

SULFIDE REMOVAL FROM PETROLEUM REFINERY WASTEWATER BY ADSORPTION ON CHEMICALLY MODIFIED ACTIVATED CARBON

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ABSTRACT

Experiments were carried out to evaluate the batch adsorption of sulfur compounds from petroleum refinery wastewater on a chemically modified activated carbon (MAC). The modification technique enhances the removal capacity of carbon and therefore decreases cost-effective removal of sulfide from refinery wastewater.

Different techniques have been used to characterize the modified activated carbon. Adsorption equilibrium and kinetics data were determined for sulphur removal from real refinery wastewater. The data were fitted to several adsorption isotherm and kinetics models.

The Freundlich isotherm fitted well with the equilibrium data of sulfur on different adsorbents, whereas, the kinetics data were best fitted by the pseudo-second order model. The MAC adsorbent was found to have an effective removal capacity of approximately three times that of non modified carbon. Using different MAC, sulfides were eliminated with a removal capacity of 52 mg g⁻¹.

Several chemical techniques were tested for the regeneration of saturated activated carbon and it was found that HCl showed high regeneration efficiency (86%). Therefore, MAC can be utilized as an effective and less expensive adsorbent for the reduction of sulfur in refinery wastewater.

Keywords: Modified activated carbon adsorbents, characterization, sulfur removal, refinery wastewater

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1. INTRODUCTION

Sulfides are generally considered among the most hazardous pollutants in refinery wastewater and they are an important parameter for refineries that crude oils are usually classified, in part, based upon the sulfur content. Thus, a sweet crude oil is one with low sulfur content, and a sour crude oil is one with high sulfur content [1,2].

Liquefied Petroleum Gas (LPG) that contains H₂S, mercaptans and other organic molecules are purified in the caustic scrubbing tower. The spent caustics generated from this tower contain mercaptans and sulfides which are reactive and odorous.

During caustic scrubbing, gaseous sulfide compounds such as hydrogen sulfide and thiols are absorbed resulting in waste streams known as refinery sulfidic spent caustic (RSC). It is a dark brown to black effluent that cause environmental problems because of their alkalinity (pH > 12) and high sulfide levels (1–4 wt%) [3].

The impacts caused by these industrial pollutants and growing concern for environmental issues have led to the search for new methods of treatment, and development of new materials that are able to reduce these environmental problems.

In fact, treatment of industrial wastewaters is a problem of major concern nowadays. More strict regulations are being imposed, which persevere on the need to develop and employ treatment technologies capable to deal with the hazardous pollutants present in many industrial waste streams [4].

Wastewater containing sulfur compounds presents a serious discharge problem due to their poor biodegradability, high toxicity and ecological aspects [5].

Several problems are related to sulfide buildup, these include corrosion of concrete sewer pipes, release of obnoxious odors to the urban atmosphere, safety hazards to sewer workers due to the toxicity of sulfide gas and negative impacts on the subsequent wastewater treatment [6,7].

Various treatment technologies have been used for the reduction of sulfur, which is a major contaminant in petroleum refinery and industrial wastewater. These techniques include filtration, ion exchange, coagulation/flocculation, reverse osmosis and electrodialysis [8-11].

Adsorption provides an attractive alternative treatment technique, especially if the adsorbent is inexpensive and readily available. Adsorption of sulphur has been previously studied to evaluate the overall adsorption behavior in wastewaters [12,13].

The use of activated carbon (AC), as an adsorbent, has proven to be effective in a wide range of applications, including the removal of both organic and inorganic pollutants from wastewater [14,15].

In fact, the adsorption process using activated carbon is of easy application, good efficiency and economically viable [16-18]. Besides, Activated carbons (ACs) are porous materials that have a high surface area and high adsorption capacity, which can remove a wide variety of pollutants such as dyes, heavy metals, pesticides and gases.

Due to its adsorptive properties, the ACs are used to purify, detoxify, deodorize, filter, discolor or alter the concentration of many liquid and gaseous materials. These applications are of great interest in various industrial sectors such as food, pharmaceutical, chemical, oil and mining [19].

The objective of the present work is to explore the viability of using MAC for the reduction of sulfides from petroleum refinery wastewater. Firstly, the different MAC was chemically characterised throughout dry-basis elemental and scanning electron microscopy (SEM) analysis.

Then, these materials were characterised under different pyrolysis times and temperatures and compared to the non modified activated carbon. Equilibrium and kinetics studies were carried out to determine the mechanisms of the adsorption process.

1.1. Adsorption isotherms

Adsorption is a process that results in the removal of a solute from a solution and concentrating it at the surface of the adsorbent, until the amount of the solute remaining in the solution is in equilibrium with that at the surface.

This equilibrium is described by expressing the amount of solute adsorbed per unit mass of adsorbent (q_e) as a function of the concentration of solute remaining in solution (C_e). An expression of this type is termed adsorption isotherm. Many theoretical and empirical models have been developed to represent the various types of adsorption isotherms.

At present, there is no single model that satisfactorily describes all mechanisms and shapes. Langmuir and Freundlich equations are examples of such models that are commonly used to describe adsorption isotherms in water and wastewater treatment applications.

The Langmuir isotherm [20] assumes uniform and constant binding of the solute on the surface of the adsorbent, which is usually described by:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

where q_e is the equilibrium amount of solute adsorbed (mg/g of solid), C_e is the equilibrium concentration of solute in solution (mg/L), and q_m (mg/g) and b (mg/L)⁻¹ are constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

Unlike the Langmuir isotherm model, the Freundlich isotherm (Eq. (2)) [21] does not have any thermodynamic basis and does not offer much physical interpretation of the adsorption data [20-29].

The model is not bound by a maximum uptake, and it does approach Henry's law at low concentrations.

$$q_e = K_F C_e^{1/n} \quad (2)$$

where, K_F (mg(1 - 1/n) l^{1/n}/g) and n are constants.

A combination of the Langmuir and Freundlich isotherms is expressed in the Sips isotherm (Eq. (3)) [30]. At low sorbent concentrations, the Sips isotherm approaches the Freundlich isotherm, whereas it approaches the Langmuir isotherm at high concentrations.

$$q_e = \frac{K_{LF} C_e^{n_{LF}}}{1 + (a_{LF} C_e)^{n_{LF}}} \quad (3)$$

where, K_{LF} (l/g), n_{LF} and a_{LF} (l/mg) are constants.

