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Treatment of drilling mud waste water of block six oilfield plant Sudan using zeolites

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Abstract

Natural zeolite samples were collected from Gedaref state (East of Sudan) and characterized using XRF, FT-IR, XRD powder and N_2-adsorption analysis. The elemental analysis by XRF showed the zeolite sample contains some impurities such as MgO, CaO and Fe_2O_3 with moderate to high percentages. FT-IR spectrum emphasized the existence of aluminosilicate core of the zeolite whereas, XRD powder indicates that zeolite of Stellerite-type was detected to dominate the natural sample. The natural zeolite material was activated with hydrochloric acid and sodium chloride solutions before applying for the heavy metals treatment process. The removal efficiency of the activated natural zeolite was studied using standard solution containing mixture of some heavy metals. Some parameters such as pH, concentration of metal ions and contact time for high removal efficiency were optimized using aqueous solution of Cr^{3+}, Fe^{2+}, Zn^{2+} and Co^{2+}ionic mixture. The results showed that at optimum conditions, the zeolite material has consistence efficiency to remove all heavy metals in the mixture i.e. ca. 77%. Then these optimum conditions were followed to minimize the level of targeted heavy metals (i.e. Cr^{3+}, Fe^{2+}, Zn^{2+} and Co^{2+}) in the wastewater of drilling mud (fluid). The experimental data showed that the respective removal percentages of these heavy species were 96.8%, 83.8%, 38.4% and 38.3% the mechanism by which the zeolite removed these metallic species was investigated using Freundlich and Langmuir models. The findings illustrated that the removal of Cr^{3+} and Fe^{2+} ions fitted well to Freundlich isotherm (model), whereas that of Co^{2+} and Zn^{2+} was found to obey Langmuir model.

Keywords: Drilling mud, drilling fluid, natural zeolites, Ion exchanger, Adsorption.

1. Introduction

Drilling fluid or mud is a mixture of barite, clay and other chemical additives in a liquid phase. It is considered the life-blood of drilling operations because an oil or gas well cannot be drilled without continuous circulation of the drilling fluid to facilitate drilling operations. Drilling mud performs numerous functions such as removal of drilled cuttings, control of formation pressure, maintenance of wellbore stability and facilitation of proper bit performance [1]. A drilling mud is used to control subsurface pressures, lubricate the drill bit stabilize the wellbore, and carry the cuttings to the surface, among other functions. The solids volume of the cutting scan range from a few cubic meters to several hundred cubic meters for each well drilled depending on the depth of the hole and on the type of the fluid used.

Over the long history of offshore development of oil and gas resources, a large number of different chemical formulations of drilling fluids have been used. The different types of drilling fluids can be separated into two basic types: water based fluids (WBFs) and non-aqueous based fluids (NABFs). WBFs, used in most offshore drilling operations, consist of water (fresh or salt), barite, clay, caustic soda, lignite, lignosulfonates and/or water-soluble polymers. WBFs may also contain low concentrations of specialty chemicals added to solve some particular problem that is affecting mud properties (e.g. tributylphosphine to control foaming, ammonium bisulfite to remove oxygen sodium bicarbonate to remove excess calcium ions) [2].

The amount of drilling waste produced by a given drilling process varies because it depends on the well depth, the kind of drilled formation, and on the mud and water management regime. Field data show that drilling a length of 1 meter of borehole produces 0.6 cubic meters of waste, and 60–80% of this waste constitutes spent drilling muds. The rest is a solid waste such as cuttings spoiled by mud and hydrated mud cakes removed from borehole walls during pipe trips. Drilling waste testing has shown that spent drilling mud has elevated values of pH, solid materials, total dissolved solids (TDS), surfactants, chloride ions, sulphate ions, dissolved organic carbon (DOC), oil hydrocarbons, heavy metals such as arsenic, barium, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, zinc, tin, and cobalt, and some radioactive materials from drilled shale formations [3].

