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An Innovated Method of H_2S Elimination from KSA Crude Oil Using Chitosan/Nano Activated Carbon/Iron Oxide Composite.

Hala M. Abo-Dief[1+*], N.A. Mostafa[2], Eman Alzahrani[3], and Ashraf T. Mohamed[4].

[1]Associate Professor, Chemistry Department, Al-Taif College of Science, Taif, KSA
[2]Professor, Chemistry Department, Al-Taif College of Science, Taif, KSA
[3]Assistant Professor, Chemistry Department, College of Science, Al-Taif, KSA
[4]Professor, Mechanical Eng. Dept., Albaha Faculty of Engineering, Albaha, KSA.
+Egyptian Petroleum Research Institute, Egypt.

ABSTRACT

The presence of H_2S in crude oil has been of great public concern and it is one of the most frequent contaminants at hazardous-waste sites. One of the easily and fast method to remove H_2S from crude oil is the adsorption desulfurization process. Adsorption-desulfurization process of crude oil was proposed and examined. Stainless steel used as material due to their low cost, good formability and proper mechanical properties. Stainless steel is susceptible to corrosion have poor wear resistance which limits its applications. Surface coating with chitosan (CH), Nano iron oxide (NFE) and Nano activated carbon (NAC) carried out at different concentrations, test periods, and degree of acidity to improve the biocompatibility of stainless steel. It has observed that chitosan shows greater corrosion inhibition efficiency than NAC and NFE respectively. The results obtained from these analyses revealed that chitosan; NAC and NFE were able to form a homogeneous mixture. NFE/NAC/CH composites showed a higher adsorption amount of H_2S at 80mg/l concentration at 80 ^{O}C followed by CH, NAC/CH, NFE/CH and NEF respectively in agreement with both TEM and SEM observations. The present work provided very promising results in the preparation of a good adsorbent composite.

Keywords: H_2S Elimination, NFE/NAC/CH.

**Corresponding author*

INTRODUCTION

Nano materials possess fundamentally new properties and functions resulting from their small dimensions [1]. According to some estimates, Nanotechnology could exceed the impact of the Industrial Revolution on society and projected to become a $2.6 trillion business in 2014 [2]. In environmental science, Nano-technology applied to smart and/or passive purification systems for air and water of which, zeolites, aerogels, chitosan and zero valent iron are already in use, [3-4]. Abo-Dief et al. [5] used Nano activated carbon in the Microwave Pyrolysis Reactors to purify the waste engine oil. Abo-Dief et al. [6-7] investigated the effect of Zn nanoparticles addition on the morphology of crystal size and corrosion properties of coated stainless steel. Clemente et al. [8] explained that metal corrosion causes big losses to the industry and one of the most widely used methods to fight it is the use of corrosion inhibitors. But Quraishi et al. [9] concluded that corrosion is a complex phenomenon occurring at the atomic and electronic scales, and no theory exist to predict corrosion inhibition efficiency. Recently, Xu et al. [10] suggested Nano materials such as carbon-based NMs are efficient, cost-effective and environmental friendly alternative to existing treatment materials. Singh et al. [11] developed Nano materials, such as Fe_3O_4, ZnO and TiO2, as well as their binary and ternary Nano composites, for the removal of various toxic metal ions and organic dyes.

Depending on the oil, there can be tens to hundreds of different sulfur compounds present in the oil. Lewand and Reed [12] deduced that there is only one single corrosive sulfur compound responsible for all corrosive sulfur issues that are present in all mineral oil. Zafour, and Fernanem [13] concluded that metal oxides have started gaining interest for removing undesirable heavy metal ions from industrial and processing oil, Nano composite of high porosity, high surface used in industry for purification and environmental remediation. Brieva et al. [14] stated that combustion of sulfur-containing compounds in fossil fuels emits sulfur oxides cause adverse effects on health, environment and economy. Amosa et al. [15] proved that sulphide scavengers is a widely adopted practice in production and processing operations in the Oil and Gas Industry.

Ayello et al. [16] concluded that the effect of crude oil chemistry on corrosion processes poorly understood. Son et al. [17] isolated a sulfur compound, from the root extract of Pleuropterus ciliinervis. Samide, and Tutunaru [18] investigated the corrosion and inhibition behaviour of iron mono sulfide (FeS) in 0.1M HCl solution. Salari et al. [19] studied the effectiveness of binary mixtures of phosphorus and sulfur compounds as coke inhibitors for naphtha pyrolysis. Pasupathy et al. [20] examined the inhibitive effect of a few thiols as corrosion inhibitors of zinc in 1N HCl and 1N H_2SO_4 by weight loss and gaso-metric methods. Sakanishi et al. [21] used ultra-deep desulfurization of gasoline and diesel fuels to produce sulfur-free fuels. Al Zubaidy et al. [22] found that one of the easily and fast method to remove sulfur from oil is the adsorption desulfurization process.