Another isotherm that has seen considerable applications is the Dubinin–Radushkevich shown in (Eq. (4)) [31].

$$q_e = q_D \exp\left\{-B_D \left[RT \ln \left(1 + \frac{1}{C_e}\right)\right]\right\} \quad (4)$$

Where q_D (mg/g) is the D–R isotherm constant related to the degree of solute sorption by the adsorbent surface and B_D (mol²/kJ²) is constant related to the free energy of sorption per mole of solute as it migrates to the surface of the adsorbent from infinite distance in the solution [32].

The shapes of various models isotherms depend on the type of adsorbate/adsorbent and the intermolecular interactions between the fluid and the surface [33]. The model that fits the

experimental data most accurately can then be used to describe the system and predict the adsorption behavior for practical process design.

1.2. Adsorption kinetics

The adsorption kinetics can be described by diffusion through the adsorbent, such as film, pore and surface diffusions, and pore-surface adsorption or any combination of these four steps. It describes reaction pathways and the time needed to reach the equilibrium, whereas chemical equilibrium gives no information about pathways and reaction rates [34].

Adsorption kinetics show large dependence on the physical and chemical characteristics of the adsorbent material which also influence the adsorption mechanism that can either be film or pore diffusion or a combination of both, depending on the system hydrodynamics.

In order to examine the controlling mechanism of an adsorption process and to determine the minimum necessary time to achieve equilibrium, several kinetics models such as the pseudo-first order, Elovich's, pseudo-second order and Intraparticle diffusion model can be used. Brief descriptions of these models are given in the following sections.

1.2.1. Pseudo-first order model

The pseudo-first order model is most commonly used to describe the adsorption of solute from a liquid solution. The pseudo-first order equation of Lagergren [35] and [36] is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

The linearized form of this model is given by:

$$\ln(q_e - q) = \ln(q_e) - \frac{kt}{2.303} \quad (6)$$

Where k is the kinetics constant of pseudo-first order adsorption (min^{-1}), q_e and q (mg/g) are the amounts adsorbed at equilibrium and at time t (min), respectively.

1.2.2. Pseudo-second order model

In this model, the rate limiting step is the surface adsorption that involves chemisorption, where the adsorbate removal from a solution is due to physicochemical interactions between the two phases [37].

The pseudo-second order chemisorption kinetic rate equation is expressed as [38] :

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

This model is usually represented by its linearized form as follows:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Where k_2 is the equilibrium rate constant of pseudo-second order equation (g/mg.min).

1.2.3. Elovich's model

In recent years, Elovich's model has been successfully used to describe the adsorption of pollutants from aqueous solutions. Elovich's kinetic model is given by [39] :

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (9)$$

The linearized form of this model is given by:

$$q = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \quad (10)$$

Where a initial adsorption rate (mg/g min); b is related to the extent of surface coverage and activation energy for chemisorption (g/mg), and $1/b$ is a parameter related to the number of sites available for adsorption (mg/g).

1.2.4. Intraparticle diffusion model

The intraparticle diffusion model describes adsorption processes, where the rate of adsorption depends on the speed at which adsorbate diffuses towards adsorbent (i.e., the process is diffusioncontrolled), which is presented by Eq. (11).

$$q = k_d \sqrt{t} + \theta \quad (11)$$

where, k_d is the rate constant of the intraparticle transport (mg/g/min^{1/2}) and θ (mg/g) is a constant related to the thickness of the boundary layer. High values of θ indicate greater boundary layer effect.

2. EXPERIMENTAL METHODS

2.1. Reagent

The activated carbon used in this study was obtained from Fluka (Fluka, France) with a particle size of 100-150 μm and a specific surface area of 1100 m^2g^{-1} .

Analytical reagent grade ethanol, sodium hydroxide, hydrochloric acid, sodium carbonate and sodium bicarbonate were obtained from Merck (Merck, Germany).

2.2. Preparation of MAC

Before use, the AC was rinsed several times with double distilled water to remove any fine powder, dried in the oven at 100°C for 24h to a constant mass and divided into 2.0 g portions. Each portion of the AC was transferred to a 500 mL solution of 0.1M H₂O₂, HNO₃ or CuSO₄ and agitated for 24h by a bottle roll apparatus at ambient temperature.

Then, it was separated from the solution and rinsed several times with double distilled water until no pH change in the washed liquid could be detected. On the other side, the AC was calcinated at three different temperatures (500°C, 700°C and 900°C). Finally, the different MAC was directly used for kinetic and equilibrium experiments.

2.3. Characterization of MAC

The sample morphology was observed using a scanning electron microscope (SEMJEOL 5400).

The specimens for SEM observation were prepared by depositing the sample onto specimen-stubs with conductive double sticky copper tapes, and then the sample surface was sputter-coated with Au–Pd to prevent electrical charging during examination (model Polaron SC7640, Quorum Technologies Ltd., UK). Imaging was done in the high vacuum mode under an accelerating voltage of 15 kV, using secondary electrons.

X-ray diffraction (XRD) patterns study of all samples were carried out using a Herzog ARL 9900 diffractometer with Co K_α radiations generated at 30 kV, 15 mA and results were monitored via a WinXRF software. Scattering angles were ranged from 2° to 80° with a scanning speed at 2° per minute.

For Infrared study, Modified Activated Carbon (0.15 g) was thoroughly mixed with KBr powder (IR-grade, Wako) to be 1.0 wt% and pressed into a disk of 20 mm in diameter. Fourier transfer infrared (FTIR) spectra were collected on a FTIR spectrophotometer BRUKER (EQUINOX 55).

The surface area and total pore volume were obtained by nitrogen adsorption–desorption at the liquid nitrogen temperature (−196°C) using a Quadrasorb S1 (Quantachrome Corp.) All samples were degassed at 200 °C for 4 h before analysis. The BET equation was applied to determine the surface area. The total pore volume was determined at P/P₀ = 0.98.

2.4. Point of zero charge pHPZC

The pHPzc of the MAC was determined by the solid addition method [40]. To a series of 50 mL capped Erlenmeyer flasks, 50 mL of 0.01M NaCl solution was transferred. The initial pH of the solutions was adjusted between 2 and 12 by adding 0.01M NaOH or HCl.

The initial pH of each solution was accurately recorded. Then 0.15g of MAC was added to each flask where they immediately capped. The suspension was stirred overnight to reach equilibrium and then the final pH of the supernatant liquid was recorded. The difference between the initial and final pH values was plotted against the initial pH. The point of intersection of the resulting curve at which final pH=0 gave the pHPzc.

2.5. Functional groups on MAC using Boehm titration

The functional groups on modified activated carbons were determined using the Boehm titration method [41]. Hydrochloric acid (HCl), sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃) solutions were used for the determining the total and specific acid sites, while sodium hydroxide solution was used for specifying the total basic sites [42].