Zeolites are highly crystalline aluminosilicate materials, consisting of either Si or Al atoms interconnected via oxygen bridges. Si and Al are also referred as “T atoms”, as they are the center of tetrahedral SiO_4 or AlO_4 structures. These tetrahedra are the building blocks forming the several crystalline lattice structures known so far, from either naturally occurring or specifically designed synthetic zeolites. Their intricate structural arrangement is also responsible for the high specific surface area of these materials, which present figures exceeding 700 mg^2 [4].

Zeolite observed in Sudan in Gedaref state in East Sudan, the most basic rocks around Gedaref and Gallabat are fine to very fine-grained, crinites and basalt. The fine –grained types with a doleritic texture are sometimes highly vesicular with zeolite amygdales and are prone to selective decomposition, zeolite include natrolite, chabazite, stablote and philipsite [5].

The Sudanese main petroleum basin called Muglad basin and it`s part of trend of cretaceous sedimentary basins of apparent rift origin, the basement adjacent to Muglad basin is predominantly Precambrian and Cambrian metamorphic rocks which include, Granitic gneiss and granodiortic gneiss, and gneiss basement is overlain by quartzite of Paleozoic age, the oldest sedimentary rocks are non-Marin of lower Jurassic salt (halite) siltstones, and premo-Triassic stones [6].

The scope of this study to remove some heavy metals from mud drilling fluid by using zeloite, to prodect the envirment from heavy metals like (Cr^{3+},Fe^{2+}, Co^{2+} and Zn^{2+})

2- Experimental

2.1 Materials

Samples of mud waste drilling were selected from block - 6 Elfulla west Kordofan state (800 km from Khartoum) according to standard sample methods. The waste drilling mud is stable colloidal mixture with high water content and it difficult to filter, Dehydrated by 80% H_2SO_4, an appropriate demulsifer was added to destroy the stability like $AlCl_3$, $CaCl_2$ and $Al_2(SO4)_3$ were chosen as potential demulsifers. Preliminary screening tests were conducted with 9 g/cm^3 H_2SO_4 to 200 cm^3 mud waste solution under stirring, then 5 g/cm^3 demulsifiers was added [7]. However another synthesize solutions containing metal ions were prepared by dissolving ($CrCl_3.6H_2O$ (93%, $(NH_4)_2.SO_4.FeSO_4.6H_2O$ (98%), $CoCl_2$ (97%) and $ZnCl_2$ (97%) in distilled water.

2.2 Zeolite collection and activation

The natural zeolite was collected from Gadarf state (550 km from Khartoum), The given amount of the material was washed with deionised water three-four times to remove any dust, it was immersed in 1.0 M HCl for 5 hours and NaCl for 24 hours to be Na-zeolite. It was ground to approximately 125 µm (120 mesh) size powder. The sample was then dried in an electric oven at 150–200ºC for 2–3 h before using for adsorption purpose.

2.3 Zeolite characterization

The quantitative analysis of structure was done using X-ray diffraction which determine the structure as well as the of zeolite purity, A Pan analytical x`pert^3 MRD, Copper Kα radiation at 40kv/0 mA with a goniometer speed at 2°/min. XRD analysis was performed from 0 to 10.0° and 20 to 30.0°.Total element analysis was performed by X-ray fluorescence. Infrared spectroscopy of all samples were obtained in KBr pellets in the 4000-400cm^{-1}, characterization was performed using FTIR spectrophotometer 84005 Shimadzu. And measure specific surface area by BET method. Nitrogen gas adsorption isotherms at liquid nitrogen temperature (77° K) were obtained with a laboratory-built volumetric apparatus equipped with a Data metrics 0-1000 Tor pressure gauge. The dried samples were mechanically ground in an agate mortar for 10 minutes and degassed overnight at (77 Kelvin) under a 0.03 Tor vacuum. Five to seven measurements of adsorbed gas volume were performed for relative pressures, P/Po, ranging from 0.05 to 0.25. Specific surface areas were calculated after the linearized BET equation. The pore size distribution was determined by Barrett-Joyner-Halenda (BJH) method using automated equipment (Autosorb 1-Quantachrome Instruments).

