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Potential of Using Limestone Rocks Accumulated in Al-Samawa Stone Quarry, South Iraq, for The Stationary Phase in A Column Chromatography Separation

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Abstract
This investigation aims to determine whether it is feasible to use the limestone rocks found in the Al-Samawa stone quarry in southern Iraq as the stationary phase in column chromatography separation. Together with the chromatographic application, the physical and chemical characteristics of the rocks are examined. SiO_2, SO_4, PO_4, NO_3, and Cl are the negative ions, while Ca, Mg, Na, K, and Li are the positive ions. The limestone samples are characterized via chromatographic analysis. The results suggest that limestone samples could be used as an adsorbent material for chromatographic separation techniques. Additionally, samples from the Nasiriyah refinery's crude oil can be used to separate oil.

Keywords: Al-Samawa stone quarry, limestone, chromatography separation column, physical and chemical properties, chromatographic application, south Iraq.

إمكانية استخدام صخور الحجر الجيري المتراكمة في محجر السماوة جنوب العراق لمرحلة الثبات في عمود الفصل الكروماتوغرافي

ميثم عبد الرضا عبد الحسين
قسم الجيولوجيا التطبيقية , كلية العلوم , جامعة ذي قار , ذي قار, العراق

الخلاصة
في هذه الدراسة تم التركيز على إمكانية استخدام صخور الحجر الجيري المتوفرة في مقالع السماوة الحجرية ، جنوب العراق كطور ثابت في أعمدة الفصل الكروموتوغرافية من خلال دراسة صفاتها الكيميائية والفيزيائية مع إجراء التطبيق الكروموتوغرافي . ومن هذه الصفات الأس الهيدروجيني ، التوصيل الكهربائي ، الكثافة النوعية ، الامتصاصية ، المساحة السطحية والتآكل الكيميائي والميكانيكي كصفات فيزيائية . تراكيز الأيونات السالبة مثل السيليكات ، الكبريتات ، الفوسفات ، النترات والكلوريدات . وتراكيز الأيونات الموجبة مثل الكالسيوم ، المغنسيوم ، الصوديوم ، البوتاسيوم والليثيوم كصفات كيميائية . بالإضافة إلى اختبار ذائبيتها في مجموعة من المحاليل اللاعضوية المختلفة التراكيز . وقد تم إجراء التطبيق الكروموتوغرافي لتمييز عينات الحجر الجيري . أشارت النتائج إلى إمكانية استخدام هذه العينات كمادة ماصة في تقنيات الفصل الكروموتوغرافي وتطبيقها في عملية فصل بعض المشتقات النفطية لعينات النفط الخام من مصفى الناصرية .

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1. Introduction

Adsorption chromatography uses natural mineralized soils containing montomonoralite, palygorskite , Caoline, bentonite, filtered clay soil, and ninivite silicate rocks rich in silica gel. Adsorption chromatography is considered a potential physical method to address the issues of chromatography separation [1]. Natural mineralized soils and silica gel, particularly the activating one, are utilized in the separation methods of hydro–carbonate compositions [2].

Silica gel has physical properties and adsorption ability at different levels. Researchers use various industrial methods to prepare silica gel to ensure matching. In many Iraqi places, Iraqi geological researchers found huge masses of mineralized soils and rocks containing uncrystallized silica gel. These rocks have been formed from clay and soil after millions of years. The rocks with uncrystallized silica gel are called ninivite rocks. These kinds of rocks were discovered for the first time in Nineveh, a historical city in Iraq [3]. From an industrial point of view, ninivite rocks are invaluable because they contain a high percentage of uncrystallized silica; they feature high porosity and very low density [1]. Previous and recent studies have reported that mineralized clay and inactive silica gel-bearing rocks are naturally used without any physical treatment. The natural balance and normal eclecticism effect in adsorption chromatography are compared with those in the industrialized silica gel. As a result, researchers used local silica gel naturally. Silica gel is pure matter extracted from siliceous rocks by a simple chemical procedure of column chromatography wherein the heavy constituents of crude oil are separated [4]. To confirm the results of the aforementioned studies, researchers revealed the relationship between these rocks' porosity and adsorption ability.

Such studies are continued using catalyst materials in petrochemical. Pursuing this line of research in this field can bring about significant benefits and income to Iraq.

