Design of sustainable geopolymeric nanomaterial matrices for treatment of produced water in oil and gas industry

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Abstract: This research aimed to develop sustainable, low-cost adsorbent materials with controlled porosity and microstructure using geopolymers prepared from natural clay Kaolin (K) and metakaolin (MK) for an advanced treatment of produced water generated during the exploration and production of oil and gas. The prepared materials were processed as ceramic composites with nanomaterial properties using geopolymerisation reaction. A range of compositions were processed under different conditions using different alkali activators, such as potassium hydroxide (KH) or potassium silicate (PS). The adsorbent materials were characterized in terms of their adsorption performance, microstructure. The adsorbent material performance was evaluated for its ability to remove dissolved impurities such as heavy metals (Lead, Zinc, and Chromium) and petroleum hydrocarbons from produced water. This study confirmed that MK is excellent adsorbent for the development of geopolymer composite membranes for treating wastewater., and provides a framework for future studies on the development of novel geopolymer composites as membranes for treatment of produced water and for residual waste encapsulation of contaminants released during oil and gas production process, and offering a sustainable, cost-effective approach that brings environmental and economic benefits in oil and gas industry.

Key Words: Geopolymer, metakaolin, adsorbent material, microstructure, heavy metals, Petroleum hydrocarbons, produced water treatment.

1 Introduction

Produced water (PW) is a by-product generated in large amount during oil and gas operations, it is basically composed from the water originally exiting in the wells, which called formation water, and any additional water injected for enhancing oil and gas recovery. During exploration and/or production of oil and gas large volume of produced water generated considered as the largest waste stream, which contains relatively higher concentration of petroleum hydrocarbons, dissolved minerals, heavy metals, and dissolved solids and other pollutants [1].

Due to the increase in exploration and production activities in oil sector in Libya and the rest of the world, its treatment for reuse becomes very important for environment protection. Furthermore, as the scarcity of freshwater supply is increasing, produced water can be a crucial source of water after suitable treatment. There has been an increased attention on reclaiming, reusing, and recycling of water that is usually wasted to meet the communities needs of freshwater source, helped to reduce its potential harm to human health and the environment [2].

Classical treatment methods for produced water usually include primary stage (Physical treatment) to remove oils and grease, secondary stage (chemically) by oxidation of organic materials and (physically) by precipitation and filtration of produced sludge, and tertiary stage including (membrane filtration, adsorption etc.) to remove the reaming traces of heavy metals and low concentrations of petroleum hydrocarbons [3].

Several researches confirm that treatment of produced water using traditional treatment methods (primary & secondary) stages were insufficient to remove heavy metals and some of organic compounds from the effluent of secondary stage in treatment plant. Pollutants were usually transferred from one stage to another, or the degradation of these pollutants was incomplete. In this case several studies advice to use tertiary stage using adsorption techniques for removal of residual heavy metals and hydrocarbons from secondary effluent of sewage in treatment plants [4].

Due to the ability of aluminosilcate materials such as zeolite and zeolite-like materials to adsorb heavy metals and organic compounds, the geopolymers composed from kaolin and metakaolin clay has become a concern of researchers. The adsorption of heavy metal by metakaoline has been widely confirmed in the natural environment [5].

The aim of this work was to synthesis metakaolin-based geopolymer using two different alkali activators, and to study the effect of activator type on formation of aluminosilcate gel and the changes in mineralogy, microstructure and morphological properties using different analytical techniques such as XRF, XRD, FTIR, and SEM analyses. Also to evaluate the adsorption efficiency of both geopolymer matrixes in removal of heavy metals and petroleum hydrocarbons from produced water using batch experiments conditions.

2 Material and Methods

2.1 Natural kaolin clay: was obtained from the Temenhint area –Libya, the samples were excavated from the sides of natural slopes and were air dried for 2 weeks, before crushing and sieving through a 1 mm sieve. Metakaolin was prepared by calcination of the kaolin clay at 700 ºC for a period of 2 h to produce thermally activated clay with high silica and alumina content. The chemical composition and crystalline mineralogy of the kaolin, metakaolin are given in table 1.

