Selective Removal of Metal Ions from Crude Oil using Synthetic Zeolites

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Abstract- The removal efficacy of three synthetic zeolite materials for the selective removal of metal ions from crude oil was investigated. The zeolite materials used for the study include; zeolite A, zeolite Y and zeolite K-L. Nickel, vanadium and sulphur were the target metals due to the problems they pose during the hydroprocessing of crude oil. The result shows that, zeolite A is able to remove all the metal ions considered (nickel, vanadium and sulphur) at concentrations of 0.035ppm, 0.25ppm and 51.13ppm respectively. Zeolite Y and zeolite K-L showed removal of nickel and sulfur, at concentrations of 0.004ppm and 52.58ppm respectively for the Y zeolite and 0.011 and 43.23ppm respectively for the K-L zeolite. The later zeolites were unable to remove vanadium from the crude oil. The study thus showed the selectivity of the synthetic zeolites for the different metal ions.

Keywords- zeolite A, zeolite Y, zeolite K-L, nickel, vanadium, sulfur, metal ions and crude oil

I. INTRODUCTION

Trace metals are often found in crude oil. Nickel and vanadium are the most abundant of the trace metals in crude oil [1]. These metals can cause a number of serious issues during crude oil processing, some of which include; irreversible deactivation of catalysts used for hydroprocessing, contribution to ‘acid rain’ by V_2O_5 as well as formation of SO_3 which deteriorates catalysts support, corrosion of engine parts and boilers. There is therefore need for the removal of these metals among other metals during hydroprocessing of crude oil.

There had been efforts in the removal of these metals which are present majorly as Porphyrins from crude oil. The metal-porphyrinic complexes are commonly associated with asphaltenes [2]. Thus, most of the currently used metal removal methods require severe reaction conditions as a result of the low reactivity of the asphaltenic aggregates. Some of the dominant methods of metal removal from crude oil include; deasphalting, hydrocracking and hydrotreating [3]. Other methods under investigation include; oxidation, adsorption, acid attack, solvent extraction etc [4-7]. The crude oil feedstock used in the hydrocracking and hydrotreating which are the methods currently used, often contain high amounts of trace metals which poisons the catalysts during hydroprocessing [3]. A pre-treatment step is therefore required to reduce the concentration of these catalysts poisons prior to the hydroprocessing.

Zeolites, having porous open framework, large surface area, catalytic and ionic exchange properties have been employed in industrial applications such as water softening, heterogeneous catalysis, separation, environmental remediation [8-9] and of course could serve as good materials for the removal of these metal ions from crude oil.

Zeolites are naturally occurring crystalline aluminosilicate minerals which are made up of three dimensional frameworks of tetrahedral molecules linked through the oxygen shared atoms [9]. Zeolites could also be synthesised from silicon and aluminium sources. The fundamental building block of all zeolites is tetrahedron of silicon or aluminium ion surrounded by four oxygen anion (AlO_4 or SiO_4 tetrahedral) which then forms the 3 dimensional frameworks with linked systems and well defined pores [9]. The tetrahedral are arranged in such a way that each of the oxygen anion is shared with another silica or alumina tetrahedron. The silica tetrahedral is electronically neutral with its +4 charge balanced by the four tetrahedral oxygen anions. On the other hand, each alumina tetrahedron has an excess charge of -1 since it is trivalent and is bonded to four oxygen anions. Hence each alumina tetrahedron requires a +1 charge from a cation (e.g. sodium) in the structure to be electronically neutral.

Zeolites are proven ion exchangers and have been successfully applied in the removal of heavy metals from aqueous solution [10-14] and for the catalytic cracking of heavy oils [15-17]. Not much work is done on the contributions of zeolites for the removal of metal ions from oil. A recent investigation showed the selective contributions of the natural zeolites in the removal of these poisonous metals from crude oil [18]. There is therefore need to investigate the contributions of synthetic zeolites to the removal of the metals, thus in the present study, the performance of the synthetic zeolites is investigated.

II. MATERIALS AND METHOD

A. Materials

Zeolite A (Na_6 $[AlSiO_4]_6.24H_2O$), zeolite Y (Na_{56} $[Al_{56}Si_{136}O_{384}].250H_2O$) and zeolite K-L ($K_6Na_3Al_9Si_{27}O_{72}].21H_2O$) and the crude oil samples were obtained from the UK. Ethylenediaminetetraacetic acid (EDTA) was purchased from sigma Aldrich, UK.

B. Experimental method

The metal ions extraction/removal was done as shown by the setup in fig.1. 1g of zeolite A powder was suspended in 50mL of the crude oil in a separating flask containing 25mL of EDTA. This mixture was properly mixed using the flask shaker for an hour at room temperature (18°C) to properly homogenize the mixture. The mixture was then left to stand for a day so as to attain equilibrium and enable the separation of the distinct layers.

The aqueous layer was then carefully separated from the organic (oil) layer and the aqueous layer analyzed for the metal ions. This procedure was repeated for zeolite Y and zeolite K-L. A similar experiment was carried out but without introducing any zeolite. This was labelled as a ‘control’ since it was used to compare the effectiveness of the heavy metal immobilization of the different zeolite materials used.

C. Characterization

The aqueous samples containing the metal ions were analyzed using the inductively coupled plasma atomic emission spectroscopy (ICP-AES), a spectro ciros ICP-AES spectrometer.