The present study uses mineralized clay and silica gel-bearing rocks to fractionate heavy crude oil petroleum in the Nasiriyah refinery into lighter and more valuable simple components. The results of this study are of substantial economic value to Iraq.

2. Experimental Procedures

2.1. Source and Preparation of Samples

Three limestone rock samples were collected from Al-Samawah stone quarries at different places and depths. Samples are marked as S1 at 1m. , S2 at 3m, and S3 at 5m. sequentially, using Silica gel (150 – 200 g / mol) as a standard specimen. Samples were crushed and then sieved by 0.4 mic. Mil. Diameter holes sieve. Through Global Positioning System, the area is located west of Al-Samawah city, South of Iraq, 280 km Southeast of Baghdad. The area coordinates Latitude 31^{0} 19ˋ 13ˋˋ N , Longitude 45^{0} 17’ 39” E, with -2 m elevation.

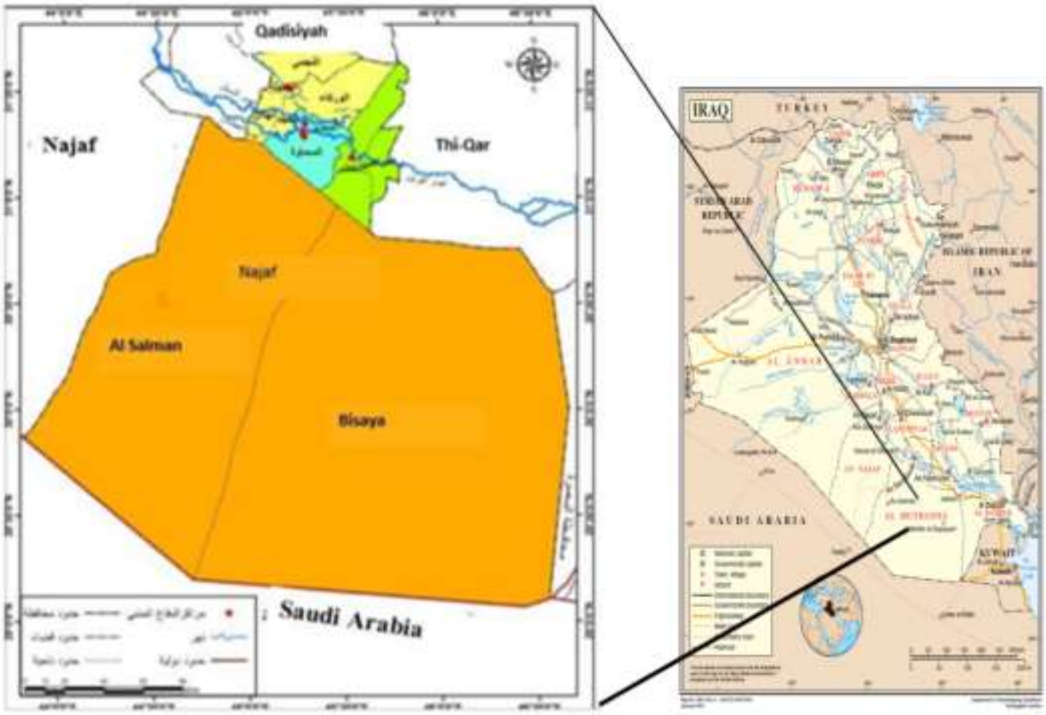

Figure 1: Location map shows the study area

Photograph 1: Area of the rock samples (Al-Samawa stone quarry)

The photograph was taken by a simple personal hand camera. The camera does not contain the Scale and Direction programs. For these reasons it has been deleted.

2.2. Chemical Properties

Concentrations of cations represented by Na, K, and Li were calculated using an atomic emission device manufactured by Corning® Inc. [5]. Ca and Mg were measured using a burette [6]. Concentrations of negative chloride ion was also measured with burette. SiO_2, SO_4, PO_4, and NO_3 were quantified by spectral methods [6].

Table 1: Values of negative and positive ions observed from rock samples.

Test	Sample (1)	Sample (2)	Sample (3)
Silicates	300	420	336
Nitrates	76	54	132
Phosphate	110	98	83
Sulfates	240	260	284
Chlorides	226	160	197
Calcium	312	457	416
Magnesium	88	136	72
Sodium	243	316	189
Potassium	78	66	159
Lithium	18	21	23

Note: All concentrations in the Table above are calculated by mg/kg.