Table.1 Chemical and mineralogical composition of kaolin& Metakaolin

Material	Units	Kaolin	Metakaolin
XRF Analysis			
L.O.I	Weight %	9.71	0.82
SiO_2		54.21	60.2
Al_2O_3		28.43	31.5
Na_2O		0.22	0.23
K_2O		3.90	44
CaO		1.80	2.01

MgO		0.40	0.44
Fe_2O_3		0.80	0.90
XRD Analysis			
Kaolin		**Metakaolin**	
Kaolinite $Al2Si_2O_5(OH)_4$, Quart SiO_2		Kaolinite $Al_2Si_2O_5(OH)_4$, Quart SiO_2	

2.2 Alkali Activation Solution. high purity potassium hydroxide, and potassium silicate (Labbox-Spain) was used as the alkali activator in this study. Solutions of KOH and K_2SiO_2 were prepared using ultra-pure water.to control the amount of Aluminum oxide and Calcium oxide in geopolymer mixtures, product called Sekar 80 contain (80% Al_2O_3, 20 % CaO) was used to adjust SiO_2:Al_2O_3

2.3 Produced water sample: Effluents after the secondary stage in wastewater treatment plant was collected to examine the efficiency of produced MK-geopolymer recipes in removal of heavy metals and petroleum hydrocarbon. Selected physic-chemical analysis of treated produced water is shown in table 2.

Table.2 Characteristic of produced water

Test	Units	Result
pH	-	3.78
Cond.	uS/cm	458400
Cr	ppm	0.298
Pb		1.85
Zn		0.55
TPH		42

2.4 MK-geopolymer recipe design: Two different MK- geopolymer mixture proportions were prepared using MK as source of aluminsilicate material, mixture MK1 prepared using potassium hydroxide, and MK2 mixture prepared using Potassium silicate as alkali activator. Table 3 shows the molar ratio of both mixtures.

Table 3. Main oxide molar ratio in both geopolymer recipes

Material	MK1	MK2
SiO_2/Al_2O_3	0.9	1.7
Na_2O+K_2O	0.1	0.2
CaO+MgO	0.02	0.02

2.5 Adsorption experiment: The adsorption experiments were performed using batch equilibration experiments. In the batch method, a 0.5 gram of adsorbent material (MK1 or MK2) was agitated with 250 ml solution using magnetic stirrer at 50 rpm at room temperature for 6 minutes to reach equilibrium. The effect of dose on removal efficiency of heavy metals was evaluated using atomic absorption spectroscopy Varian 220G for measuring concentration of lead, cadmium and chromium, while gas chromatography Agilent A6890 equipped by FID Detector was used to measure the concentration of petroleum hydrocarbons.

3 Result and discussion

3.1 Geopolymerisation of metakaolin and effect of alkali activator type.

The degree of transformation of MK clay to geopolymers using two different alkali activator was evaluated by measuring the degree of alkali activation reaction and measure the quantity of aluminosilcate gel formed. The degree of geopolymerisation reaction was evaluated using acid attack test proposed by Fernández-Jiménez [6].

Figure1, shows that both proposed geopolymer recipes (MK1 and MK2) successfully produce aluminosilcate gel in similar quantities, and transformed into a solid matrix due the effect of alkali activator type and concentration.