2.4 Removal of heavy metals

To remove metal ions from solution there are many parameters affected like pH, contact time and concentration.

2.4.1 The effect of pH

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent, It has been identified as the most important variable affecting metal adsorption onto adsorbent, this partly because hydrogen ions themselves are strongly competing with adsorbate [8]. Adsorption experiments were carried out in pH range of 2 to 8 keeping all other parameters constant in batch solutions contain initial concentrations 200 ppm using HNO_3 and NaOH to adjust pH (pH meter model 3305 Jenway UK). To study the effect of pH on adsorption capacity of zeolite the mechanism of adsorption at the Zeolite surface reflects the nature of physicochemical interaction of the metal ions in the solution and the active sites of the Zeolite [9].

2.4.2 The effect of contact time

The adsorption of (Cr^{3+},Fe^{2+},Cd^{2+} and Zn^{2+}) invesegated in on to adsorbents as a function of shaking time in the range of 10 to 120 Minute using Hot stirrer Model: LMS-1003 Scott science UK.

2.5 Batch study

Batch adsorption was performed to for types of synthesis ions (Cr^{3+},Fe^{2+},Co^{2+} and Zn^{2+}), In typical adsorption run 40ml of solution with 0.4g of dry zeolite in polyethylene flak. With particle size 125-130 µm zeolites. Kept in hotplate stirrer at room temperature 27± 0.5 with 80 minutes, and (2, 4, 6, 8, 10) pH, during experimental period to prevent any sedimentation, and to provide proper agitation, The residual metal ion concentration of the filtrate was determined using Atomic adsorption spectrometer ICE 3000 series Thermo Scientific-USA.

The removal percentage by zeolite was calculated according to equation:-

$$\text{Metal removal\%} = \frac{Co-C}{Co} * 100 \qquad (1)$$

Where Co and C are initial and final concentration (mg/l) of the metal ions solution contact with the mass of zeolite.

The amount of Ca^{+2}, Fe^{+2} and Mg^{+2} adsorbed by zeolite was determined by using mass balance equation $qe = \frac{v(Co-C)}{m}$ (2)

Where q_e is the metal concentration on the zeolite (mg/l) at equilibrium, C is metal concentration in solution (mg/l) at equilibrium, Co is initial metal concentration in solution (mg/l), v is volume of initial metal solution used (ml) and m is mass of zeolite used [10]. The final metal concentration in the supernatant (liquid phase) was measured on Atomic absorption.

2.6 Adsorption isotherms

The sorption data have been subjected to different sorption isotherm Freundlich and Longmuir. The equilibrium data for metal cations over the concentration range from 100 to 500 ppm at room temperature for 80 minutes, the mixture was filtered and the filtrate analyzed for metal ions concentration using AAS. The data was fitted into the following isotherms Freundlich & Longmire isotherms [11].

2.6.1 Freundlich Adsorption Isotherm

Freundlich model supposes that uptake or adsorption of ions occurs on heterogeneous surface by monolayer, these data often fit the empirical equation proposed by Freundlich:

$$q_e = K_f (Ce)^{1/n} \qquad (1)$$

The Freundlich equation can be linearized by taking logarithms and constants can be determined. The above equation can be linearized as follows:

$$\text{Log}\,(q_e)=\log(k_f+1/n\,\log\,(C_e) \qquad (2)$$

Where k_f and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The initial concentrations of Cr^{3+} were varied and adsorbent dose was kept constant in order to determine the equilibrium isotherms.