A weighed amount of 2 ± 0.1 g of modified activated carbon was placed in 100 mL of the prepared 0.1M solution and shaken for about 48 h. After filtration, the excess base and acid were titrated with 0.1M HCl and 0.1M NaOH, respectively.

The concentration of acidic sites was calculated using the assumption that NaOH neutralizes carboxylic, phenolic and lactonic groups, Na₂CO₃ neutralizes carboxylic and lactonic and NaHCO₃ neutralizes only carboxylic groups.

2.6. Potentiometric titration

The residual concentrations of sulfides were measured by a titroprocesseur (titrando 716 automatic titrator, Metrohm) using Ag/Ag₂S electrode and AgNO₃ as titrant solution.

2.7. Batch adsorption

Refinery wastewater samples were collected from a local petroleum refinery and preserved in dark color plastic containers at room temperature. The main characteristics of the refinery wastewater are given in Table 1. Batch adsorption equilibrium experiments were carried out by contacting a known amount of MAC with 50 mL wastewater sample in a sealed glass bottle. Real refinery wastewater samples with different initial sulfur concentrations were tested (100, 300, 500, 800 and 1000 mg/L). The bottles were kept on a shaker at a constant temperature for 24 h to reach equilibrium. For the kinetics study, samples were withdrawn at regular intervals and filtered.

The sulfur concentration was then measured with the potentiometric method. All experiments were carried out in duplicates and the average values were reported. The uptake, q , was calculated from the difference between the initial and the final sulphide concentrations as follows:

$$q = \frac{(C_i - C_f)V}{m} \quad (12)$$

where, q (mg/g) is the uptake, C_i and C_f (mg/L) are the initial and final sulphide concentrations, respectively, m is the adsorbent dosage (g) and V is the solution volume (L).

2.8. Fixed bed treatment

Three samples of MAC were packed in glass column (200 mm height, 20 mm i.d). In order to study the ability of oxidation and calcination to enhance the adsorption capacity, these columns were used for sulphide removal from the real spent caustic wastewater. The wastewater was introduced through the columns and the effluent concentrations were determined. The initial pH were adjusted to 11 and the flow rate for the three columns were maintained at 2 mL/min.

2.9. Desorption/Regeneration of MAC

Regeneration is an important aspect in evaluation the capacity and practicality of any adsorbent. In this study, the effectiveness of chemical regeneration was investigated. These include different solvents using 1 M HCl, 1 M NaOH and ethanol (70%). An amount of 4 g of spent activated carbon was placed in 50 mL of the prepared solution and shaken for about 2 h. The regenerated MAC was then washed with distilled water and dried at 105 °C.

The efficiency of regeneration was then tested by subjecting the regenerated MAC to a batch equilibrium experiment, similar to the one described in Section 2.7. The procedure was repeated for four cycles. The regeneration efficiency (RE%) was determined using the following equation:

$$RE (\%) = \frac{q_r}{q_e} \times 100\% \quad (13)$$

Where, q_e is the adsorption capacity of non modified activated carbon (mg/g) and q_r is the adsorption capacity of regenerated carbon after the re-adsorption equilibrium (mg/g).

3.RESULTS AND DISCUSSION

3.1. Chemical surface characterization

[Table 2](#) lists the different functional groups available on modified activated carbon. The use of chemical reagents in the activation process provides an increase in the amount of acid groups present in the ACs surface, as observed in other studies [43, 44].

As can be observed in Table 2, there was a gradual increase in the amount of acid groups (lactonic and phenolic) for MAC, which consequently caused an increase in the amount of total groups. The carboxylic groups have not been detected and basic groups too.

Additionally, it can be seen that acid characteristics are more evident for AC-HNO₃. On the other hand, the basic character is absent for all MAC. The basicity is due to Lewis basic sites, oxygen free, on the graphene layer, and from some surface groups containing oxygen such as carbonyls, pyrone, and chromene type structures [45].

The pH drift method provides important information about the characteristics of acidity and basicity of activated carbons, as the pH_{pzc} value, which has helped in the understanding of the adsorption mechanism. According to Table 2, the pH_{pzc} value of 3.8 for the AC-HNO₃ was lower than for AC-500°C (7.2) and AC-H₂O₂ (7.8), respectively. Indeed, the acid characteristic of the three MAC agrees with the results obtained by Boehm method and by other researchers which produced ACs from a chemical activation [46,47].

The crystalline phases of MAC samples determined by XRD analysis are shown in Fig. 1. In different MAC, the major phases are quartz. The XRD patterns show no difference between nitric acid treated samples and the H₂O₂ treated samples, which suggests that phase transformation has taken place. The intensities of quartz also show a significant enhancement, making them the dominant phases in MAC samples.

SEM pictures provide surface morphology of the different MAC samples at micro-scale. From Fig. 2, the contrast in surface features between the non modified AC which is relatively smooth and flat, and the acid treated specimen, AC-HNO₃, provides clear visual evidence for the new surface area generated by strong acid treatment. The acid treated sample shows many new cavities and coarsened exterior probably due to removal of some acid-soluble salts. FT-IR spectra of the different MAC samples are presented in Fig. 3. The broad peak at 3130–3450 cm⁻¹ corresponding to OH vibrations, appears for different MAC. By examining the four spectra above, there is a great similarity between them with the presence of some differences.

On the one hand, the spectra of oxidized AC-HNO₃ and H₂O₂ are almost identical with four bands: those between 3500 and 3700 cm⁻¹ correspond to the vibration of OH groups, those near 2300 cm⁻¹ correspond to a carbon atoms, while one located around 1100 cm⁻¹ corresponding to a CO bond. Regarding the spectrum of AC-500°C, there is only two bands corresponding to the carbon-carbon bonds and carbon-oxygen band.

The spectrum of non modified AC contains the bands corresponding to OH, CO and CC bonds. The N₂ adsorption isotherms at 77K of both untreated sample and chemically activated carbons are shown in Fig. 4. The characterization by adsorption and desorption of nitrogen allows us to determine the specific surface and the distribution of the pore size.

The adsorption isotherms of the activated carbons are type I isotherms, indicating the presence of large fractions of micropores and in some cases mesopores, while the untreated sample can be considered as non-porous. Isotherm data were analyzed for BET area, total

pore volume, micropore volume and average pore width. Specific surface areas were calculated according to the BET method.

Total pore volumes were directly derived from the adsorbed quantity at high relative pressures ($p/p_0 \sim 0.95$, while p_0 is the saturation pressure of Nitrogen at 77.36K and equals to 101.38 KPa). The results obtained from nitrogen isotherms are presented in [Table 3](#).