Yadav et al. [23] improve the biocompatibility and other activities of CS by fabrication of composites with metal oxide nanoparticles. Wang et al. [24] investigated catalytic oxidative desulfurization of benzothiophene in n-octane with hydrogen peroxide (H_2O_2) over catalysts of activated carbon (AC) supported iron oxide under mild conditions. Bolbukh et al. [25] synthesized composites which contain iron oxide nanoparticles and unmodified or laminated silica by in situ precipitation of ferrous salts in chitozan or glucose solution. Sikdera et al., [26] concluded that CS is an important natural polymer, obtained by the deacetylation of chitin and has found extensive application in the green synthesis of Nano scale materials because of its excellent biocompatibility, biodegradability, and lack of toxicity. Yadav et al. [27] prepared iron oxide/graphene oxide/chitosan (Fe_3O_4/Go/Cs) composite by a simple solution mixing-evaporation method. The results obtained from these analyses revealed that chitosan, iron oxide and graphene oxide were able to form a homogeneous mixture.

The present work aimed at detailed investigation of H_2S adsorption using NAC, NFE and CH deposition and their composites at different concentrations, test periods, temperatures and degree of acidity. The effect of the adsorbents deposits individually and composites on the H_2S adsorption, corrosion rate, inhibition efficiency at various test variables is carried out and investigated. The TEM and SEM observations used to indicate the effectiveness of the adsorbents used.

EXPERIMENTAL WORK

Specimen preparation

A stainless steel specimens of 10 mm diameter and 30 mm length cut from steel rod. Polishing was done in two phases includes paper polishing and cloth polishing. Hifin solution used to give the final touch on the polished surface. Further, they degreased with acetone in an ultrasonic bath to remove the impurities, then rinsed thoroughly with double distilled water and dried in air. Prior to each experiment, the specimens treated as described and freshly used without further storage.

Solution preparation

Chitosan dissolved in the solution of 4 ml acetic acid in 396ml of distilled water followed by filtration to remove the impurity. Thereafter, solution was taken in ten separate beakers of 100 ml each of 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mg/l concentration that are used with paraffin oil containing 1.0 M H_2S. The pH of the solution will be changed from pH = 4.0 to pH = 10.0. Then all the solutions magnetically stirred for 2 hours at room temperature.

Preparation of NFE/NAC/CH composite films

NFE/NAC/CH composites prepared by a simple solution mixing-evaporation method. The iron oxide first swelled in 40 mL of distilled water and ultrasonicated for 15 min. Then, the iron oxide suspension added into the CH solution with 0.5 %wt. iron oxide content with respect to CH, followed by stirring at 27 ^{O}C for 5 h. Subsequently, 1% wt. NAC suspension added into the mixture solution. The stirring rate kept at a speed of 350 rpm for 1 h. The resulting CH concentration in mixture solution controlled to 1% (w/v) by evaporating water. The solutions degassed for 30 min under vacuum. After that, NFE/NAC/CH solutions were poured into a Teflon mold and dried at 70 ^{O}C for 8 h to remove the solvents. The degassing and curing cycles applied using the basis of trial and error. The dried membranes were soaked in 2% wt. aqueous NaOH for 1h to remove the acid and washed with water to neutrality and then dried at 70^{O}C for 6 h. The obtained composite film peeled from the glass plate and stored at room temperature. Mean thickness of the film was 0.04 mm.

Experimental procedure

The experiments started only after a stable open circuit potential (OCP) achieved usually within the exposure time of 30 min. The electrochemical cell, assembled in a 750 mL round-bottomed flask, consisted of a saturated calomel electrode (SCE) as a reference electrode, carbon steel working electrode, and the graphite counter electrode (5 mm diameter). The SCE electrode connected to the cell using a Luggin-Haber capillary salt bridge, the tip of which separated from the surface of the working electrode by a distance of 2 mm.

In the adsorption operation, chitosan, NFE (Nano Fe_3O_4) and NAC (Nano activated carbon) loaded individually onto the plating solution. Then NFE/NAC, NFE/CH, NAC/CH and NFE/NAC/CH composites immersed in the plating solution individually. Then the adsorption tests (corrosion tests0 were carried out.