2.3. Physical Properties

The physical properties investigated are absorbance (%), surface area (gm/cm^2), density (gm/cm^3), electrical conductivity (ms/cm), pH, and chemical and mechanical corrosion. The chemical properties of the limestone rocks are tested by dissolving liquid extractions of different concentrations of negative and positive ions in inorganic solutions
The pH and electrical conductivity of the extracted water were measured with instruments made by WTW [6]. Density is the mass of an object divided by its volume
Weight / mass =30 kg / volume =15 m^3 Density = 2 kg / m^3
The total surface area is calculated by adding all the areas on the surface: the areas of the object's base, top, and lateral surfaces (sides). This is done using different area formulas and measured in square units.
Absorbance (A) is the flip side of transmittance and states how much of the light the sample absorbed. It is also referred to as “optical density.” Absorbance is calculated as a logarithmic function of T: $A = \log10 (1/T) = \log10 (Io/I)$.

Table 2: Values of physical characteristics of rock samples.

Chemical Corrosion (%)	Mechanical erosion (%)	pH	Electrical Conductivity (ms/cm)	Surface Area (gm/cm^2)	Absorbance (%)	Density (gm/cm^3)	Sample No.
1	30.3	8.3	3260	3	2.8	0.52	1
1.6	28	8.1	3520	4.7	2.5	0.32	2
0.4	30.9	7.8	3211	2.8	2.8	0.39	3
---	---	---	---	3.0	0.6	0.33	Manufactured Silica – gel .

2.4. Solubility in Inorganic Solution

The limestone samples were treated using several concentrations of HCl (30%), H_2SO_4 (30%), NaOH (30%), and NaOH (60%).

Table 3: Solubility percentages of rock samples at different concentrations of inorganic acids and bases.

Sample No.	Solubility in 30% HCL solution	Solubility in 30% H_2SO_4 solution	Solubility in 30% NaOH solution	Solubility in 60% NaOH solution
1	18	34	15	25
2	16	23	13	34
3	32	28	12	23

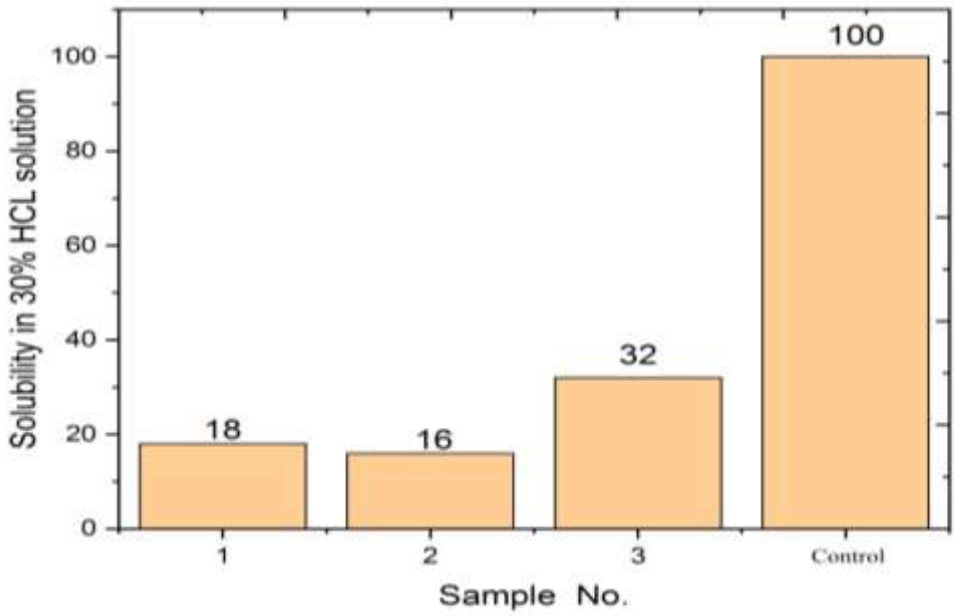

Figure 2: Percentage of the separation efficiency of rock models in HCL solution (30% soluble).