Hence, as shown on Table 3, the MAC provides a quite high BET surface (945 m²/g as an average value) and has essentially a mesoporous structure. Indeed, 40% of its total pores are mesopores with pore width comprised between 2 and 50nm. The micropore proportion in that case is 20% of the total created pores.

3.2. Effect of adsorbent amount

In any adsorption process, the amount of adsorbent plays an important role. In order to evaluate the effect of adsorbent amount on sulphide adsorption, various amounts of MAC (0–10 g/L) were used. The effect of adsorbent amount on the removal capacity of sulphides is shown in Fig.5.

It was found that the concentration of sulphide decreased with an increase in adsorbent amount. This is expected, as increasing the adsorbent amount at a fixed sulphide initial concentration provided more available adsorption sites and hence the removal is enhanced. For the refinery wastewater an adsorbent amount of 4 g/L was sufficient to remove most of the sulphides from the wastewater. K8.

3.3 Adsorption kinetics

Kinetic studies are important to understand the dynamic of the reaction in terms of order of the rate constant. Since the kinetics parameters provide information for designing and modeling the adsorption process. The results shown in Fig. 6. indicate that most of the sulphide removal takes place during the first 30 min.

After that the sulphide concentration remained almost unchanged, which is assumed to be the equilibrium amount. The adsorption data shows a curvature in the initial period, which is attributed to the intraparticle diffusion or external mass transfer effects. The sulphide adsorption rate was determined for the three adsorbents by contacting refinery wastewater samples with different initial sulphide contents (100, 300, 500, 800 and 1000 mg/L) using an adsorbent dose of 4g/L.

The data of adsorption kinetics for the different MAC were fitted to the different kinetic models described in Section 1.2, namely: Lagergren's pseudo-first order (Eq. (5)), pseudo-second order (Eq. (7)) and Elovich's (Eq. (9)). [Fig. 7](#), shows the relationship between $\ln(q_e - q)$ and t , according to the linearized Lagergren's pseudo-first order equation (Eq. (6)).

It is observed that the results deviate significantly from a straight line, which indicates that the pore diffusion is not the sole rate controlling step, as the Lagergren's pseudo-first order model suggests.

Similar results were found by plotting q vs. $\ln(t)$ according to the linearized Elovich's equation (Eq. (10)), shown in [Fig.8](#). for different adsorbents, which also proves the incompatibility of the Elovich's model to describe the adsorption mechanism.

The best straight lines that pass through the data points were used to determine the kinetics parameters of both models, which are shown in Table 4. The deviation of the values of R^2 from unity is a measure of the incompatibility of each respective case. On the other hand, when t/q was plotted against t , according to the linearized pseudo-second order model (Eq. (8)), a clear linear relationship was observed for different adsorbents, as shown in Fig. 9.

The data were fitted perfectly well by straight lines, with R^2 values too near to 1.00. This proves that the adsorption kinetics is more accurately described by pseudo-second order model. The kinetics parameters of the model are shown in Table 4. To further confirm this conclusion, q was plotted against \sqrt{t} , which would, according to Eq. (11), give a straight line if intraparticle diffusion was the limiting process.

However, the results in Fig. 10 show that this is not the case. The early stage sharper portion is assumed to be due to the mass transfer external resistance; whereas the later linear portion is an indication of some intraparticle diffusion control.

3.4. Adsorption isotherms

The adsorption isotherms describe how the adsorbate molecules are distributed between the liquid phase and solid phase when the system reaches the equilibrium [48]. The analysis of isotherm data by fitting them to different models is important to find a suitable model that can be used [49].

The modeling of the equilibrium data is very important in the design of adsorption systems. In this study, the linear and non-linear regression analysis of experimental data has been carried out using two-parameter isotherm models including Freundlich and Langmuir as they are known as two-parameter models, which provide information on the adsorption capacity and constants related to the activation energy.

The values of the maximum adsorption capacity (Q_m), correlation coefficient (R^2), and other constants obtained for the models from experimental data are shown in Table 5. In order to optimize the design of an adsorption system of different MAC, the two adsorption isotherm models namely the Langmuir and Freundlich, isotherms in their nonlinear forms, were applied to the equilibrium data, and the results are shown in Fig. 11. and Fig. 12.

The Langmuir model assumes that the adsorption is a process which occurs in a homogeneous surface, in which the molecules form a monolayer of adsorbate on the surface of the material, saturating the pores and preventing the transmigration [50, 51].

However, the Freundlich model is an empirical equation based on the adsorption on heterogeneous surface [52, 53]. Comparing the R^2 values (Table 4), it can be observed that the Freundlich model yielded the best fit with the highest R^2 value. The fit of the experimental data to the Freundlich model indicates a heterogeneous nature of the different MAC surface [54].

The Q_m value of 52 mg g⁻¹ describes the high adsorption capacity of the MAC. Considering that, we can notice that sulphide molecules can diffuse from solution into the MAC, which justifies the high value of Q_m . In addition, the adsorption is favored due to the acid characteristics of the MAC surface, which was described by Boehm and pH drift methods. The negative surface of the different MAC interacts effectively with sulphides, due to cationic property of sulphur compounds.

3.5. Fixed bed treatment

The modified activated carbons were used directly in fixed bed-columns for a sulphide removal from a real refinery wastewater sample, containing 1000 mg/L of sulphide. To explore the effect of applied modifications on the adsorption capacity of activated carbon, the amounts of sulphide adsorbed onto NM-AC, AC-HNO₃, AC-H₂O₂ and AC-500°C carbons are measured as a function of total added wastewater (Fig. 13).

The amount of sulphide adsorbed during the breakthrough experiment is calculated using the equation (12). It is seen that all investigated carbons adsorbed relatively an important amounts of sulphide, following the same trend found in the batch adsorption experiments. The differences between adsorption capacities, found by batch type sorption experiments and fixed bed procedure, could be attributed to the competitive adsorption of organic and mineral species present in the rinsate effluent.

Another alternative explanation that could be attributed to the applied flow rate and, as a consequence, to the contact time which was not sufficient to reach equilibrium and to have complete removal of sulphide.

3.6. Regeneration of activated carbon

The regeneration of spent modified activated carbon was evaluated using different regeneration solvents, and the results are shown in Fig.14. Chemical regeneration using HCl achieved the highest regeneration efficiency of 86%. NaOH and Ethanol, showed good regeneration efficiency reaching 76%.

3.7. Conclusions

The effectiveness of modified activated carbon for the removal of sulphide from real refinery wastewater was evaluated. Kinetics and equilibrium data for the adsorption of sulphide were obtained and fitted to different kinetics and isotherm models.

