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Study Of the Optimum Conditions for Removing Phosphate from House Water in City of Mosul Using Some Local Clays

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ABSTRACT

The aim of this study is removal of phosphate from domestic waste water using different local clays and soils. Waste water was collected in July and August from five lift water stations in Mosul City (Bab Sinjar, Al-Sandooqi, Al-Hadbaa, Al-Qarazee and Al-Shurtaa). The phosphate concentration average is (3 ppm). According to the Iraqi determinants of the quality of water suitable for the aquatic environment within the limits of (3 mg/liter), the upper value is in Bab Sinjar (6.8 ppm), while the lower is in Al-Shurtaa (2.2 ppm). Other experiments related to the analysis of soil materials for adsorption such as (Bentonite, Tulkeef and, Al-Qobah) are carried out. Selected Al-Qobah soil is of more efficiency (quantity of soil, concentration of phosphate, volume of sample, particle size and flow rate) is 2.5 g, 30 ppm, 40 ml, 125 micron and 1.5 ml/min respectively) as adsorption experiment efficiency reaches 98%. Thermal equilibrium of material is calculated following the Langmuir equation, where R2 gives a good linear relationship.

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دراسة الظروف المثلى لإزالة الفوسفات من المياه المنزلية لمدينة الموصل باستخدام بعض الأطيان المحلية

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الملخص

الهدف من الدراسة هو إزالة الفوسفات من مياه الصرف المنزلي باستخدام أنواع مختلفة من الأطيان والترب المحلية، وتم جمع مياه الصرف الصحي في شهري تموز وآب من خمس محطات رفع لمطروحات مياه المنازل في مدينة الموصل (باب سنجار ، الصندوقي، الحدباء، الخزازي، الشرطة)، وكان متوسط تركيز الفوسفات (3 ppm) حسب المحددات العراقية لنوعية المياه الصالحة للبيئة المائية، إذ كانت القيمة العليا في محطة باب سنجار (6.8 ppm) ، بينما القيمة الأدنى كانت بحدود (2.2 ppm) ، وتم استخدام اطيان وترب (البنتونايت، تلكيف، ترب الكُبة) في إزالة الفوسفات وتقليل تركيزها. وبعد المقارنة بين الترب الثلاثة، تم اختيار ترب الكُبة بكفاءة عالية ودراسة الظروف المثلى (كمية التربة، تركيز الفوسفات، حجم العينة، حجم حبيبات الترب، معدل التدفق، وكانت افضل الظروف (2.5 g، ppm30 ، 40 مل، 125 مايكرون، 1.5 مل/ دقيقة على التوالي). بلغت الكفاءة بنسبة 98% كما تمت دراسة التوازن الحراري للمادة بتطبيق معادلة لانكماير حيث أعطت علاقة خطية R^2 جيدة.

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Introduction

Many local clays and soils have ability to exchange or absorb cations and anions. Thus, it contains on its surface such as (H^+, Mg^{2+}, Na^+, Ca^{2+}, NO_3^- $PO_4^{-3}$and SO_4^{2-}), which can be exchanged without change the geometry, which has a large surface area (Bergaya and Lagaly, 2006). They easily absorb dyes, heavy metals and organic matter from pollution, electrical conductivity (EC) and (pH). Bentonite shows the best removal efficiency of calcium and magnesium Phosphate, Nitrate, followed by Ninavite and Kaoline respectively. Removal of (COD) gives for (BOD_5) at optimum doses (Nabeel and Abid, 2009). Phosphate concentration shows five times in the of the Al- Khosar River, (BOD) and (COD) increase by (1.5, 1.48) times respectively compared to the Iraqi standard No. (25-B1) of the conservation of water supply according to the load of organics (Hazim, 2009). Phosphate is essential for life, developed a sophisticated system to regulate the phosphate of evolution.

Also it has a critical factor in the pathogenesis of bone disorders and mineral associated with chronic kidney(Komaba and Fukagawa, 2016), phosphorus is released to the soil water, and so phosphorus pollution is reaching dangerous levels in the rivers and others, hoping to use bacteria in the soil to overcome the unused phosphorus, boosting crop growth (Paul Simons, 2018)**.** Pollution of water caused by human activities and industrial is one of the major problems in the world, as it is the leading cause of 80% of diseases worldwide, there is almost (1.1) billion people that cannot get portable water (Al-Hayani *et al*., 2022). In the aquatic environment, phosphate is found in wastewater as a result of agricultural phosphate fertilizers, household detergents and organic waste, knowing that its high concentrations in drinking water have health problems, including osteoporosis (Lanjwani *et al*., 2020) aquatic plants and plants due to the increase in the proportions of green algae known for their toxicity. This leads to a decrease in the amount of dissolved oxygen in the water, factors resulting from weighting, water springs, tourism in the adjacent soil (0.3-3) mg. kg^{-1} (Mustafa *et al*., 2019).