Inhibitor efficiency was determined by hanging the stainless steel coupon into an oil beaker containing oil with 1.0 M of H_2S in the absence and presence of the adsorbents at temperature ranges from 10^{O}C to 100 ^{O}C for 72 h. All subsequent concentrations of adsorbents expressed in mass fraction concentration. At the end, the coupons were cleaned with distilled water, abraded lightly with emery paper, then washed with distilled water, acetone and dried at 110 ^{O}C. The corrosion rate calculated by the following Eq. (1):

$$V_{Corr} = [(W_O - W_f)/At] \times 100 \qquad (1)$$

V_{Corr} (mg/cm^2.h) is the corrosion rate of steel coupons; W_O (g) is the steel mass before corrosion; W_f (g) is the mass of metal steel removal from corrosion solution; A (cm^2) is the surface area of hanging sheet and t (h) is the immersion time.

The percent inhibition efficiency calculated according to the following formula;

$$\eta = [(V_O - V_f)/ V_O] \times 100\% \quad (2)$$

where; V_O is the corrosion rate (mg/cm^2.h) in the absence of the adsorbent and V_f is the corrosion rate (mg/cm^2.h) in the presence of the adsorbent.

RESULTS AND DISCUSSIONS

Effect of test period

Fig. 1 showed the relation between the remaining amount of H_2S in the presence of (NAC), (NFE) and chitosan (CH) inhibitors individually at various test periods. It is clear that as the test period increases, the amount of the remaining hydrogen sulphide decreases that indicated the ability of the inhibitors in the rapid and stable reaction with H_2S that usually found in the crude oil and their ability on the H_2S adsorption. Also, it is clear that CH has higher effect followed by NAC and NFE respectively.

Effect of degree of acidity

Figure 2 showed the relation between H_2S corrosion rate and the three adsorbents concentrations; Nano iron oxide (Fig. 2.a), Nano activated carbon (Fig. 2.b) and CH (Fig. 2.c.) at different degrees of acidity. It is clear from the figure that the H_2S corrosion rate increases up to a concentration of 25 mg/l for all the three adsorbents at all the degrees of acidity followed by a rapid decrement. Also, it is shown that as the degree of acidity (pH) increases, the corrosion rate decreases in all the three adsorbents at different concentrations that illustrates the higher effect of the three adsorbents with the degree of acidity increment in agreement with Singh et al. [11] and Amosa et al. [15] because molecular H_2S predominates in the acidic range. In the range of 7 to 12, monovalent CH- predominates and above pH 12, divalent S_2- predominates. It is clear that Chitosan has the higher effective adsorption due its ability to close the vacancies in the specimen surface that prevent the H_2S attack followed by both NAC and NFE respectively.

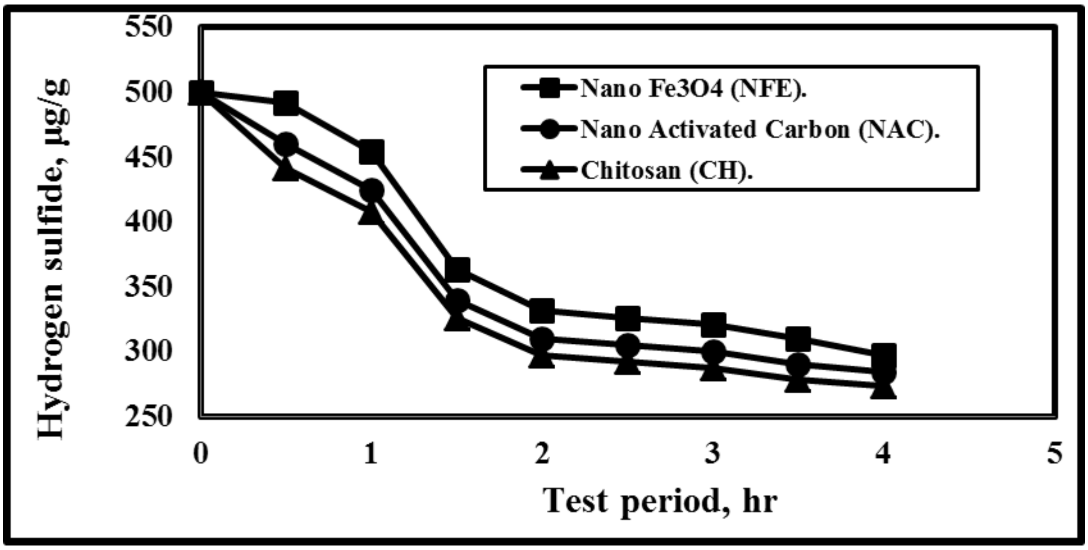


Figure 1: Effect of test period on the sulphur content remaining in the oil after using the three inhibitors individually.