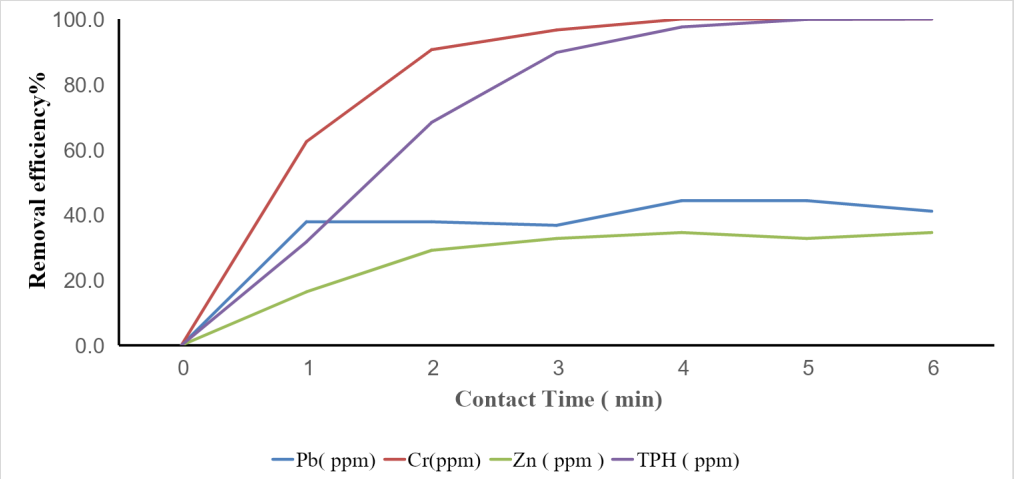

Fig 1. Effect of alkali activator type in improvement of formation of geopolymer gel

The results shown in Figure 1 indicate that the amount of reacted materials was high, and the degree of geopolymerisation and formation of geopolymer gel in both recipes was similar.

3.2 FTIR analysis

In general, the FTIR spectra obtained from both MK1& MK2 matrix contains bands at approximately 1025 cm^{-1} which assigned for typical Si–O vibrations and considered as indication of the excitation of quartz as reported by Tchakoute [7]. There are also major bands at approximately 3500, 1650, 1410, 1000, and 780 cm^{-1}. Bands at 3500 and 1640

cm^{-1} are typical of the O–H stretching and the H–O–H bending vibration respectively, and used as indication of existence of hydroxyl groups resulting from either the alkali activator (KaOH) or water.

The band at 1440 cm^{-1} is assigned to carbonate
compounds. Bands at 870 and 910 cm^{-1} are assigned to the stretching of the Si–O and Al-O
formation. This important peak is attributed to the amorphous nature of the geopolymer gel and indicative of short-range order of Si and Al tetrahedral [8]. The band is considered as fingerprint of geopolymer matrices and used as evidence to prove the formation of sodium or potassium aluminosilcate hydrated gel (NSAH) or (KSAH)

In figure 2, formation of geopolymer gel in both geopolymer recipes is indicated in FTIR spectra by the broad, intense X–O band (X=Si or Al) located in the 950–1000 cm^{-1} range attributed to the Si-O-Si and Si-O-Al vibrations, representing the combination of both Al–O and Si–O and reflecting the extent and magnitude of the incorporation of aluminates and silicates in gel groups and the band around 789 cm^{-1} is indicative of the vibration of Al–O or Si–O–Al groups.