Materials and Methods

Location

Water samples are collected from five pumping stations in geographical locations with latitudes and longitudes shown in Table (1). Water samples are collected for laboratory measurements and biological analyses using clean glass bottles that are well washed with distilled water several times. As for the samples related to the determination of dissolved oxygen (DO) and the requirement of Bio-oxygen BOD5 is used to collect special bottles of 500 ml without creating air bubbles as much as possible, refrigerated boxes away from light for the purpose of preserving samples until reaching the laboratory at 4ºC, and a special iron canister tied with a rope for the purpose of collecting the sample from the basins of the lifting stations with special gloves for sample collection. The location address, date of sampling, weather conditions, the pH and electrical conductivity are calculated in the field at the studied sites.

Table 1: The longitude and latitude values

Locations of Station	latitude Lines	Longitude Lines	Actual Energy h/m^3
V Al-Qarazee	N36º36'07"	E13º43'83"	8700
Al-Shurtaa	N37º36'64"	E12º43'78"	5200
Al-Hadba'a	N38º36'48"	E15º43'14"	3900
Bab Sinjar	N34º36'30"	E11º43'52"	2900
Al-Sandooqi	N25º36'12"	E15º43'19"	6000

Fig. 1. Satellite image of sample collection sites.

Laboratory analysis

Turbidity, phosphate, chloride, nitrate, nitrite, COD, BOD, sulphate, hardness, Ca, Mg, Na, K, E.C and pH, are analyzed according to standard method for examination of water and waste water (APHA, 1998).

Materials Adsorbent

Bentonite, Tulkeef and Al- Qobah clays, which are locally available in large quantities are used as an inexpensive raw material. They are available in the environment areas. After collecting them, the samples are crushed and sieved with a grain open size of 175 micron and kept inside a plastic container for measurement (Khan, 2020). A mass of (2.5 g) of absorbent materials is separately used (batch and column) techniques. The volume of stock solution 25 ml at different concentrations (7.5, 15, 22.5, 30, 37.5) ppm of PO4 –as KH2PO4 are added, then standing time for (15 min) with stirring in batch technique, and the other used 1.5 ml/min flow rate for column (see schematic 1), finally absorbance is read of phosphate according to ammonium molybdate- meta vanadate mixture (Tandon et al., 1968) spectro-photometrically at maximum wavelength 400 n.m.

Then phosphate is calculated before adsorbed according to equations:

$$\mathrm{PO4} - \mathrm{ad} = V(Cin - Cf)/W \dots\dots\dots\dots (1)$$

Where:

PO4-ad: phosphate adsorbed in ppm, *V*: the quantity of phosphate in ml, *W*: weigh of dry material in gram. The equilibrium concentrations of the phosphate according to Langmuir single-surface equation are determined to get free energy, binding capacity preference factor, and maximum adsorption capacity.

$$X = KbC/(1 + KC) \dots\dots\dots\dots (2)$$

Where:

X: the quantity of phosphate adsorbed in µg g-dry clay, *K*: the binding factor of the phosphate on the clay surface. energy coefficient in ml µg-unit, *b*: maximum adsorption in µg. g^{-1}, *C*: phosphate concentration in the equilibrium in µg.ml^{-1}, and the values of constants are calculated after plotting the relationship between C/X values and C values to get a straight line, so the slope of the line is 1/b, and the intersection with the y-axis Intercept is 1/Kb.

$$\frac{C}{X} = \frac{1}{Kb + C/b} \dots\dots\dots\dots (3)$$

Maximum Buffering Capacity (MBC)

This value is expressed mathematically by multiplying the binding energy K in the maximum adsorption capacity of the surface Xm of the Langmuir equation, which is a specify of ion adsorption. The Langmuir equation, as noted by Yassen and Fakher, 2016; Al-Hassoon *et al*., 2019) is as follows:

$$MBC = dx/dc = (KXm) \dots\dots\dots\dots (4)$$

The samples were collected once in month starting from July 2021.