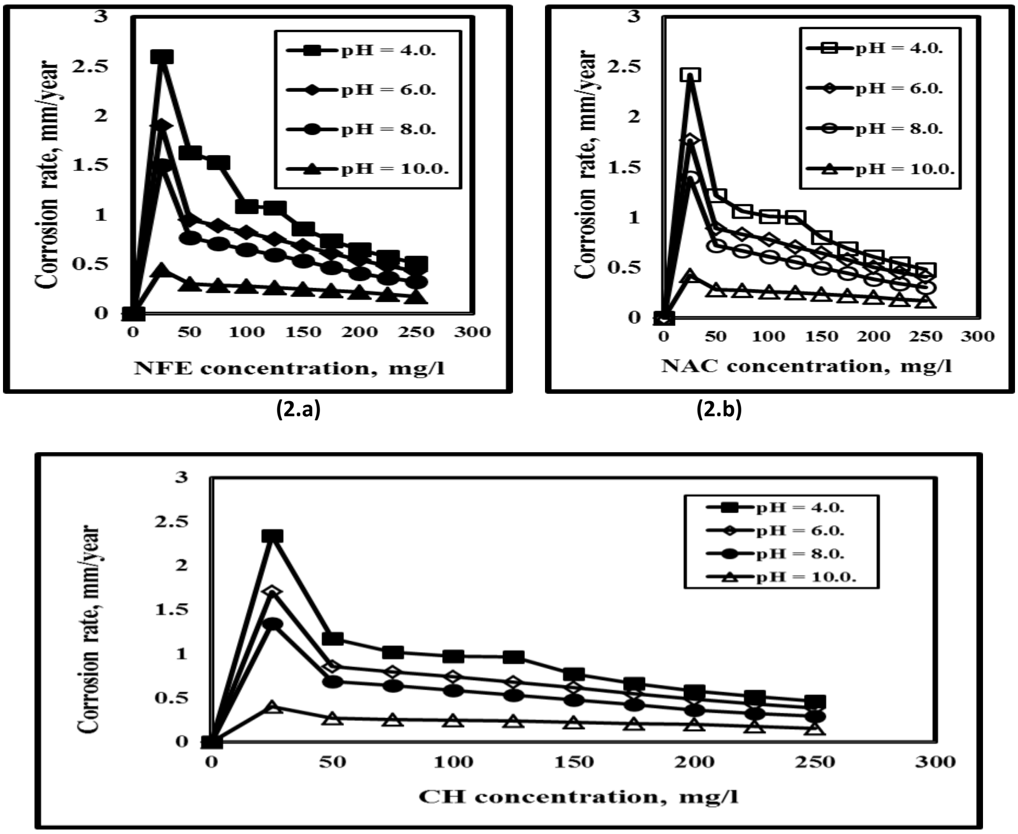
Figure 3 illustrates the relation between the adsorbent concentration and the adsorbent (inhibitor) efficiency at various degrees of acidity for the three adsorbents. It is clear that as the adsorbent concentration increases, the adsorbent efficiency increases. As pH increases, the adsorbent efficiency increases for the used three adsorbents. The CH trends shows its higher adsorption effect compared to both NFE and NAC respectively.

Effect of temperature

Figure 4 illustrates the effect of adsorbent concentration on adsorbition amount at different test temperatures for the three adosrbents. Figure 4.a showed that as the adsorbition temperature increases, the adsorbiton amount of H_2S increases up to 40 ^{O}C, then at temperatures higher 40 ^{O}C, an inflection occurs for NFE. While Figure 4.b illustrates the same trend, but the inflection occurs at 90 ^{O}C for NAC. But Figure 4.c showed that the inflection occurs at 80 ^{O}C for CH. So, it is clear that at low temperature and the adsorption process governed by weak van der Waals forces, however at higher temperature chemisorption, and probably chemical reaction is dominant showing an increase in the sorption capacity in agreement with Brieva et al. [14]. Higher condition of temperatures and pressures contributed to higher corrosion inhibition efficiencies as observed during the corrosion tests.