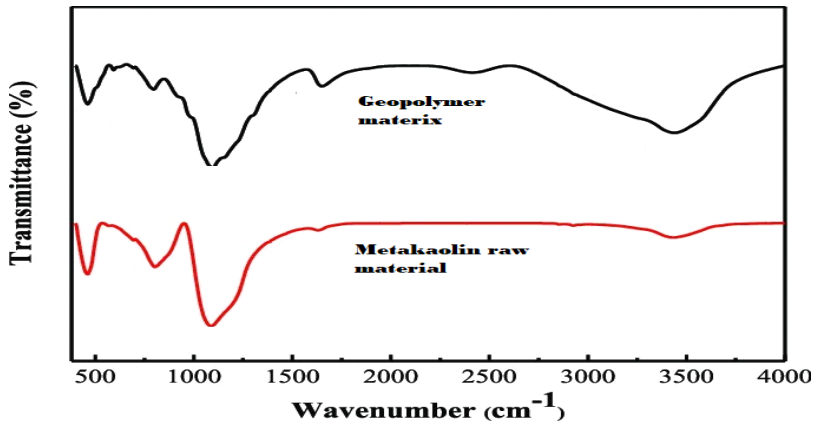

Fig. 2. Transformation of metakaolin to metakaolin geopolymer after activation

3.3 Scanning Electron Microscope

Figure 3(a&b) representative SEM images of both metakaolin recipes (MK1 & MK2). After the geopolymerisation. In both microscopic images it is clear that both alkali activator has different effect on transformation of metakaolin of geopolymer reaction. Morphological change observed in both synthesized geopolymers is due to the dissolution of metakaolin aluminosilcate in the activator solution leading to the formation of aluminosilcate gel. The morphology of both geopolymers is constituted by a chain of polyalumino-silicate layers by the complete disappearance of metakaolin particles

Figure3a. shows surface morphology of MK1 activated by KOH and illustrate that MK1 matrix are lower homogeneity that MK2 which activated by K_2SiO_3, and that MK2 matrix consisting of regular shaped particles (Figure 3b). Which contains more

voids and higher surface area which help in adsorption of different contaminants for environmental applications

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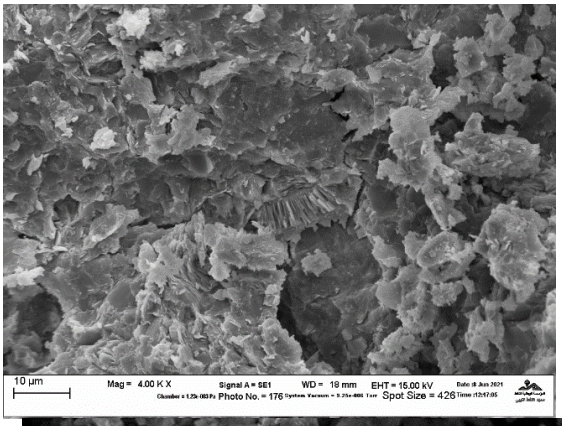

Fig.3a SEM micrograph of geopolymer MK1

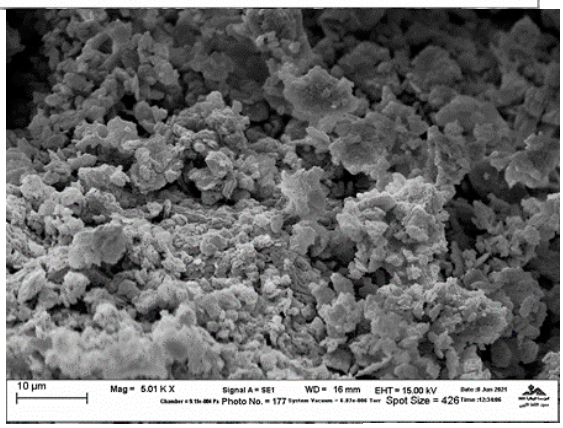

Fig.3b. SEM micrograph geopolymer MK2

This observation confirms the fact that metakaolin activated by potassium Silicate in MK2 improve the geopolymerisation reaction by formation of aluminosilcate gel which expected to improve the adsorption properties for this matrix.

3.4 XRD Analysis

The XRD patterns of both geopolymer recipes (MK1&MK2) are shown in figure 4 a&b, after the geopolymerisation process, a number of characteristic peaks in the XRD diffractograms indicate remaining of part from raw materials unreacted both geopolymer systems. The remaining materials present the phases introduced from the raw material such as quartz, kaolinite from kaolin binder which indicate incomplete alkali activation reaction.

The new peaks appeared on the XRD patterns in geopolymer matrixes such as hydrosodalite and katoite formed as result of geopolymerisation reaction, both of those phases have the properties of zeolite materials