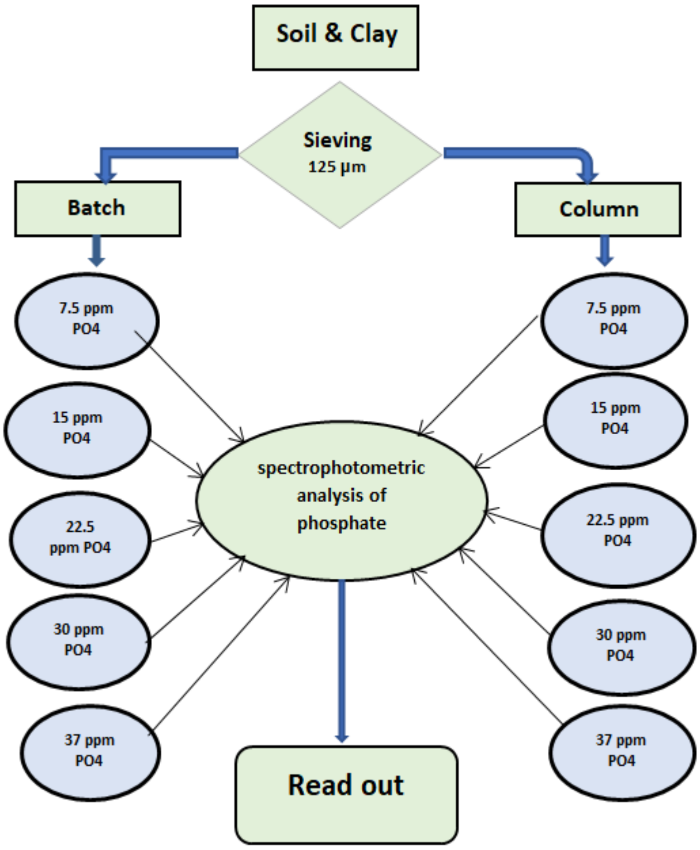


Fig. 2. The diagram of different materials treatment.

Results

Composition of clay and soils:

A property of natural adsorbents (bentonite, Tulkeef and Qobah) clays are used as listed in tables (2 and 3).

Table 2: Composition of bentonite.

	L.O. I	Fe_2O_3	Na_2O	K_2O	MgO	CaO	Al_2O_3	SiO_2	Total
Wt%	12.49	5.12	1.11	0.60	3.42	4.48	15.67	56.77	99.9

Table 3: Properties of soil.

Soil texture	Organic Matter %	E.C(ds/m)	pH	Sand%	Silt%	Clay%
Salty clay	2.7	3.4	7.6	13.3	50	36.7

Analysis of house water

After collection of water from lift pump station, many chemical parameters and biological were examined, all value listed in table 5 were with permissible limit, except phosphate.

Table 4: Chemical and physical analysis of water lift stations from domestic waste water

analysis	WQI (*)	Bab Sinjar		Al-Sandooqi		Al-Hadba'a		Al-Qarazee		Al-Shurtaa	
		July	August	July	August	July	August	July	August	July	August
pH	9−6.5	7.1	7.5	7.2	7.4	7.3	7.1	7.6	7.0	6.0	7.0
E.C micromos/cm	2250	772	772	635	635	700	609	1035	981	688	507
Turbidity (NTU)	18−10	25.2	25.2	23.6	23.6	13.8	31.3	6.45	27.1	6.77	12.4
TDS (ppm)	1500	392	392	327	327	355	294	518	480	338	248
TSS (ppm)	40	90	24	14	140	94	52	56	48	14	34
DO	5	2.6	5.5	6.1	4.3	4.1	3.2	2.2	2.9	3.5	1.5
Phosphate(ppm)	3	3.4	6.8	2.3	4.3	.42	4.6	2.3	2.9	.20	2.2
Fluoride (ppm	1	0.35	1.06	0.49	0.99	0.7	0.96	0.5	1.07	1.4	0.86
Chloride (ppm	400	124	70	80	38	92	55	70.4	45	150	38
Nitrate(ppm)	50	2.7	4.2	1.7	1.9	4.2	4.2	6.2	6.2	3.1	7.3
Nitrite(ppm)	Nil	0.2	0.5	0.1	0.1	0.2	0.3	0.3	0.4	0.17	0.15
COD (ppm)	100	96	76.8	64	41.6	99.2	160	112	54	134.4	48
BOD (ppm)	40	60	43.1	40	20.2	42		35	28.1	27	25
Sulphate (ppm)	400	136	235	73	230	138	152	20	264	107.5	87.1
Hardness (ppm)	500	300	245	290	290	310	280	520	495	270	225
Ca^{+2} (ppm)	200	58	45	64	64	60	52	116	112	48	44
Mg^{+2} (ppm)	50	37.5	32.4	31.2	31.2	38.4	36	55.2	48	36	36.4
K^{+}1(ppm)	20	4.5	5.4	3.27	3.27	5.6	3.9	3.3	3.1	4.48	2.4
Na+1(ppm)	35	13.8	11.5	9.2	9.2	14.4	22.4	13.6	20.6	15.7	10.2

(*): water quality index (Al-Saffawi and Al-Assaf, 2018).