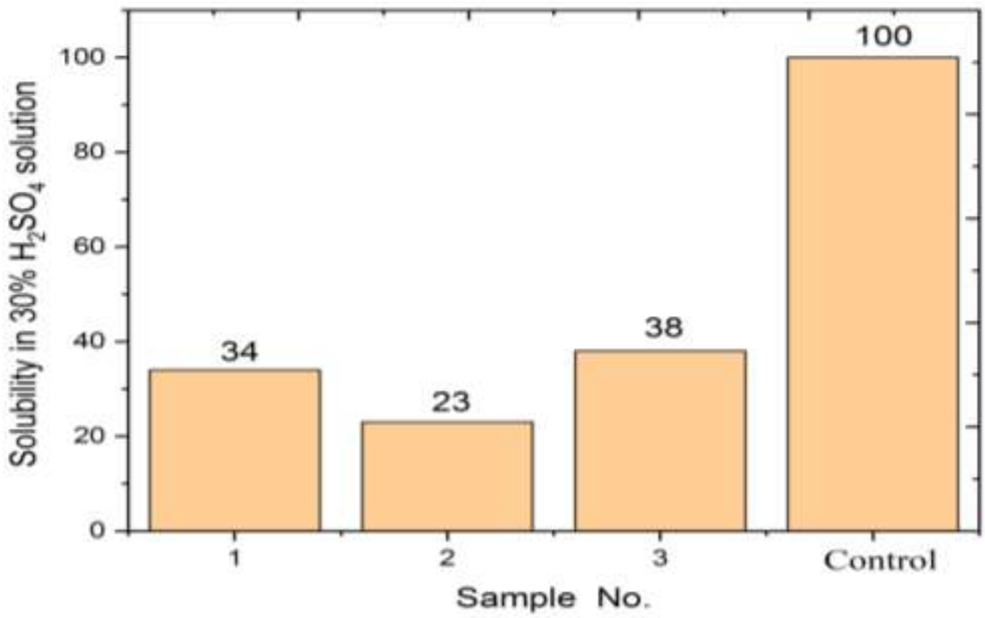

Figure 3: Percentage of the separation efficiency of rock models in H_2SO_4 solution (30% soluble).

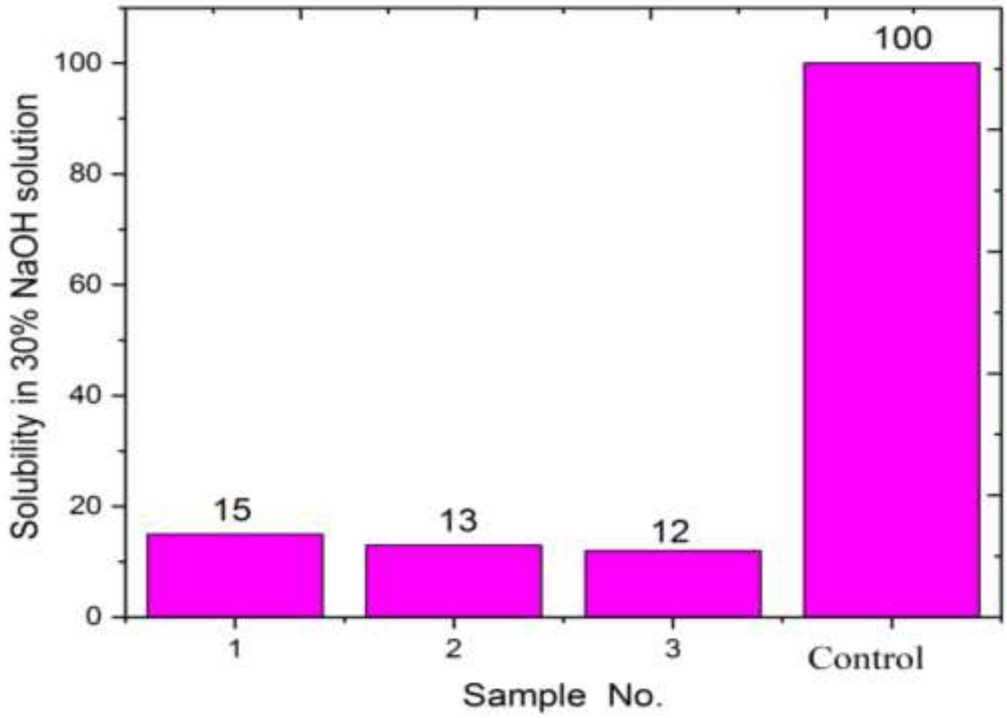

Figure 4: Percentage of the separation efficiency of rock models in NaOH solution (30% soluble).