Adsorbent concentration

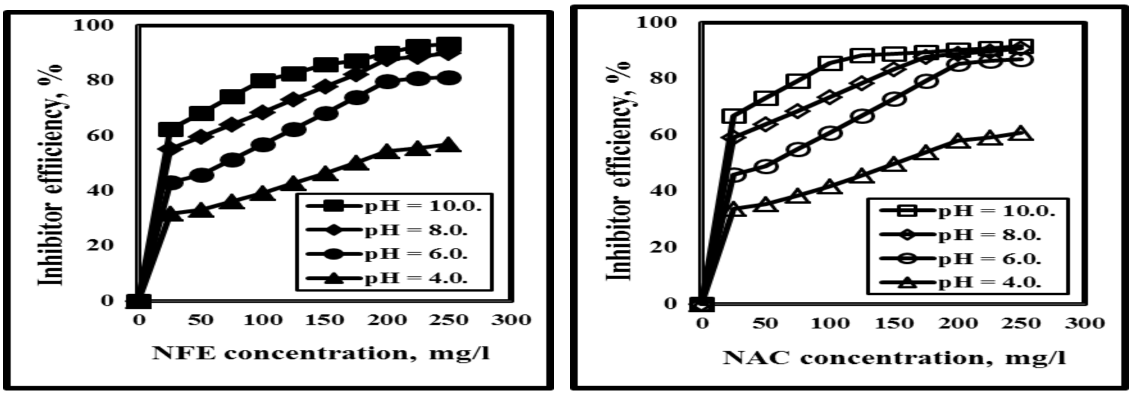
Figure 5 showed the variation of adsorbent concentration on adsorbition amount at various adsorbent types and compsites at 80 ^{O}C. It is clear that as the adsorpent concentration and adsorpent compsites concentration increases, the adsorbition amount increases up to 250 mg/l concentration, then an inflection occurs for all adsorpent and adsorpent composites of concentrations. It is clear that NFE/NAC/CH trend has the higher adsorption amount of H_2S with an optimum condition at 250 mg/l of equal constituents at 80 ^{O}C followed by CH, NAC/CH, NFE/CH, NAC and NFE trends respectively. It is clear that as the adsorbent concentration increases, the inhibitor efficiency increases in all cases of the three inhibitors indicated valuable effect of the inhibitors in adsorption of H_2S in agreement with Amosa et al. [15]. Also, it is shown that the sulfur removal rate in the reaction system with NFE/CH was much lower than the system containing NAC/CH. This result is in agreement with the study conducted by Wang and his coworkers [28], who reported that the presence of NAC/CH can significantly improve the efficiency of the reaction system and correlated to the good adsorptive property of NAC/CH. As is known, activated carbon usually used as adsorbent due to their high adsorption surface and developed porosity.



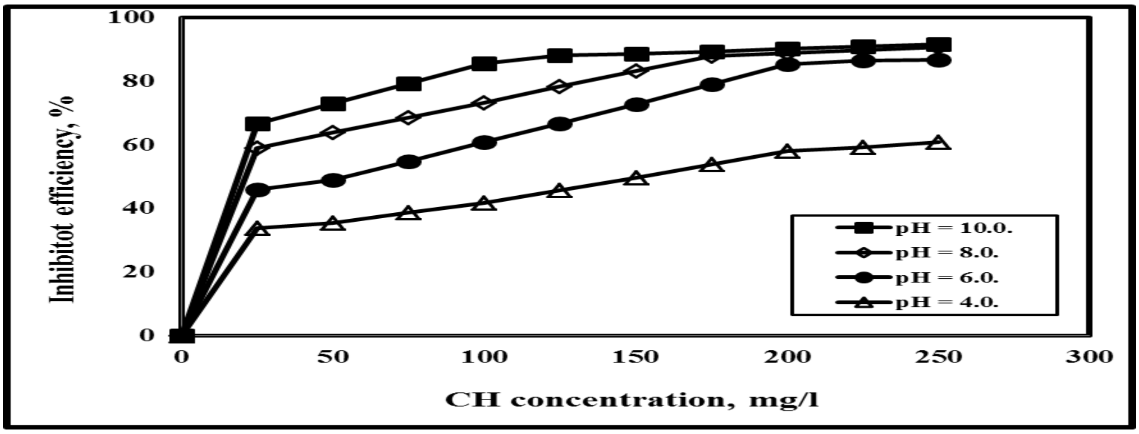
(2.a) (2.b)

(2.c)

Figure 2: Effect of pH on various corrosion rate.