The relative increase in the concentration of orthophosphate ions (6.8 ppm) in Bab Sinjar station, and this is due to the increase in the use of detergents rich in phosphorus compounds, as well as agricultural waste containing pesticides and fertilizers through the disposal of outfall water thrown to the river.

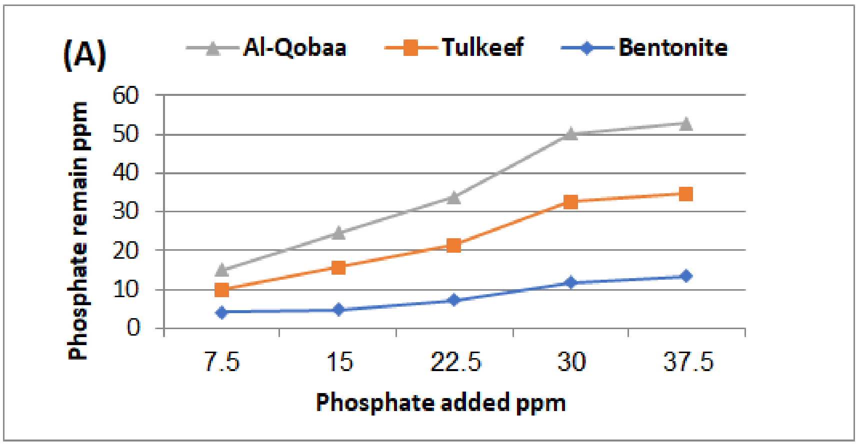
Table 5: Comparison between clays

PO_4 Added	Bentonite				Tulkeef				Al-Qobah			
	Batch		Column		Batch		Column		Batch		Column	
	Release found (ppm)	Absorb %	Release found (ppm)	Absorb %	Release found (ppm)	Absorb %	Release found (ppm)	Absorb %	Release found (ppm)	Absorb %	Release found (ppm)	Absorb %
7.5	4.20	44.00	0.05	99.33	5.79	22.80	2.04	72.71	5.10	31.90	4.08	45.5
15	4.81	67.89	0.09	99.4	10.86	27.55	2.20	85.33	8.94	40.38	4.42	69.51
22.5	7.277	67.65	0.251	98.88	14.25	36.66	5.12	77.23	12.24	45.58	4.57	80.32
30	11.73	60.87	0.815	97.28	20.81	30.61	7.58	74.72	17.58	41.39	5.54	81.52
37.5	13.41	64.18	2.303	93.86	21.17	43.53	15.53	58.57	18.25	51.33	6.13	83.65

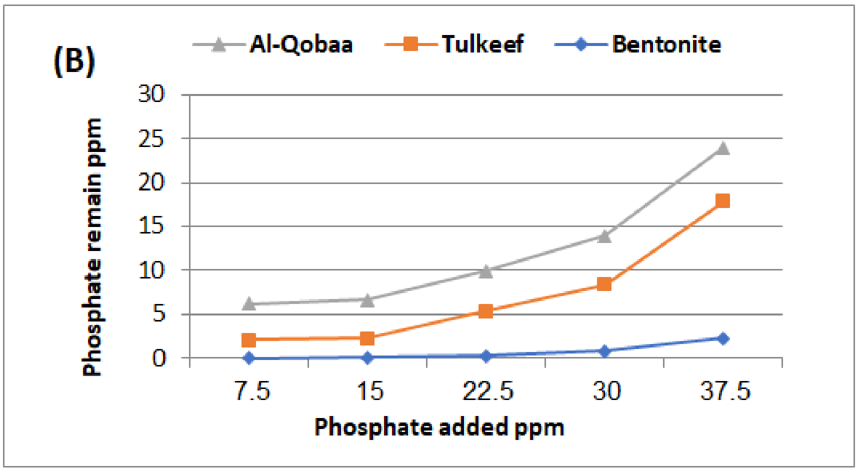
Optimum condition for adsorption of clays

In the beginning, three clays (2.5 gram) of (bentonite, tulkeef and Qobah) are selected in order to make a comparison between them to choose the best, where five duplicate concentrations of phosphate (25 ml) are prepared, the first is placed in five glass beakers for a period of a quarter of an hour, while the second concentrations are passed on columns with a diameter of 1 cm at a flow rate of 2 ml/min and the samples are collected for the determination of phosphate by colorimetric analysis (see Table 5, Fig.2).