2.6.2 Langmuir Adsorption Isotherm:

Langmuir adsorption Isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. Although the model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The model is described in the following equation:

$$\mathbf{q_e} = \mathbf{q_{max}}\frac{KL\ Ce}{1+\ KLCe} \qquad (3)$$

The above equation can be also linearized by the following process:

$$\frac{1}{q}=\frac{1}{q\,max\,KL}\cdot\frac{1}{Ce}+\frac{1}{qmax} \qquad (4)$$

Where qe denotes the amount adsorbed at equilibrium and q max is the Langmuir constant, which is equal to the adsorption capacity. The parameter K_L represents the Langmuir adsorption equilibrium constant and Ce is the equilibrium concentration. Plots of log Ce vs. log q and 1/Ce vs. 1/qe evaluated. The parameters for the Langmuir and Freundlich isotherms were evaluated based on the data from present experimental systems [11, 12].

3. Results and Discussions

3.1 Characterization of zeolite

3.1.1 X-ray diffraction

XRD pattern of the sample is presented in Fig(1), the two major peaks were found in zeolite in 9.7◦ and 21.8◦ in 2ɵ it`s corresponded to type called Stellerite, the remaining peaks in the pattern may be attributed to the presence Chabazite 23.5%.It demonstrate that the natural zeolite has typical to orthorhombic micro porous structure [13].

The structure can be verified by observation of four distinct diffraction peaks indexed as, (020), (311), (060) and (319).in low 2ɵ region.

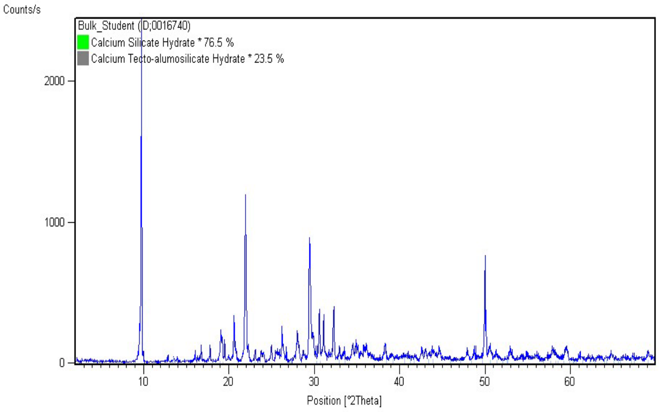

Fig 1: XRD pattern of Natural zeolite

3.1.2 FT-IR

The FT-IR spectrum of the natural zeolite sample is shown in Fig. 2. It is very obvious that the absorption bands at around 440cm^{-1} which is attributed to Silicon Aluminum lattic. The strongest infrared absorption band at 1020 cm^{-1} assigned to valence vibration of (Al,Si)-O bonds. OH- observed at 3568cm^{-1}, H_2O observed at 1645.17cm^{-1} [14].