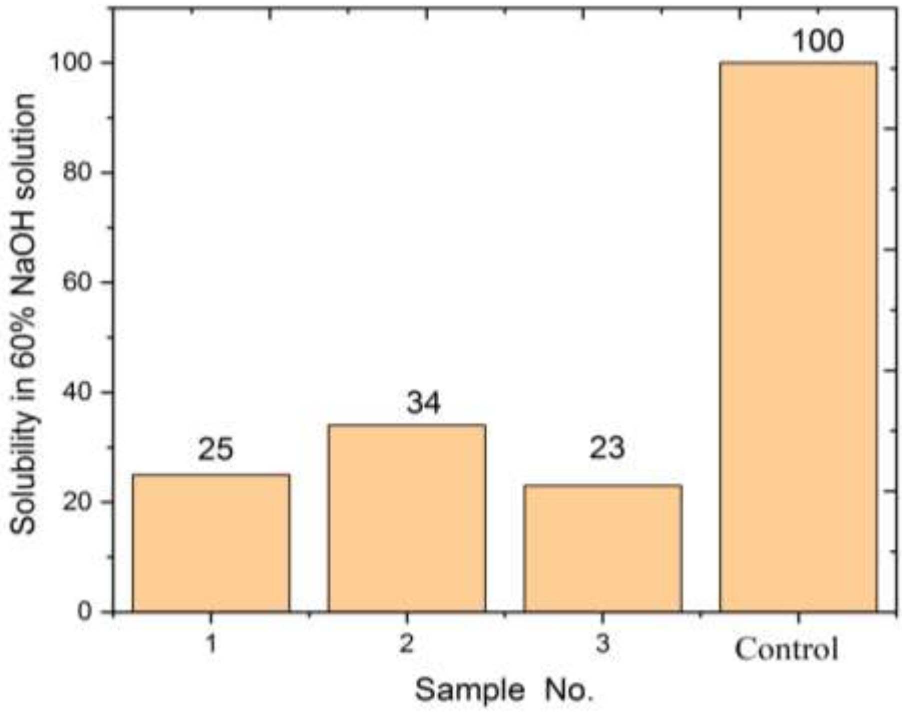

Figure 5: Percentage of the separation efficiency of rock models in NaOH solution (60% soluble).

Table 4: Separation efficiency of rock samples for crude oil passed through separation columns compared with manufactured silica gel.

Sample No.	Separation efficiency %	Separation efficiency %	Separation efficiency %	Separation efficiency %
1	36	28	32	22
2	42	36	45	48
3	15	12	10	12
Manufactured silica – gel	60	55	54	52

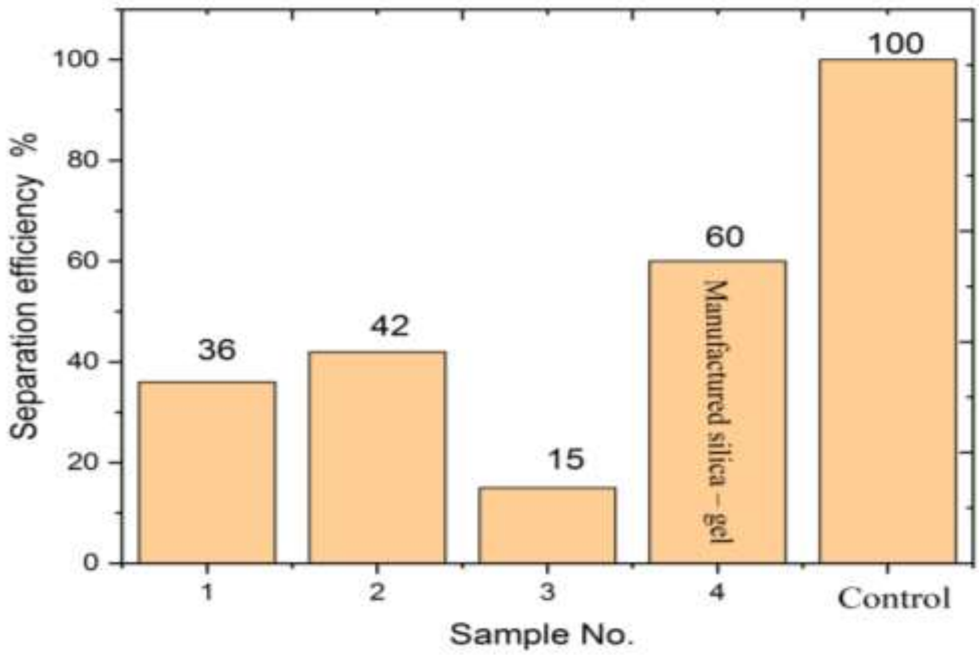

Figure 6: Separation efficiency of rock samples for crude oil passed through separation columns compared with manufactured silica gel (60%).

