated carbons (ACs) were prepared from coconut shell (CNS), palm kernel shell (PKS) and wood saw dust (WSD) wastes. These materials were used as precursors to produce the activated carbon (ACs). The removal operation conditions of H_2S (aq) from waste water like initial H_2S concentration, adsorption contact time, dosage, pH, agitation speed are screened. The result found that the initial H_2S (aq) concentration, adsorption contact time and dosage are significant. Thus, it is concluded that the activated carbon derived from palm kernel shell is very useful green and economical adsorbent due to their easy availability and absence of any toxic. Therefore, it is very suitable for the removal of H_2S (aq) from petroleum waste wasters.

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