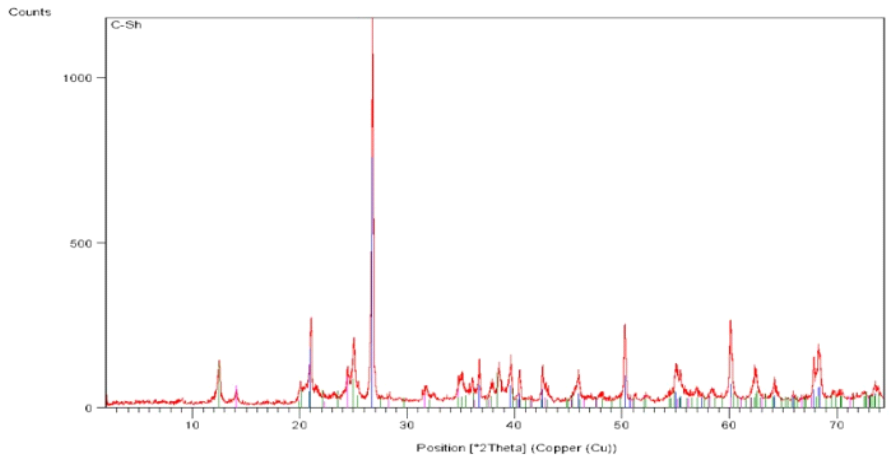

Fig. 4a. Mineralogical composition of MK1

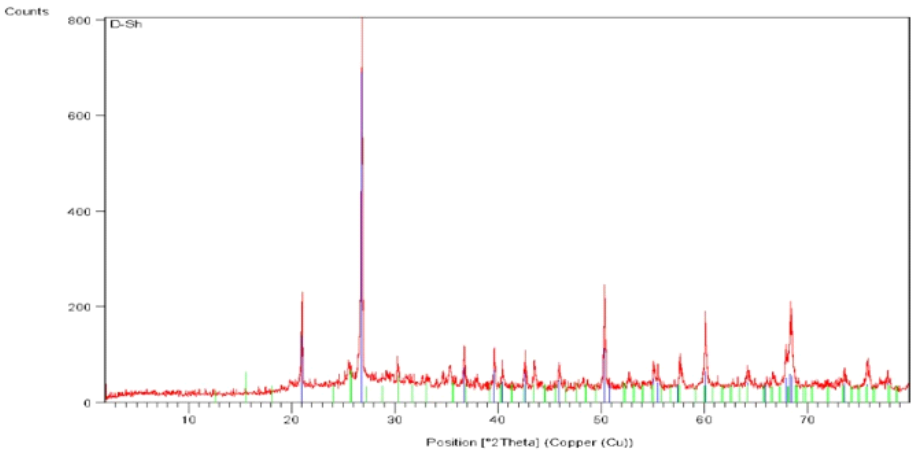

Fig. 4b. Mineralogical composition of MK2

3.5 Batch study. Figure 5 a&b represented the effect of contact time with constant parameters (Temperature 25^{o}C, adsorbent material dosage (0.5 g MK1 or MK2) and produced water volume (250 ml) for adsorption of various heavy metals onto geopolymer matrixes.

It shows that removal percentage were increased with increasing contact time until passing of approx. 4 minutes and then, removal were constant thereafter, which revealed that equilibrium attainted at very short time for heavy metals and petroleum hydrocarbons.