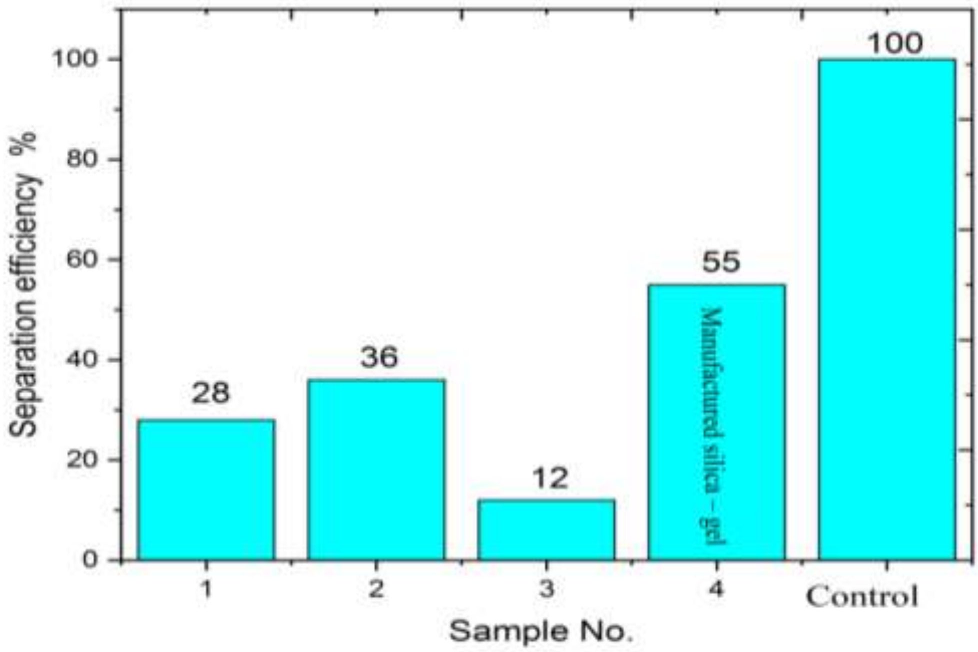

Figure 7: Separation efficiency of rock samples for crude oil passed through separation columns compared with manufactured silica gel (55%).