From above table 5 choice Al-Qobah clay in Subsequent experiments which are of more efficiency and cheaply available comparing to others.



Batch



column

Fig. 3. Capacity adsorbed of different clays; (A):by batch technique (B):by column

From Figure (3)., the adsorption capacity of phosphates in the column technique was better than the batches, especially bentonite clays, but choice the more availability Al-Qobah soil.

Study the condition parameters of adsorption on Al-Qobah soil:

1-Study the quantity of Al-Qobah soil:

After optimum condition for different adsorbe material, select Al-Qobah in next application, firstly study the quantity of soil (Table 6):

Table 6: The Effect of quantity al- Qobah soil on adsorption

weigh soil (g)	PO_4 Remain (ppm)	PO_4 Remain (%)	PO_4 adsorb (%)
2.5	6.650	22.166	77.834
5	4.721	15.736	84.264
7.5	3.959	13.198	86.802
10	3.249	10.829	89.171
With out treatment	30.000	100.000	0.000

2-Study volume of phosphate:

Table 7: Effect of phosphate volume on adsorption of al-Qobah soil

Volume (ml)	PO_4 Concentration remain	PO_4 remain (%)	PO_4 adsorb (%)
10	0.798	7.980	92.020
20	1.732	8.659	91.341
30	3.056	10.187	89.813
40	4.211	10.526	89.474
50	13.243	26.486	73.514
With out treatmen	30.000	100	0.000

3- Effect of particle size:

Table 8: Effect of particle size of Al-Qobah soil on adsorption of phosphate

Particle size Micron	PO_4 Concentration remain	PO_4 remain (%)	PO_4 adsorb (%)
75	2.011	6.702	93.298
125	3.016	10.053	89.947
300	6.931	23.104	76.896
1100	7.884	26.279	73.721
2000	14.074	46.914	53.086
2360	15.820	52.734	47.266
With out treatment	30.000	100	0.000

4-Effect of flow rate:

Table 9: Effect of flow rate phosphate on adsorption of Al-Qobah soil

Flow rate ml/min	PO_4 Concentration remain	PO_4 remain (%)	PO_4 adsorb (%)
0.25 (4 drops/min)	2.222	7.407	92.593
0.5 (8 drops/min)	0.741	2.469	97.531
1.0 (17 drops/min)	1.164	3.880	96.120
1.5 (20 drops/min)	0.053	0.176	99.824
2.0 (34 drops/min)	1.005	3.351	96.649
With out treatment	30.000	100.000	0.000

5-Study the phosphate concentration on adsorption:

Other parameter was study, the quantity of phosphate adsorbed (see Table 10).

Table 10: The effect of concentration phosphate on adsorption of Al-Qobah soil

PO_4 added ppm	PO_4 remain ppm	PO_4 remain (%)	PO_4 adsorbed (%)
20	4.656	23.280	76.720
30	4.762	11.905	88.095
60	5.979	9.965	90.035
70	8.148	11.640	88.360
100	10.053	10.053	89.947