The MAC adsorbent was found to have an effective removal capacity of approximately three times that of non modified carbon. Using different MAC, sulphide were eliminated with a removal capacity of 52 mg g⁻¹.

The results show that the capacity of AC-HNO₃ is comparable to other adsorbents, which proves that it can be considered as a better solution to enhance the capacity of the removal of sulphide from spent caustic refinery wastewater than the commercial activated carbons. Kinetics data were best fitted by the pseudo-second order model, and the equilibrium data followed the Sips isotherm. High regeneration efficiency was achieved using HCl.

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TABLES

Table. 1 Characterization of used refinery wastewater

Characteristic	Value
pH	12.9
Conductivity (ms cm ⁻¹)	126.7
Sulphide (mg/l)	17 200
NaOH (Wt%)	7.5

Table. 2 Surface functional group and pH drift on different MAC

MAC	Functional group (mmol/g)				Total Basic sites	pH drift
	Carboxylic	Lactonic	Phenolic	Total Acid Sites		
AC-HNO ₃	0.000	0,110	1,658	1,768	0.000	3.8
AC-H ₂ O ₂	0.000	0,159	1,222	1,381	0.000	7.2
AC-500°C	0.000	0,119	1,314	1,433	0.000	7.8

Table 3 : Surface and porous texture parameters of different MA

	NM-AC	AC-HNO ₃	AC-H ₂ O ₂	AC-500°C
BET surface area (m²/g)	521	836	986	1012
Total surface area (m²/g)	532	846	993	1014
t-Plot external area (m²/g)	568	867	1007	1053
Total pore volume (cm³/g)	0,280	0,338	0,446	0,718
Micropore volume (cm³/g) (d < 2 nm)	0,169	0,143	0,100	0,262
Mesopore volume (cm³/g) (2nm < d < 50 nm)	0,050	0,066	0,160	0,423

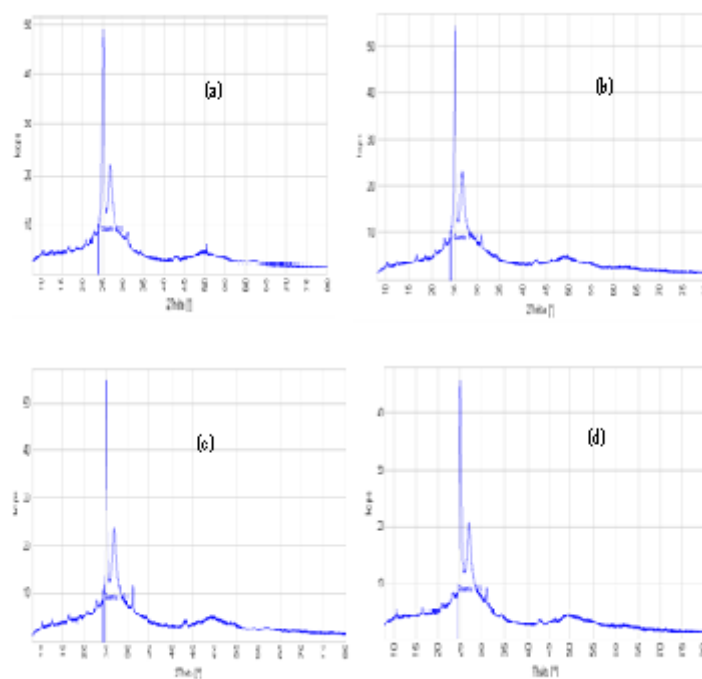
d: pore diameter

Table 4 : Fitted kinetic parameters for adsorption of Sulphide onto AC-HNO₃, AC-H₂O₂, AC-500°C at 25°C.

Pseudo-first order	q_e (mg/g)	k(min⁻¹)	R²
NM-AC	13,92	0,018424	0,984
AC-HNO ₃	91,10	0,396116	0,944
AC-H ₂ O ₂	92,11	0,370783	0,912
AC-500°C	122,97	0,398419	0,817
Elovich's equation	a (mg/g/min)	1/b (mg/g)	R²
NM-AC	0,04457	15,79	0,923
AC-HNO ₃	0,04457	15,79	0,923
AC-H ₂ O ₂	0,08953	15,51	0,942
AC-500°C	0,08906	17,87	0,897
Pseudo-second order	k (mg/g.min)	q_e (mg/g)	R²
NM-AC	0,6053	19,2307	0,978
AC-HNO ₃	10,8695	52,6315	0,997
AC-H ₂ O ₂	11,1111	52,6315	0,997
AC-500°C	7,6923	58,8235	0,991

Table 5 : Langmuir and Freundlich isotherm model parameters and correlation coefficients for adsorption of Sulphide on different MAC.

Langmuir	Q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2
NM-AC	22,727	0,0068	0,930
AC-HNO ₃	55,555	0,0030	0,955
AC-H ₂ O ₂	52,631	0,0038	0,996
AC-500°C	58,823	0,0022	0,998
Freundlich	K_F	$1/n$	R^2
NM-AC	0,1347	1,172	0,933
AC-HNO ₃	0,0877	1,128	0,972
AC-H ₂ O ₂	0,1089	1,119	0,979
AC-500°C	0,0438	1,249	0,989

FIGURES**Fig. 1: XRD patterns of (a) Non modified AC, (b) AC-HNO₃, (c) AC-H₂O₂, (d) AC-500°C.**