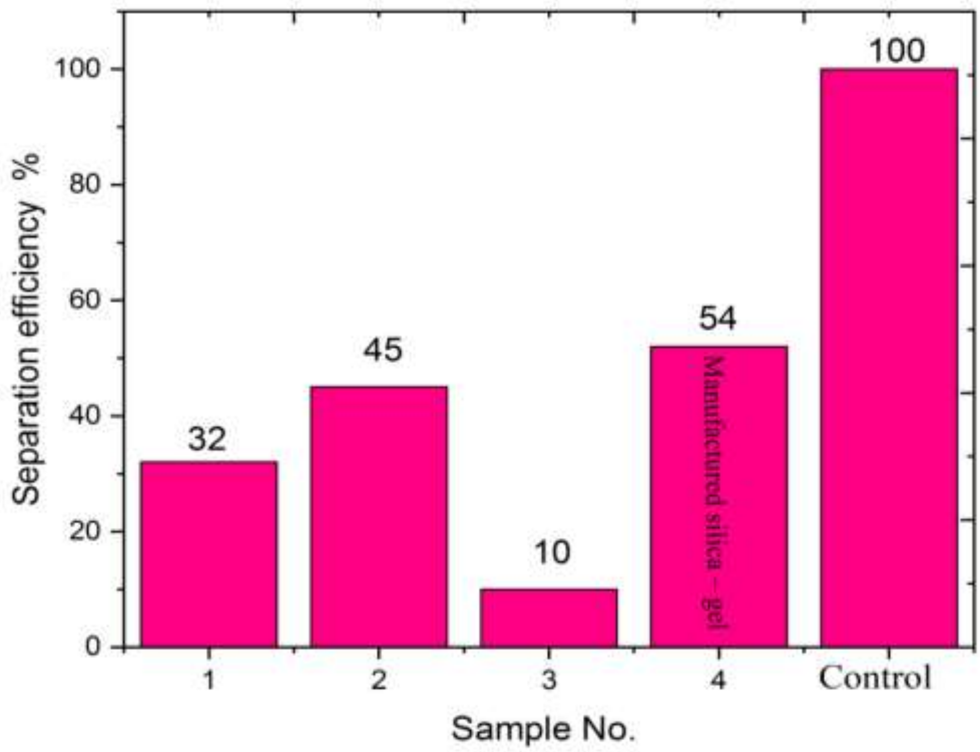

Figure 8: Separation efficiency of rock samples for crude oil passed through separation columns compared with manufactured silica gel (54%).

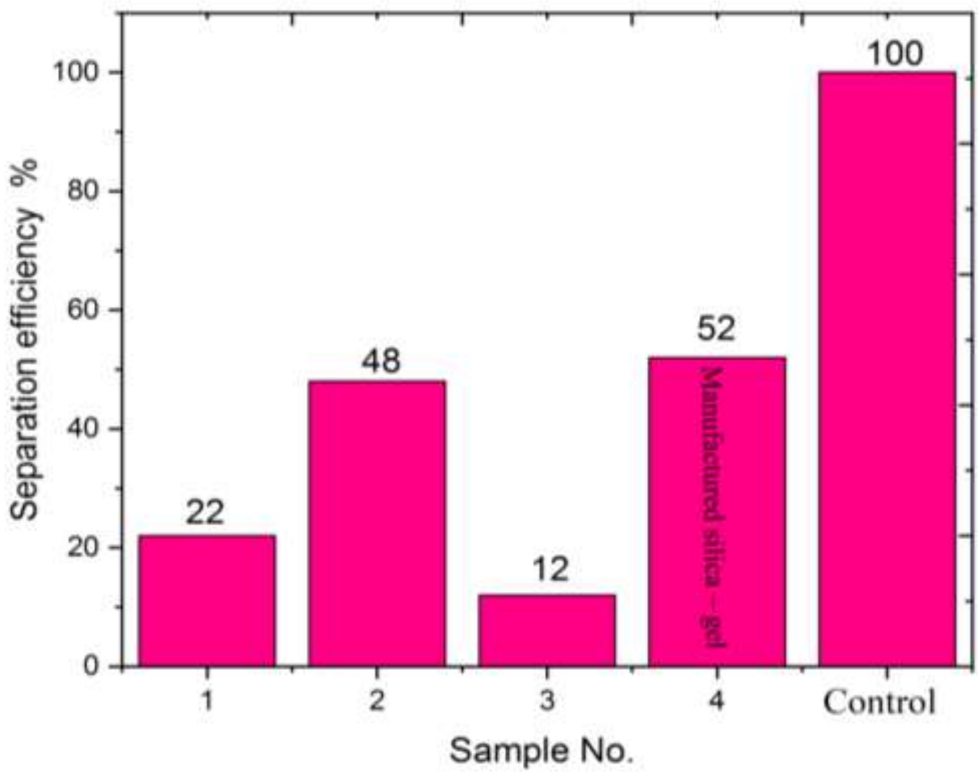

Figure 9: Separation efficiency of rock samples for crude oil passed through separation columns compared with manufactured silica gel (52%).

2.5. Explanation of Thin Sections

Facies, in general, limestone for all layers to the formation of the Euphrates limestone, as it reflects the sections that were analyzed as a chemical environment of deposition. Consisting of :-

1- 10% of the granules of limestone are called (Lime mudstone). It is of equal size to the size of mud, which indicates the calmness of the shallow basin. A quiet environment due to the absence of a strong water current.

2- 20 – 80 % of the calcareous stone granules (Pelletal Wackstone), which are Pellets of unknown origin, may be due to animal waste, particularly Al-Gastropoda waste which is generally called (Fecal pellets).

The remainder of the facies is clearly traces of green algae and some calcined Gastropoda, as well as traces of melt (melt veins) reflecting the calmness in the waves with the coastal and shallow environment and isolated beach basins.

The thin sections were analyzed at the (Center for Marine Science, Basrah University).