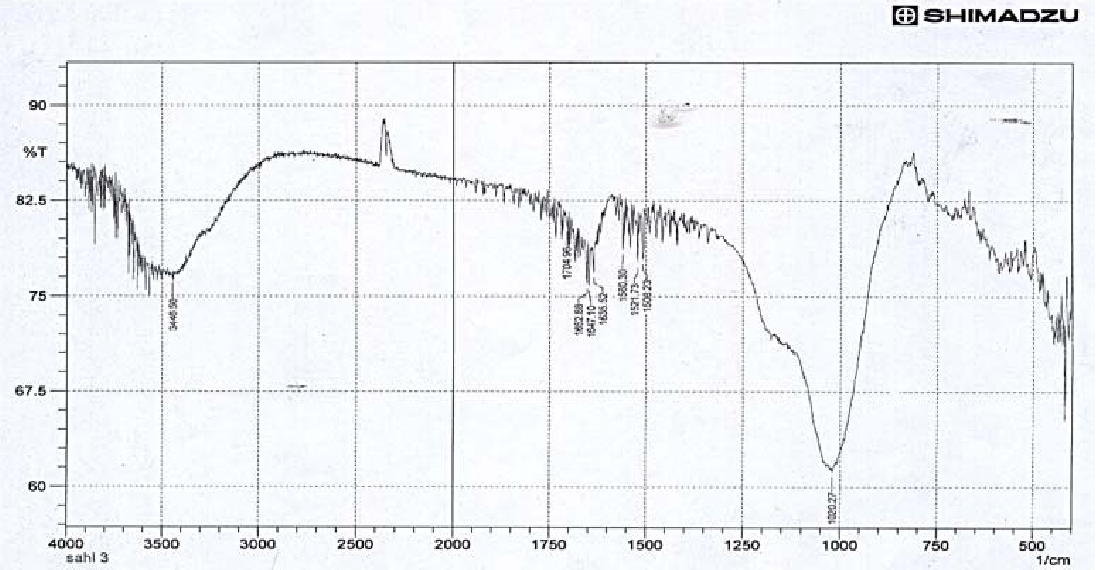

Fig 2: T-IR spectrum of natural zeolite

Table 1: Total metal oxide of natural zeolite by XRF

Compound	%
SiO_2	62.94
Al_2O_3	19.81
CaO	9.12
MgO	2.71
Na_2O	2.12
Fe_2O_3	2.28

3.1.3 N_2 adsorption – desorption isotherm

The hysteresis between the adsorption and desorption isotherms are thought to be due to the different size pore being combined. Classified as types (v) of adsorption of microporous or mesoporous based on International Union of Pure and Applied Chemistry (IUPAC) isotherm classification as it was shown in Fig 3.The type (v) isotherm concentrated on the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents [15]. The BET surface area of natural zeolite is around 204.4 m^2/g, and the BJH mean pore diameter is 0.3 nm.

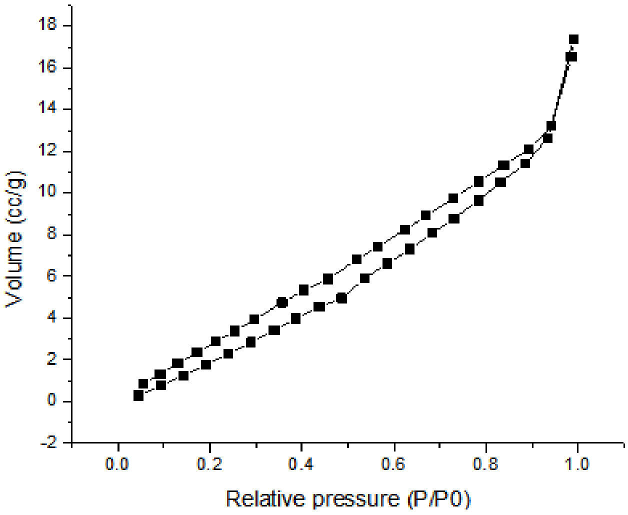

Fig 3: N_2 adsorption – desorption isotherm of natural zeolite

Table 2: physical properties of mud in progress

Sand content	0.75%
Viscosity	9.18 centipoise (pa. s)
Solid content	20.3%
Water content	10%
Oil content	15%

3.2 Removal of heavy metals

3.2.1 The effect on contact time

The effect of contact time on adsorption of Cr^{3+} on natural zeolite was studied over a contact time of 10 to 120 minutes using different initial Cr^{3+} concentration, fig(6). The adsorption increasing in the first time rapidly for 40 minutes and then achieves the adsorption equilibrium in 80 minutes.