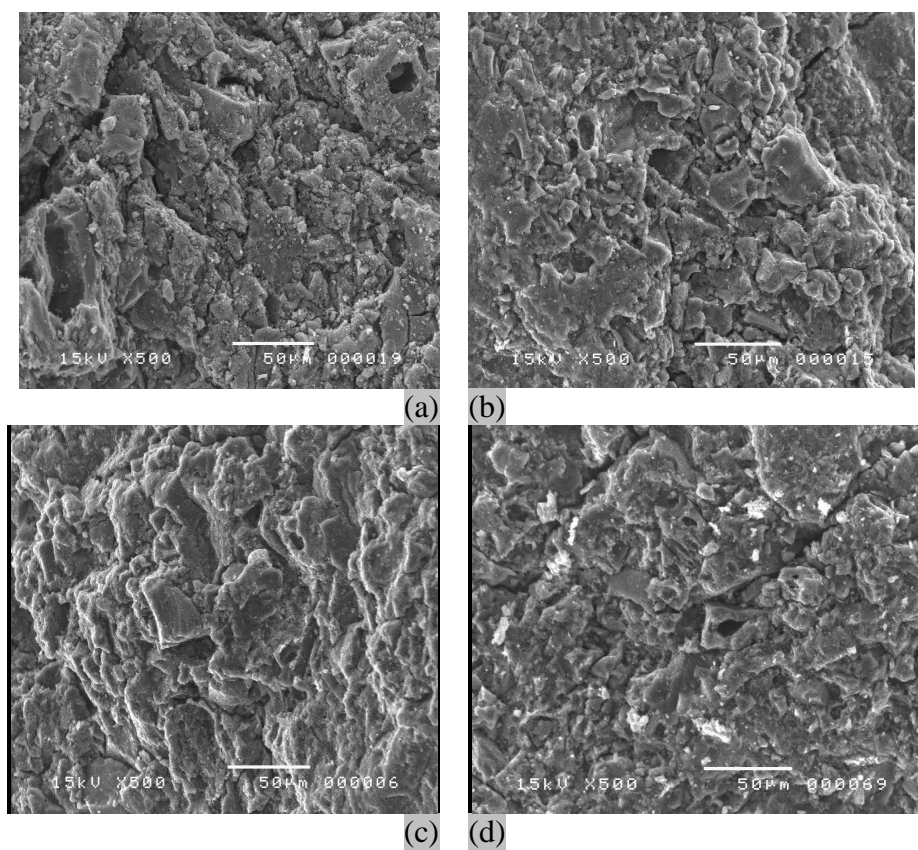


Fig. 2: SEM photographs of (a) Non modified AC, (b) AC-HNO₃, (c) AC-H₂O₂, (d) AC-500°C.

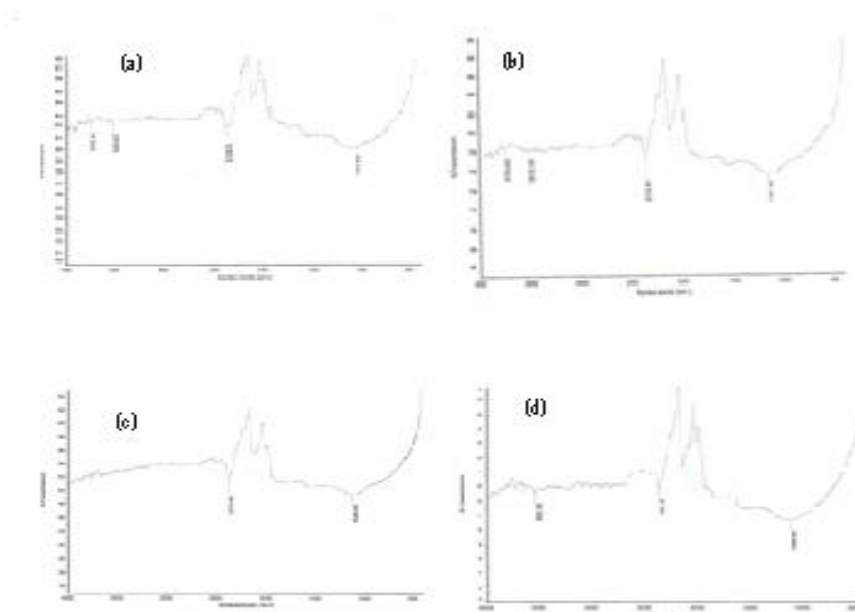


Fig. 3: FT-IR spectra for (a) Non modified AC, (b) AC-HNO₃, (c) AC-H₂O₂, (d) AC-500°C.

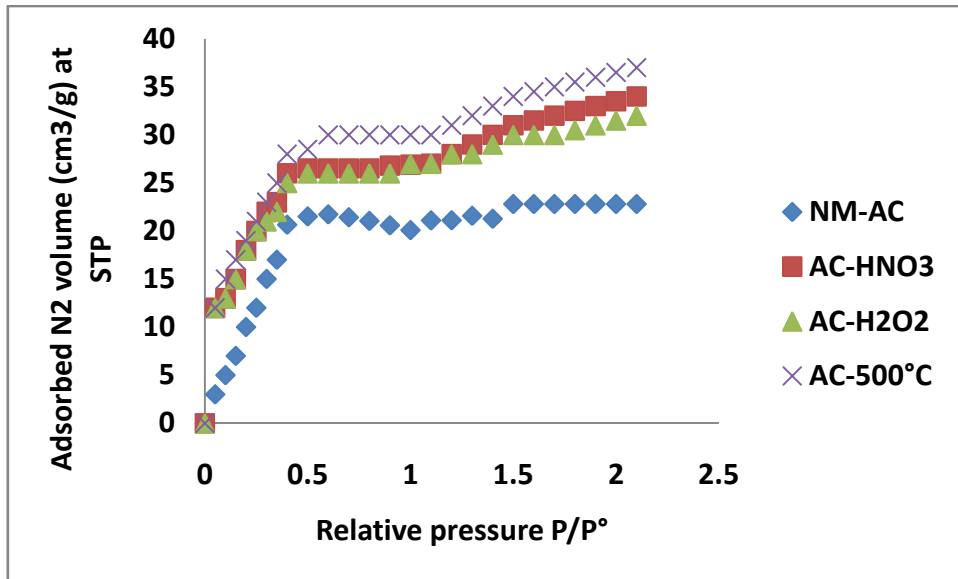


Fig. 4 : Adsorption isotherm of nitrogen at 77 °K by different MAC.

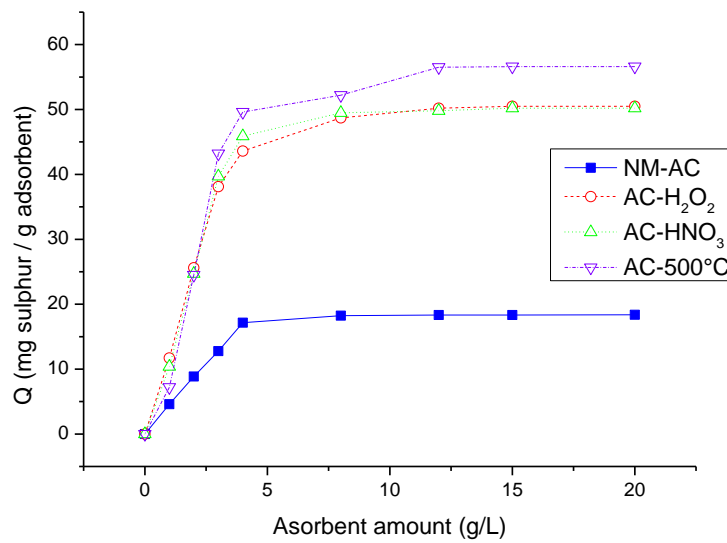


Fig.5: Effect of adsorbent amount on sulphide removal at 25°C.