2.6. Chromatographic Application

Adsorption chromatography was then employed in the rock samples and was compared with similar techniques. The fractionation of QP was employed. QP is an analyzer that filters the ions passing the specified mass according to the applied voltage. The results are presented in Table 5. The table details the fraction's percentages eluted using different solvent polarities. The chemical composition of the eluted fractions was adopted for comparison. The QP, in general, is composed mainly of straight aliphatic hydrocarbons, which have lower polarity than branched aliphatic ones. The QP also contains naphthenic and polyaromatic hydrocarbons, which have higher polarities than the above constituents. Moreover, a regular manual fractionating column was applied. The following results are expected:

1. The eluted fractions by using low polar solvents were mainly saturated paraffinic hydrocarbons. The polarity of the eluted solvent increased the percentage of naphthenic obtained, followed by aromatic hydrocarbons.
2. Treated and activated samples appeared to be the best adsorbent in terms of activity and selectivity actions.

Table 5: Chromatographic fractions (%) of QP using different adsorbents.

Solvent	Polarities (Debby)	QP (%) of Sample 1	QP (%) of Sample 2	QP (%) of Sample 3
Ethanol	51.9	65	32	41
Toluene	33.9	42	57	25
Chloroform	43.0	52	35	27
Cyclohexane	42.7	43	32	53

Note: QP composition: 38% straight chain aliphatic, 27% branched aliphatic, 18% naphthenic, and 17% aromatic compounds.

3. Results and Discussion

In Table 1, S1 is characterized by high concentrations of Cl and PO_4, compared with other samples. S2 is characterized by high concentrations of SiO_2, Ca, Mg, and Na. S3 is characterized by high concentrations of NO_3, SO_4, K and Li.

According to the movement, the transfer and separation of the compounds in natural systems depend on the status of the chemical compounds. These processes are controlled by the system's physico- chemical and geological behaviors [7].

Table 2 shows the convergence of the physical characteristics of the three samples with those of the manufacturer silica gel. Low specific gravity and high surface area increased separation efficiency [8], as evinced in Table 4.

The electrical conductivity of S2 is superior to those of the other samples. This result indicates high polarity. Consequently, polar compounds in petroleum compounds are attracted, thereby increasing separation efficiency. A clear relationship between the other physical properties and separation efficiency is not observed.

Table 3 indicates that S3 is the lesser soluble in acidic and alkaline mediums. This result may be due to the high dilution of the values of its constituent salts, mostly salts of calcium silicate [9], as shown in Table 1. The proportion of the effective isolation of ions belonging to the chemical forms and the readiness of the isolated constituents in the sample are determined through chemical extraction. The isolated movement is the total amount dissolved in the solution and the quantity that can be transmitted to the liquid phase [10].

Table 4 proves that S2 is the best sample used as absorbent matter in the stationary phases of chromatography separation. The separation efficiency increases after setting thermal activation and adding more inorganic impurities [6].

In addition, sequential extraction methods are employed. They are partly beneficial in interpreting the geochemistry of the deep-sited presence of rocks by using the selected chemical extraction techniques that can move or melt different isolated ions in a phased manner depending on the strength associated with the elements [11].

Table 5 indicates that S1 derives a QP of 65% by using the ethanol solvent with a polarity of 51.9. This QP is the highest among the experiments conducted to pass the dissolved crude oil with different polar solvents. This result explains why S1 has a high content of naphthenic and polyaromatic compounds and straight aliphatic hydrocarbons compared with S3, wherein the chloroform solvent with somewhat less polarity is used.

Furthermore, QP laboratories provide specialists in the analytical industry with many advantages by finding materials of natural origin. They can be well employed to produce materials with high selective porosity. Good separation coefficient and better dispersal in various oil components can be found in these materials.

Conclusion

1- The transfer and separation of the compounds depend on the chemical compounds' status.
2- Low specific gravity and high surface area increased the efficiency of separation.
3- The electrical conductivity of sample No.2 is superior, indicating high polarity. Consequently, polar compounds in petroleum compounds are attracted, thereby increasing separation efficiency.
4- Sample No.2 is the best sample to be used as absorbent matter in the stationary phases of chromatography separation.
5- Sample No.1 derives a QP of 65% with a polarity of 51,9. This QP is the highest among the experiments conducted to pass the dissolved crude oil with different polar solvents.
6- QP laboratories provide specialists in the analytical industry with many advantages by finding materials of natural origin. They can be well employed to produce materials with high selective porosity.

Good separation coefficient and better dispersal in various oil components can be found in these materials.

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