“Recovery of some organic matters from resultant condensate from natural gas industry”

Presented By

Rania Fathy Abdallha Eid Abu Neama

B.Sc. in Major Chemistry, 1996

A Thesis Submitted in Partial Fulfillment

Of

The Requirements for the Master Degree

In

Environmental Science

Department of Environmental Basic Science

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Approval Sheet

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This Thesis Towards a Master Degree in In Environmental Science

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Abstract:

Exhausted molecular sieves sorbent media (EMSSM) used in the purification of natural gas is considered industrial waste causing disposal problem. This work was carried out to utilize this waste in the treatment of produced wastewater and to recover organic matters. X-Ray analysis revealed that the main constituents of EMSSM are like bentonite and most clay. EMSSM material was tested in different forms (untreated, chemically treated, thermally treated) for the removal of pollutants from industrial wastewater as(organic matter, oil and grease, turbidity and some metals) which tested using jar test with and without ferric chloride as coagulants. The using chemically and thermally treated EMSSM in order to increase its adsorption efficiency. Characteristics of these sorbents were investigated by X-ray diffraction, Energy Dispersive X-Ray (EDX), Thermogravimetric analysis (TGA). The untreated, chemically treated, thermally treated EMSSM were found to remove organic matter from industrial wastewater with removal percentage reached to (70.47%), (78.63%) and (86.81%) respectively. Factors affecting the removal percentage such as time, dose, pH and temperature were investigated to assess the optimum conditions for turbidity, organic matter and oil and grease removal. These parameters were further used in thermodynamic and kinetic modeling of the adsorption processes. In the uptake evaluation part of the study, adsorption ratios of negative charge particles on EMSSM match to Langmuir, and Freundlich, adsorption isotherm data.

Key word; molecular sieve, adsorption, wastewater treatment, clay, isotherm, organic matter.

C O N T E N T S

List of Abbreviations

EMSSM	: Exhausted Molecular Sieve Sorbent Media
AAS	: Atomic absorption spectroscopy.
ASTM	: American Society for Testing and Materials.
AWWA	: American Water Works Association.
BOD	: Biochemical Oxygen Demand.
COD	: Chemical Oxygen Demand.
OM	: Organic matter.
TDS	: Total dissolved solid.
TGA	: Thermogravimetric analysis.
O&G	: Oil and grease.
PW	: Produced Water.
API	: American Petroleum Institute Separators
CPI	: Corrugated Plate Interceptors
WWTP	: Waste Water Treatment Plant.
DAF	: Dissolved Air Flotation
NG	: Natural gas.
MS	: Molecular sieves.
AOPS	: Advanced oxidation process.
BTEX	: Benzene, Toluene, Ethyl benzene, Xylene.
FTE	: Freeze Thaw Evaporation.
TG	: Thermo Gravimetric.
DTG	: Differential Thermo Gravimetric.
WW	: Wastewater
NTU	: Nephelometric Turbidity Unit

Bbl.	: Barrel
FT-IR	: Fourier-Transform Infrared Spectroscopy
EDX	: Energy Dispersive X-ray spectroscopy
RSE	: Rapid Spray Evaporation
C.V	: Calorific Value
XRD	: X Ray Diffraction
EPA	: Environmental Protection Agency

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1-Introduction

1-1. Introduction

Natural gas is a valuable resource both as a clean source of energy and as a chemical feedstock. Before use, it has to pass through several processing steps. These steps are necessary to be able to transport the gas over long distances and for the recovery of valuable components contained in the gas.

Produced water is the hugest waste current is produced from petroleum and natural gas industries. It is a mixture of different inorganic and organic compounds. Recently because of the rising quantity of waste all over the world, the effect and the outcome of produced water discharging on the environment has got a significant concern of environmental interest. Produced water is traditionally treated through different chemical, physical and biological methods. Compact physical and chemical methods favorable using in offshore platforms because of space limitations. But, current technologies cannot remove small suspended oil particles and some dissolved elements. Besides, many chemical treatments, spend high initial or running cost and also produce hazardous sludge .However, biological pretreatment of oily wastewater can be used in onshore facilities because of low cost and environmental friendly method. Combined physio-chemical and biological treatment of produced water can be used to meet limits of discharge or reuse. (**Ahmadun, et al., 2009).**

Oil and gas industry produces about 14 billion barrel (bbl.) of produced water annually **(Rodney, 2003 and Veil, et al., 2004).**

The water varies greatly in quantity and quality, either can be a useful by-product **(Arthur et al., 2005).**

During petroleum or natural gas exploration and production, huge quantities of petroleum hydrocarbon containing 'produced water' are simultaneously recovered. During the recovery of oil in onshore sites, separation of the petroleum hydrocarbon and water mixture is made through various units where the water recover is also discharged into storage facilities above ground, or re-injected into a subsurface formation as a permanent disposal. In many cases, regular disposal process like these caused extreme environmental petroleum hydrocarbon contamination to ground, surface and coastal waterways. Thus, can assess the performance of a field for removing petroleum hydrocarbons from generated produced water (**Telleza et al., 2002).**

Molecular sieve is one of potential stages for natural gas purification that could be applicable for removal of mercury, water, others, this sieve depends on zeolite structure, numerous zeolite species that differ in chemical composition, crystal structure and adsorption properties are known (**Flanigen et al., 2001).** After several times of operation, molecular sieves were exhausted. The amount of exhausted molecular sieves is approximately high, where total quantities of molecular sieves contaminated is 500 ton / year in natural gas sector in Egypt (**personal communication**).

Clay minerals, such as bentonite and zeolite, are the probable alternatives, while they have large surface areas with negative charge, which can be electrically charged for organic and inorganic cations from wastewater **(Konig et al., 2012)**. Their

sorption efficiency come from their large surface areas and exchange spaces (**Babel and Kurniawan, 2003).** Lately, the synthesis of zeolite is from other materials, for example clay, fly ash and rich material with aluminates and silica typically, zeolites are commonly produced from the hydro gels of silicate and sodium aluminate (**Breck 1974).** The production of zeolites from clays, as a source of Silica and alumina is a common source, but it is still continual investigated with positive results **(Chandrasekhar and Pramada, 1999)**.

Clay used in concurrence with alum or ferric chloride, result in enhance turbidity and colour moving from wastewater **(Mittal and Mehrotra, 1981).**

Kendall (1996) demonstrate that, the efficiency of clay could be enhanced with acid activation of some clay .The "thermal activation process" suggested by **(Juang et al., 1997)** was else applied.

Furthermore acid treatment was used to remove cations from the crystal structure to give clay with enhanced porosity and higher surface area, which improve both chemical properties and adsorption capacity, like catalytic activity and ion exchange capacity **(Kendall, 1996).**

(Dilek and Bese, 2001; Stephenson and Duff, 1996), was found that, the using of clay like a coagulant aid in water treatment by alum, lime and ferric chloride the turbidity and colour removal efficiency was enhanced especially, at combinations with low ferric chloride or alum dose, for the clays tested.