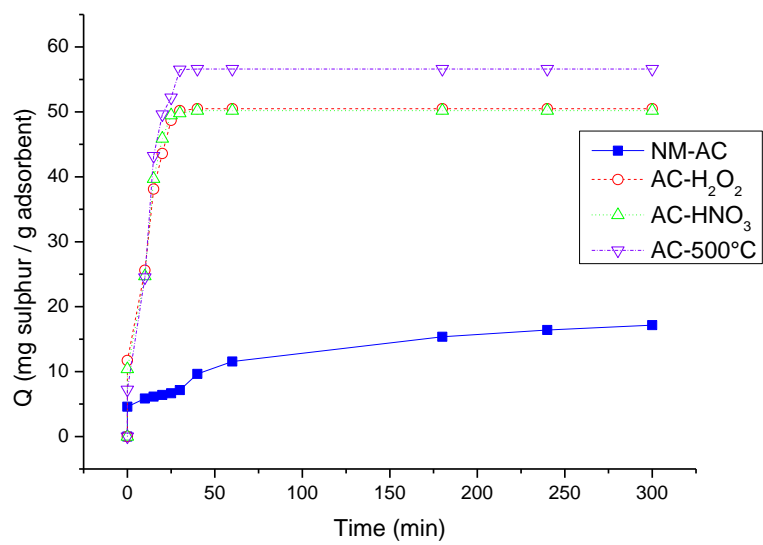


Fig.6: Kinetics of sulphide uptake at 25°C for different MAC.

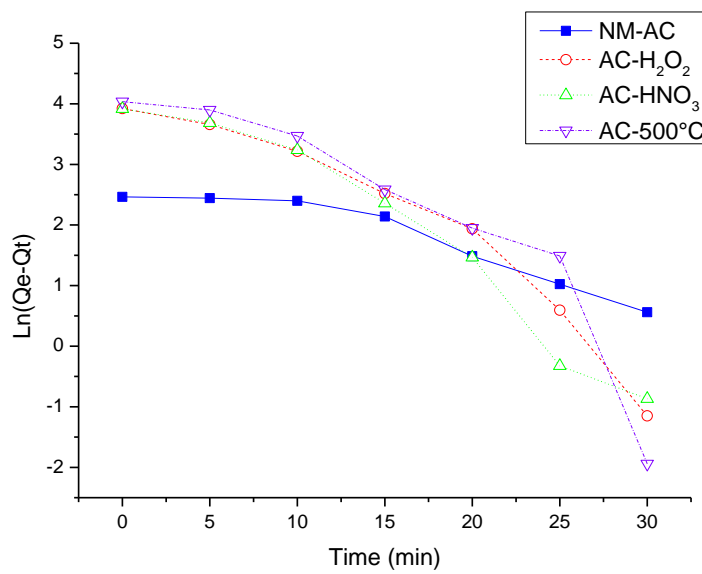


Fig.7: Ln (Qe – Q) vs t according to pseudo first order model for different MAC.

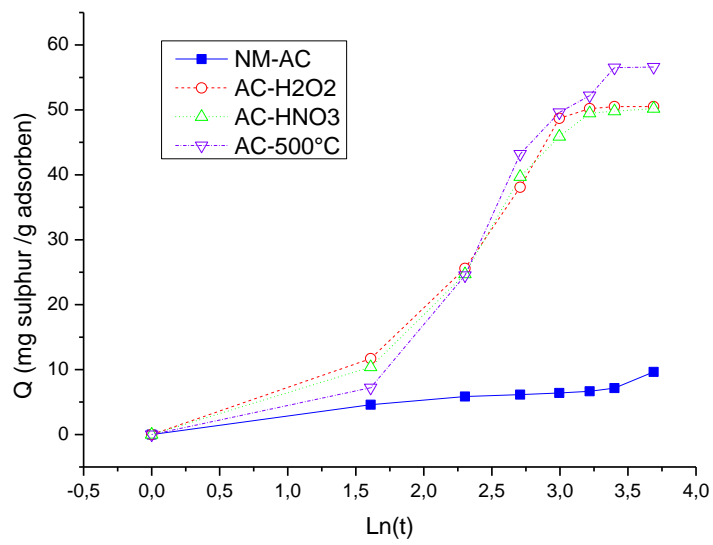


Fig.8: Q vsLn(t) according to Elovich’s model for different MAC.

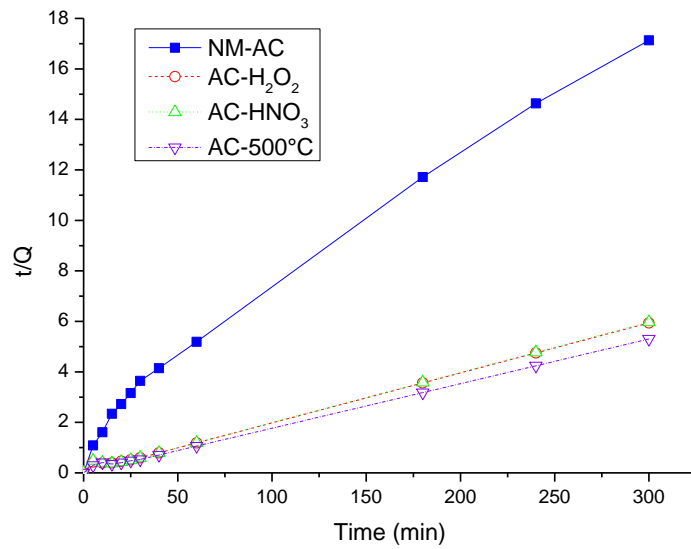


Fig.9: t/Q vs t according to pseudo-second order model for different MAC.

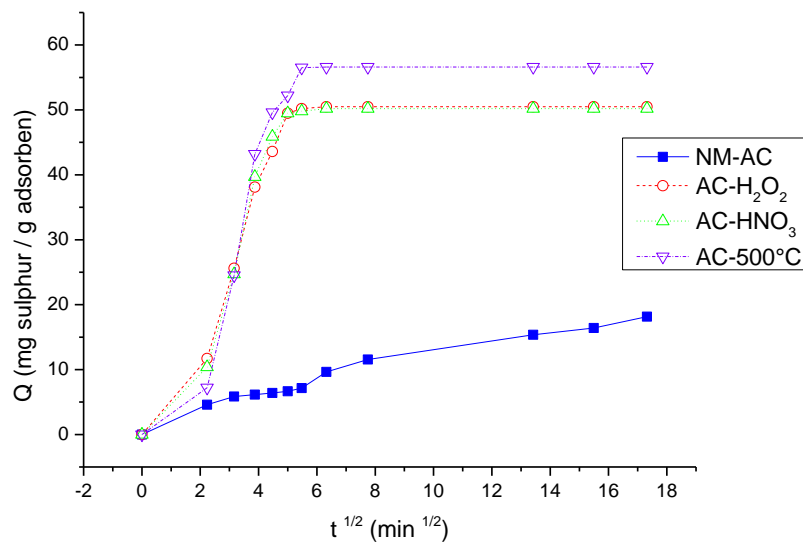


Fig.10:Q vs \sqrt{t} according to the intraparticle diffusion model for different MAC.