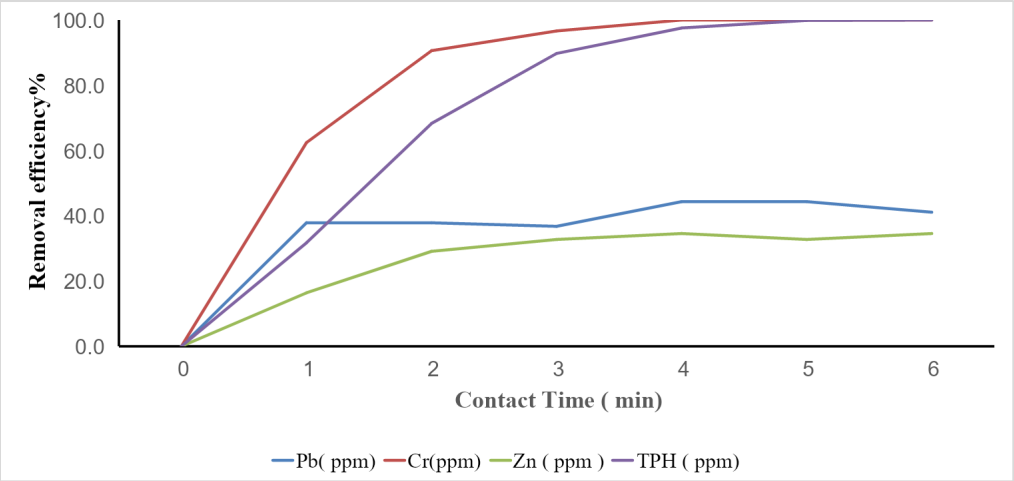

Fig. 5.a Efficiency of geopolymer MK1 in removal of heavy metals and petroleum hydrocarbon

Figure 5.a shows the efficiency of MK1 geopolymer matrix activated by KOH. The order of adsorption capacity for heavy metals after reaching the equilibrium are 100 % for Chromium ion, 45% for lead ion and around 38% for zinc ion, where its reached approximately 100% for petroleum hydrocarbons,

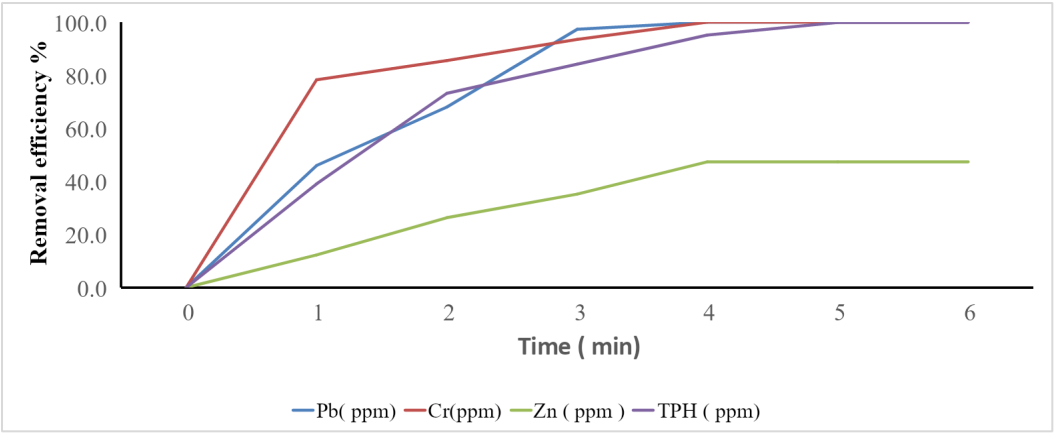

Fig. 5b. Efficiency of geopolymer MK2 in removal of heavy metals and petroleum hydrocarbon

Figure 5b illustrate that the efficiency of matrix MK2 activated by potassium silicate was better in removal of heavy metals, the approximate percentage of removal of heavy metals was 100% for chromium and lead ions and close to 48% removal of zinc ion which is more efficient than MK1.Figure 5b also shows that the matrix MK2 has good efficiency in removal of petroleum hydrocarbon compounds from produced water.

4 Conclusion

The study of the effect of the type of alkali activator on the characteristic of geopolymer made from metakaolin is reported. The main conclusions drawn are the following:

- Geopolymer materials prepared by alkali activation of metakaolin using KOH or K_2SiO_3 have the great potential to provide useful adsorptive material and provide solutions to environmental remediation issues in produced water advanced treatment.

- Both metakaolin geopolymers activated by KOH, or K_2SiO_3 could produce high adsorpant material which may use to remove petroleum hydrocarbons and heavy metals from produced water and industrial wastewater.

- Using of potassium silicate as alkali activator helps to improve the microstructure properties of the metakaolin geopolymer by increasing the aluminsilicate gel phase of the material through providing of active silica which promote the dissolution of silicon–aluminum raw materials and make the reaction more complete.

- The addition of K_2SiO_3 Increase the SiO_2:Al_2O_3 molar ration to 1.7 in MK2 comparing to 0.9 in MK1

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