Figure 1: Experimental setup

III. RESULTS AND DISCUSSION

The efficiencies of the synthetic zeolites for the selective removal of the metal ions from crude oil have been clearly demonstrated from the ICP analysis as shown in figure 2. This is evident from the appearance of metal ions such as nickel and vanadium that were initially absent from the ‘control’. This behaviour could be explained based on the fact that, the metal ions (nickel and vanadium) are present in crude oil mainly as porphyrinic complexes which are usually associated with asphaltenes fractions. The asphaltenic aggregates thus have to be broken so as to expose the metal ions for removal. The synthetic zeolites due to their catalytic property could have broken down these aggregates into lower molecular weight fractions thus exposing a significant amount of the metal ions for removal from crude oil.

The efficiencies of the metal ions removal by the different zeolites are as shown in Figures 2-4. The zeolites were observed to show metal ions removal at varying degrees particularly for zeolite A that was able to remove all the zeolites considered. Zeolite Y and zeolite K-L each showed selectivity for nickel and sulphur. This could be due to the nature of acid sites for the different zeolites. The result of the analysis shows, zeolite A to be efficient at removing all the metal ions, however, the extent/amount of removal varied; nickel was removed at concentration of 0.035ppm, vanadium at 0.25ppm and sulphur at 52.13ppm. Zeolite Y was found to be efficient in the removal of nickel at a concentration of 0.004ppm and sulfur at concentration of 52.58ppm. The metal selectivity for zeolite K-L, was found to be similar to that for zeolite Y. The K-L zeolite was found to efficient for removal of nickel and sulfur at a concentration of 0.011ppm and 43.23ppm respectively. The concentrations of sulfur from the experiment were found to increase from concentration of 31.557ppm to 58.068ppm. The two later zeolites were not able to remove vanadium ions from crude oil.

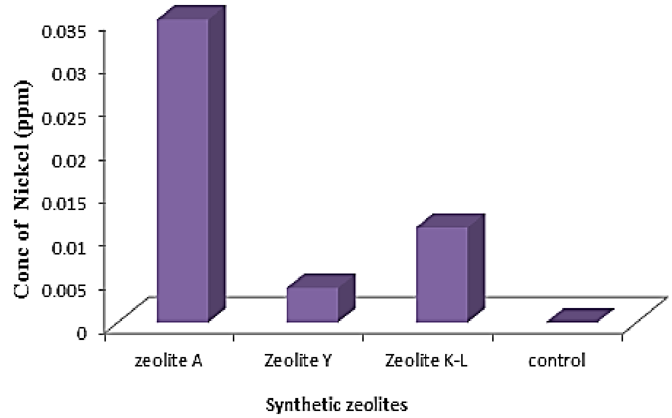

Figure 2: Nickel concentrations indifferent zeolites

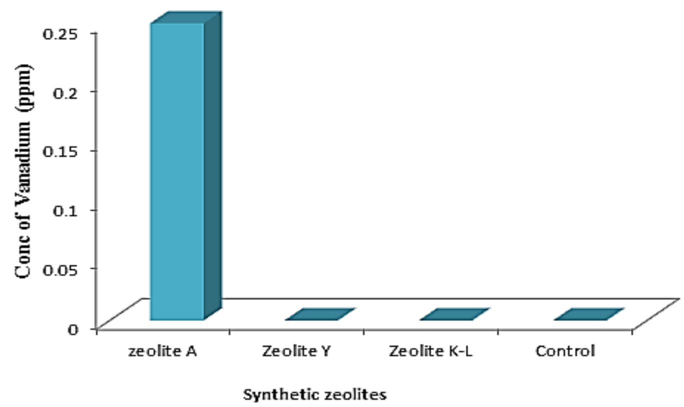

Figure 3: Vanadium concentrations in different zeolites

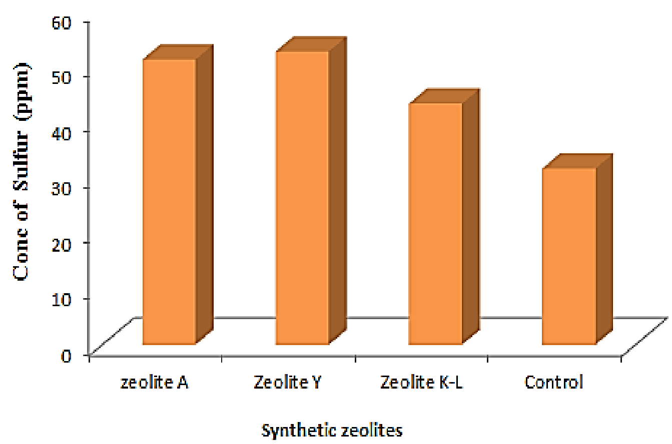

Figure 4: Sulfur concentrations indifferent zeolites

IV. CONCLUSION

The synthetic zeolites investigated have proven to contribute positively in the removal of the metal ions (nickel, vanadium and sulfur) from crude oil. The different zeolites were observed to be selective at removing the metals. These zeolites with dual catalytic and ion exchange properties could be used in a pretreatment stage to remove these metal ions prior to the hydroprocessing of crude oil, thus, reducing the overall cost to crude oil processing.

ACKNOWLEDGMENT

The Authors would like to express profound gratitude to Prof. Craig D. Williams for his guidance and support during the course of this research. The financial support received from Benue State University Makurdi, Nigeria is also appreciated.

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