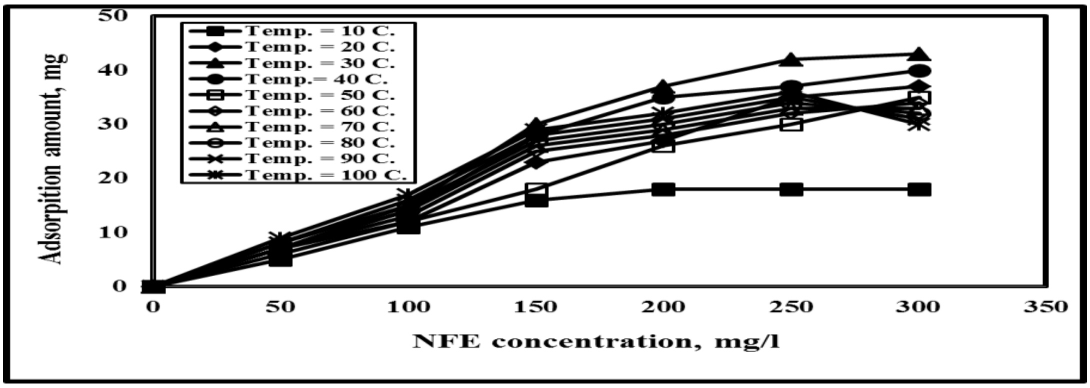


(3.a) (3.b)

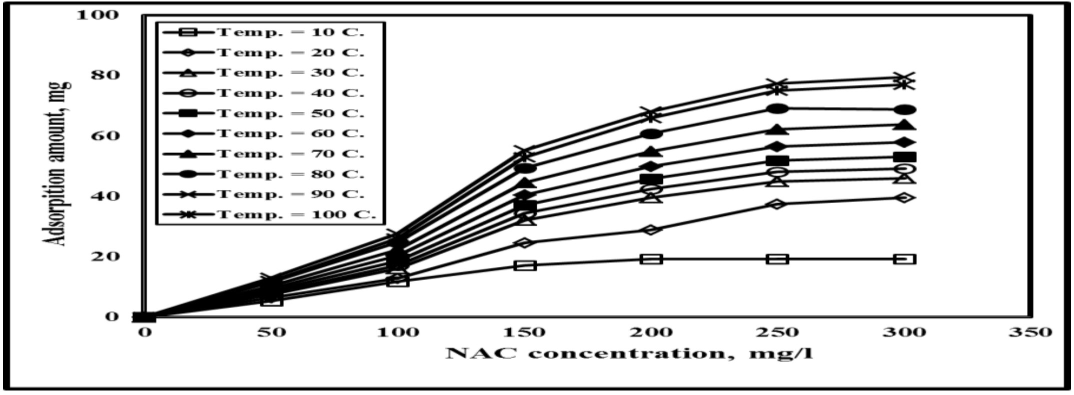


(3.c)

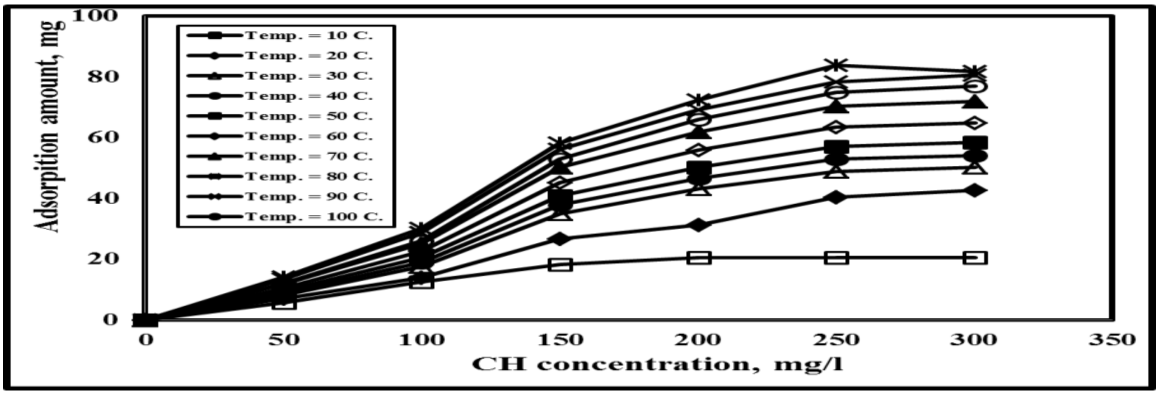
Figure 3: Effect of NFE, NAC and CH concentration and degree of acidity on inhibitor efficiency.