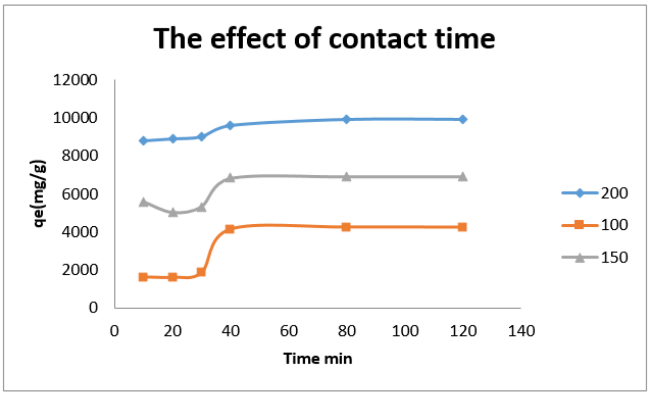

Fig 4: effect of contact time

3.2.2 Effect of pH

Fig (4) showed metal ions adsorption on natural zeolite at room temperature in the range from 2 to 8, the results indicate that the strongly uptake of (Fe^{2+}, Co^{2+}, Cr^{3+} and Zn^{2+}) in range between 3 to 5, the optimum pH for ions was found to be 4.5 with (76.64%, 76.59%, 77.2 and 76.63% respectively. In addition the results suggested that acidic pH are favorable to the adsorption

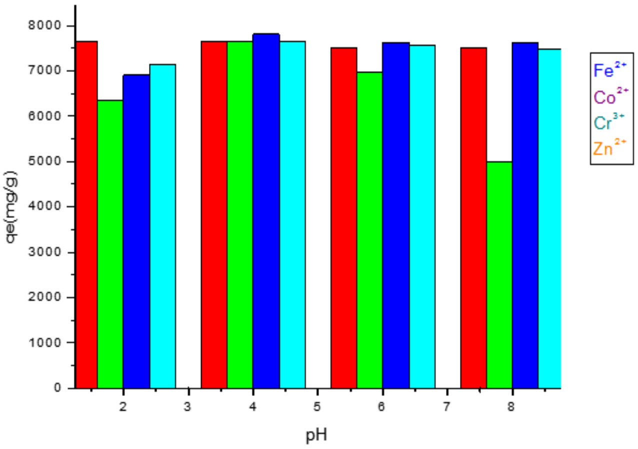

Fig 5: the effect of pH on natural zeolite

Fig (6) Effect of Cr^{3+} initial concentrations and contact time on the adsorption of Cr^{3+} onto zeolite.

Table 3: the removal percentage of mud samples and synthesis samples

%	Fe^{2+}	Cr^{3+}	Zn^{2+}	Co^{2+}
Synthesis	76.58	78.2	76.63	76.59%
Fluid solution	83.8	96.8	38.4	38.3

3.4 Adsorption isotherms

Analysis of equilibrium data is important for developing an equation which can be used to design purposes, the linearized Freundlich and Langmuir adsorption isotherms of (Cr^{3+},Co^{2+}, Zn^{2+} and Fe^{2+}) ions obtained at concentration (100 to 500ppm) table (3) and (4), the correlation coefficient between 0.942 to 0.756 for freundlich and 0.949 to 0.842 for Langmuir. Cr^{3+} and Fe^{2+} fitted well to freundlich model, whereas that Co^{2+} and Fe^{2+} obey Langmuir model.

Table 4: Freundlich isotherms

Metals	K(mg/g)	1/n	R^2
Cr^{3+}	0.13	3.5	0.756
Co^{2+}	0.86	16.6	0.941
Zn^{2+}	1.1	5	0.942
Fe^{2+}	1.08	12.5	0.864

Table 5: Langmuir isotherms

Metals	Q$_{max}$(mg/g)	K(l/g)	R^2
Cr^{3+}	57.1	0.12	0.887
Co^{2+}	5.8	0.44	0.983
Zn^{2+}	4.9	0.2	0.842
Fe^{2+}	4.5	0.34	0.906

3.5 conclusion

Natural zeolite is important low coast materials for water and waste water treatment due to the nature of ion exchange and high performance in adsorption of cations in aqueous solution. Oil industrial spite of harmful effects waste on environment especially drilling fluids because it contain Hazard materials. The present study focus on remove some heavy metals from drilling mud (fluids) by natural zeolite and it`s parameters, most studies concentrated on biodegradable treatment.

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