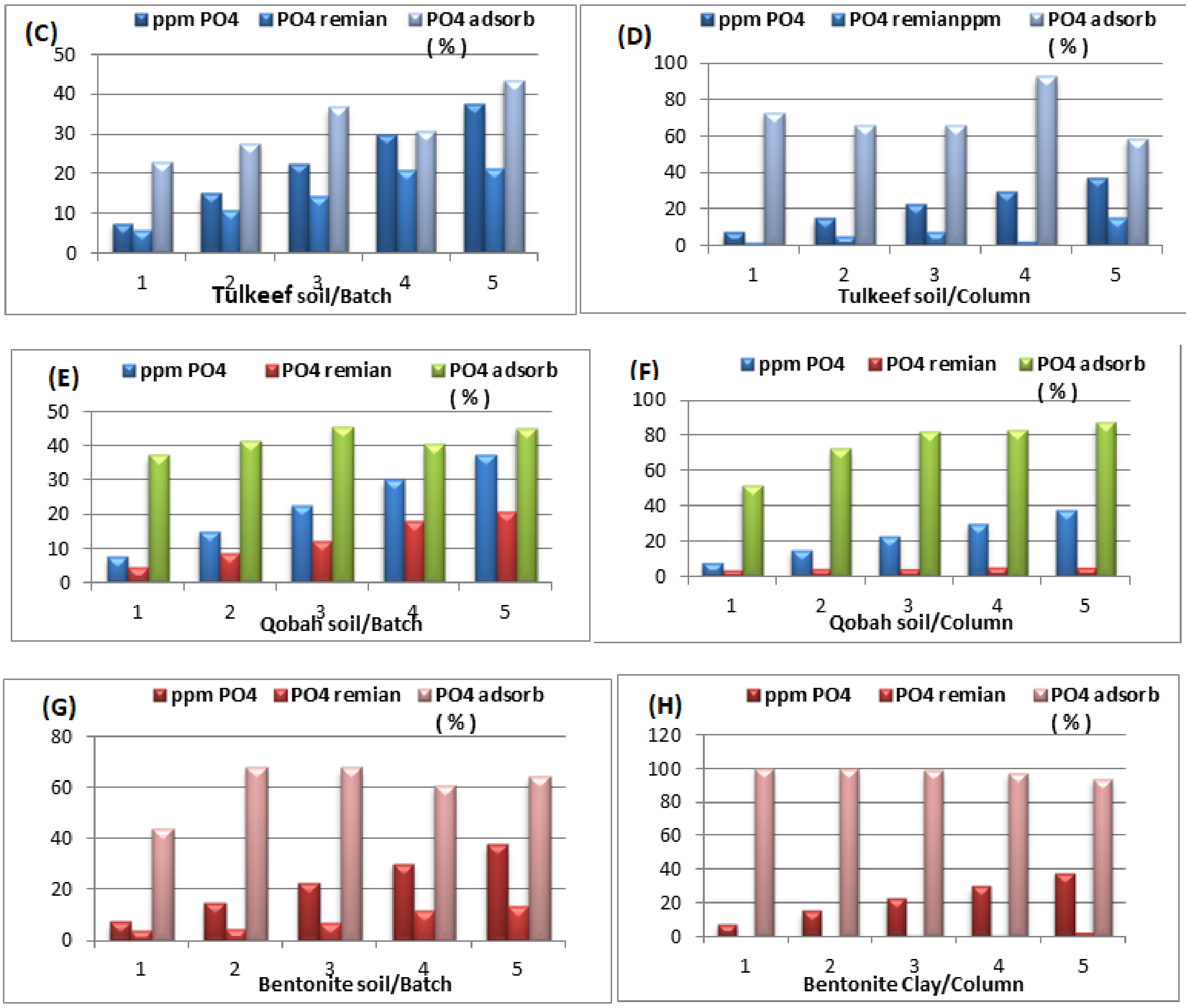


Fig. 4. Diagram for Phosphate removal efficiency and percentage by column and meal technique using (Qobah, Tulkeef and Bentonite soil).

From Table (11), the adsorption reactions are spontaneous with different clays and that the reaction are negative and that these values are in line with the values of the preference factor (separation coefficient, R^2) with negative free energy value (Yassen and Fakher, 2016).

Table 11: Regulatory capacity at equilibrium regulatory capacity at maximum free energy.

Treatment		Langmiur equation			
Clay and Soil		Correlation coefficient R2	Gibbs free energy ΔGx10+3 (Joule. mole-1. degree-1) Xm	Bonding Energy k x10 +6 (ml.g-1) KL	MBC
Bentonite Clay	batch	0.9627	-5.61 E+3	1.31 E+04	-7.37 E+07
	column	0.9432	-8.04 E+3	79.1 E+04	-6.36 E+09
Tulkeef Soil	batch	0.9636	-2.48 E+3	-6.77E+01	1.68 E+05
	column	0.5902	-6.04 E+3	2.73E+04	-1.65 E+08
Al-Qobah Soil	batch	0.9539	-3.16 E+3	-21.0E+01	6.65 E+05
	column	0.5797	-2.3 E+3	-7.24 E+01	1.84 E+05

Conclusion

1- We conclude that the water of the houses exposed to the river through the pumping stations is higher than the surveyed limit.

2- The deterioration of the waste water requires treatment, and for this reason we have prompted us to carry out the treatment process.

3- Soil of Tulkeef region was the best compared to the bentonite clays and Al-Qobah regions in terms of adsorption efficiency.

4- Finally, Langmuir equation was applied.

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