(4.a)



(4.b)



(4.c)

Figure 4: Effect of adsorbent concentration on adsorbition amount at different test temperatures.

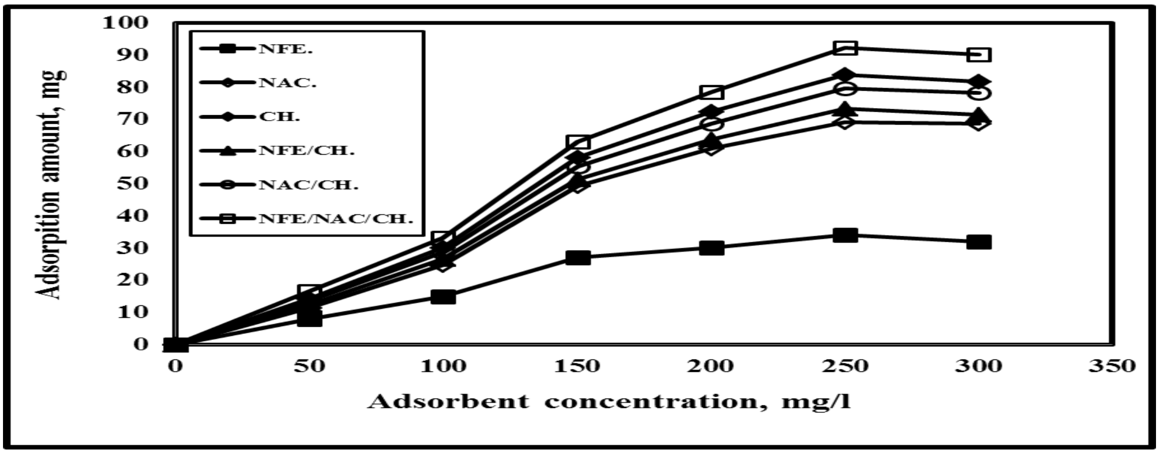


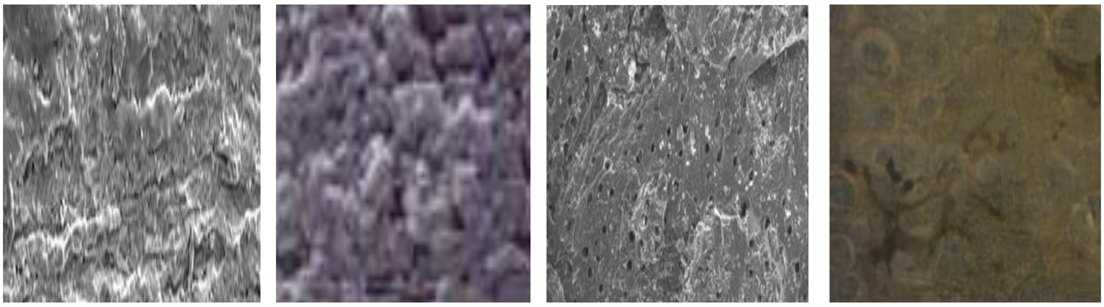
Figure 5: Variation of adsorbent concentration and amount at various adsorbent types and compsites at 80^{O}C.

Surface morphology

Figure 6.a illustrated the micrograph of H_2S corroded steel, and steel coated with NFE, or NAC or CH are shown in Figs. 6.b to 6.d. Fig. 6.b illustrated that NFE surface containing a lot of aggregates with small bright areas. While Fig. 6.c showed the NAC surface had many pores in a generally smooth surface. The adsorbent coating clearly loose with non-uniformity. The porous structure seen clearly. Fig 6.d showed that uniform layer of chitosan was formed which covered the entire steel surface.