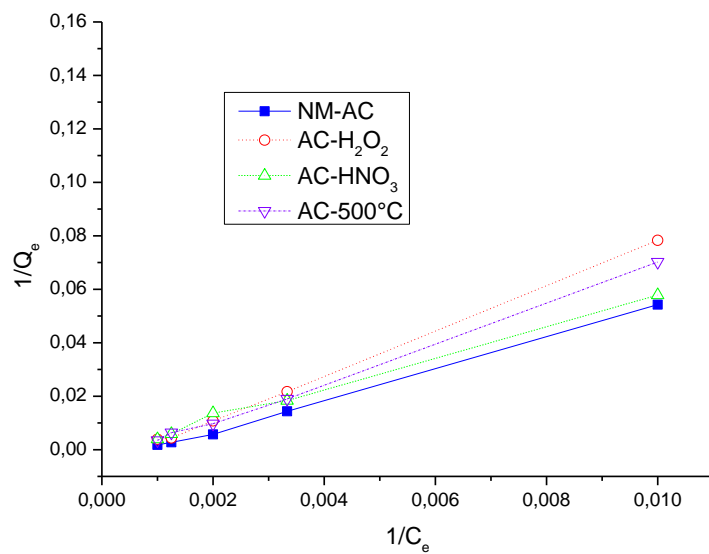


Fig. 11: Langmuir fitting for the equilibrium isotherm data of the sulphide adsorption on different MAC- Adsorption experiments were carried out in batch mode using 0,4 g of modified activated carbon and 100 mL of sulphide solution (100–1000 mg L⁻¹). Samples were agitated for 24 h at 25°C.

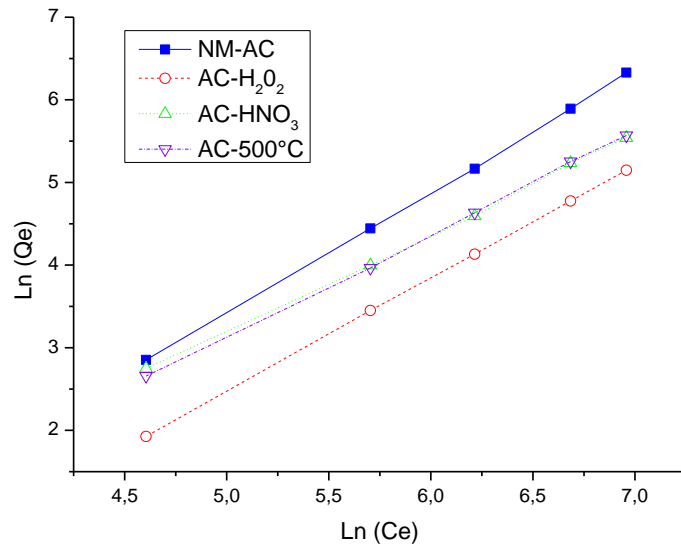


Fig. 12: Freundlich fitting for the equilibrium isotherm data of the sulphide adsorption on different MAC
 Adsorption experiments were carried out in batch mode using 0,4 g of modified activated carbon and 100 mL of sulphide solution (100–1000 mg L⁻¹). Samples were agitated for 24 h at 25°C.

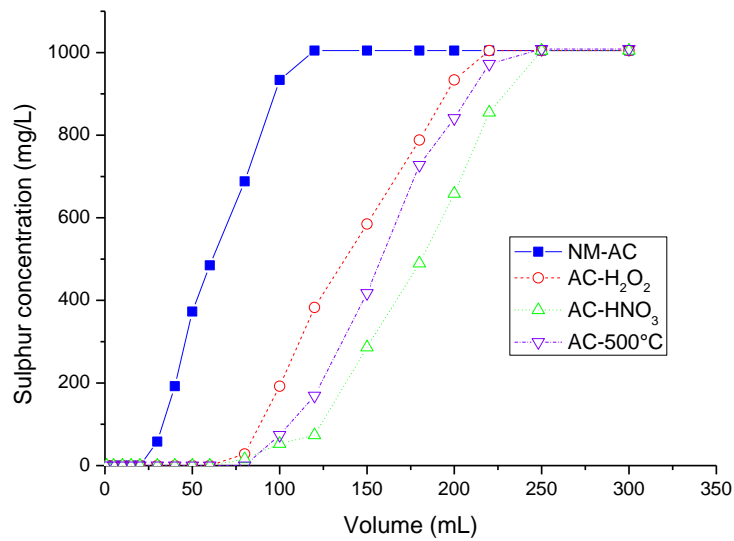


Fig. 13: Breakthrough curves of sulphide onto different MAC, columns wastewater contained 1000 mgL⁻¹ of sulphide.

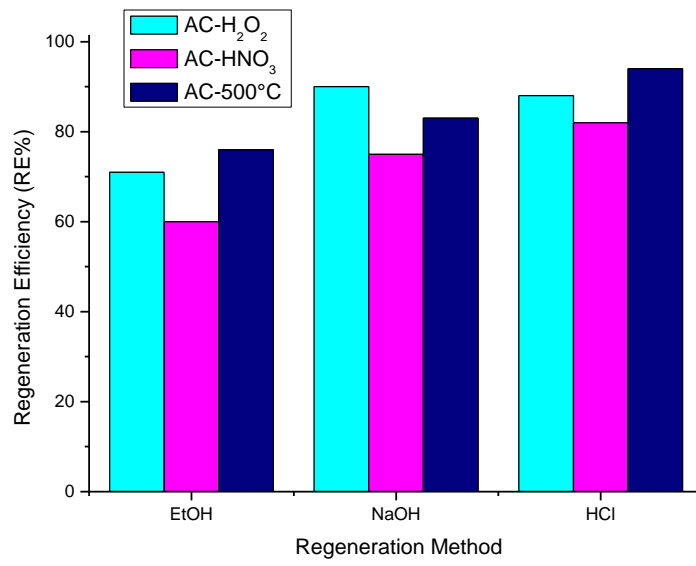


Fig. 14: Regeneration efficiency for batch experiments using different solvent for one cycle of regeneration.