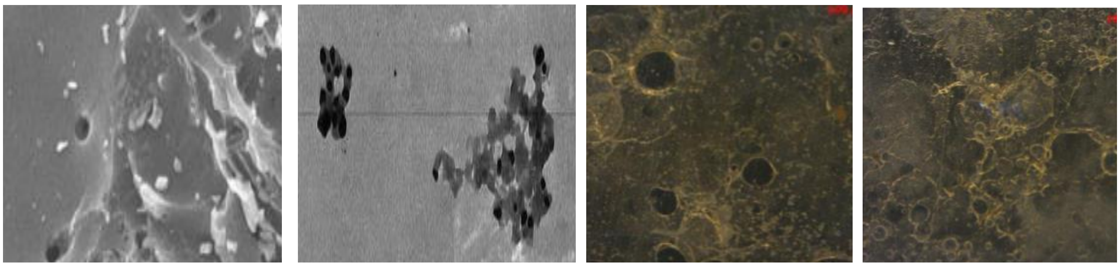
Figure 7 illustrates the NFE/NAC composite coating on the steel surface. The scattered white highlights are iron oxide particles which suggesting the formation of iron oxide particles well-dispersed covering the AC pores. The microstructure of Fe_3O_4 particles contained NAC are nearly spherical which was confirmed by scanning electron microscopy. All the nanoparticles well separated and no agglomeration was noticed and exhibiting inverse spinel facets due to the electrostatic repulsion between the positively charged nanoparticles as shown in 7.b. While Figs. 7.c and 7.d illustrate both NFE/CH and NAC/CH composites respectively. Addition of NFE leads to the formation of tiny globular particles on the surface similar to micro spheres. On close observation of the images, it depicted that addition of NFE increased the roughness of the coating due to the formation of the microsphere on the material surface. While the addition of NAC to CH produce less formation of tiny globular particles on the surface which leads to a more compact and strengthening coating of NAC/CH compared to NFE/CH coating.

Fig. 8 a, shows the SEM micrograph of the steel surface after exposed to H_2S without any adsorbent, where it can be seen that the steel forms a porous layer full of micro cracks. The aggressive solution can penetrate through these defects and corrode the underlying metal. However, in presence of adsorbent, Fig. 8.b, the surface has remarkably improved with respect to its smoothness, less porous and micro cracks, indicating considerable reduction of corrosion rate. This improvement in surface morphology is due to the formation of a good protective film on carbon steel surface is responsible for inhibition of corrosion. These pictures show that NFE/NAC/CH has a strong tendency to adhere to the steel surface and regarded as good adsorbent.



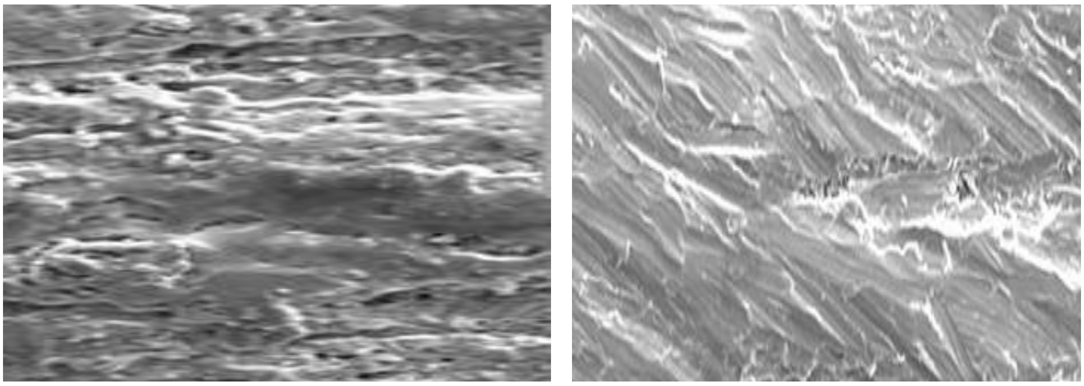
(a) (b) (c) (d)

Figure 6: Micrograph of H_2S corroded steel, NFE, NAC and CH (X2000).



(a) NFE/NAC. (b) TEM of NEF/NAC (c) 25% NFE/CH (d) 25% NAC /CH.

Figure 7: NEF, NAC and CH composites.



(8.a) (8.b)

Figure 8: Micrograph of stainless steel subjected to 1.0 M H_2S (8.a) and that of a stainless steel subjected to 1.0 M H_2S of a solution containing a composite of NFE/NAC/CH at 250 mg/L concentration and 80 ^{O}C.

CONCLUSIONS

The following conclusions obtained;

- CH, NFE and NAC deposits and composites are successfully adsorbed H_2S.
- Chitosan deposits found effective in H_2S adsorption compared to Nano activated carbon and Nano iron oxide.

- NEF/NAC/CH composites showed a higher adsorption amount of H_2S at 80mg/l concentration at 80 ^{O}C followed by CH, NAC/CH, NFE/CH and NEF respectively in agreement with both TEM and SEM observations.
- As the test period, adsorbent concentration and degree of acidity increases, the amount of the adsorbed H_2S and the corrosion inhibition efficiency increases.
- As the test temperature increases, the amount of the adsorbed H_2S adsorbed increases with an optimum value at 80^{O}C for all adsorbent types and composites.
- The TEM and SEM observations indicate the effectiveness of the adsorbents used.

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