



Ferric Iron, Manganese Sorption from Waste Water by Commercial Activated Bentonite clay as Low Cost Adsorbents

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Abstract

Sorption of Fe (III), Mn(II) from wastewater using a solid phase extractant via utilizing clay bentonite. Thermal bentonite clay was prepared as adsorbent by heating at 800°C (B- 8).

The adsorption of Fe (III), Mn(II) from waste water onto thermal bentonite Likewise are should be were studied. The parameters that affect Fe (III), Mn(II) adsorption as, sorption time, pH, Fe (III), Mn(II) concentration, (rpm), sorbent amount and temperature were considered .

Stability line used to calculate occupied adsorption ability of Fe (III), Mn(II) and the experimental results were to be about 22, 35 mg/g respectively. Adsorption process of Fe (III), Mn(II) on wastewater have been proven.

Description keywords: thermal bentonite; Fe (III); Mn(II); polluted water; sorption.

1. Introduction

As a result of the addition of heavy elements, water pollution will occur, and that is a result of the use of industrial activities such as mining and waste treatment, which leads to disturbances and an increase in anxiety in terms of pollution,[1,2] because these wastes are biodegradable in nature in the soil[3].

Therefore, many methods have been used to reduce water pollution; among these methods are sedimentation, exchange between ions, extraction, filtration and absorption [4].

Natural clay has high properties, so this study was done on a type of clay used from nature in order to absorb heavy elements from polluted water, which are used in drinking. Adsorption and also due to its availability, ease of obtaining it, and its low price [5-11] Natural clay has many uses. Among these uses is the extraction of heavy elements from the water used in drinking, as well as waste from industries, which is called wastewater, such as the manufacture of fertilizers and pesticides. Manufacture of tiles, paints and materials used for gluing objects and raw materials produced from the factory, animal feed and building materials. Also, bentonite or natural clay has the following advantages: high porosity of the surface, its

ability to exchange cations, and its cheap price. Among the disadvantages is that it requires treatment and modification in order to work on the adsorption of anions. This requires treating the clay to be used in the various processes of adsorption according to the type of study used [12, 13]. In contrast to what has been mentioned, this study focused on the preparation of natural and thermally treated clay used in the processes of adsorption of Fe (III), Mn (II) from polluted waters. Then, the adsorption process was studied in the way it was exploited and used in the adsorption process, and the efficiency was calculated

2. Experimental results

2.1. Tools and Chemicals

The clay found in Egypt was found from the company located in Cairo and it is called Al-Amir Ceramica Company. The used clay samples were plated, and the samples were sieved into small and equal sizes about 200 mesh, and the composition of natural clay or chemical bentonite in Table 1, the clay sample was washed and dried in an electric oven at 110°C until completely dry. The polluted water in this study was obtained from the 10th of Ramadan City and its chemical composition is shown in Table 2.

Table 1. Chemical structure of the employed bentonite example

Constituent	%	Constituent	%
Al ₂ O ₃	16.60	MgO	2.13
SiO ₂	41.10	CaO	7.96
TiO ₂	0.98	Na ₂ O	5.46
Fe ₂ O ₃	7.41	P ₂ O ₅	0.17
MnO	0.04		

Table 2. Results of analysis of a chemically polluted water sample.

Element	ppm
Fe ³⁺	149.96
Zn ²⁺	15.69
Mn ²⁺	271.12
Cu ²⁺	11.98
Cd ²⁺	0.52
Al ³⁺	13.4

2.1.1. Equipment

Regulator shaker, water steam bath having a temperature difference of $\pm 0.5^\circ\text{C}$ used for group balance investigates, was gained from Joshi Technical Organization. All substances and chemicals were of A.R. ranking and used without further decontamination. Fe

(III), Mn (II) was definite by Atomic Absorption Spectrometer.

2.2. Preparation of thermal bentonite:

Current Modified natural clay bentonite was organized as creased, powdered in a mortar, separated 200 mesh size, the pounded rock-hard clay samples were dried in an electric heater at 110 °C until complete dryness. The calcined process was approved at temperature of 805 °C for 2 h (B- 8) [14].

2.2.1. Characterization of treated bentonite

external belongings of the natural bentonite clay on alteration were persistent by numerous procedures as, Fourier transform infra-red spectroscopy (FTIR), and scanning electron microscopy (SEM) [15, 16].

2.3. Balance Preparations

Collection sorption investigations were achieved by trembling 0.121 g bentonite clay with 15.00 mL of waste water in a thermo stated shaker bath at $(25 \pm 1^\circ\text{C})$. After the conforming time wait, the solutions were clarified complete a 0.45 μm pore size tissue. Fe (III), Mn (II) concentration in the clarified results was determined with Atomic Absorption Spectrometer. Numerous sequence of trials have been achieved by Fe (III), Mn(II) and several influences were planned. These influences included, shacked time, Fe (III), Mn(II) concentration, pH and temperature. After the found effects, Langmuir and Freundlich isotherms were determined. On behalf of eluting loaded of Fe (III), Mn(II) after bentonite clay, investigational of these were recycled by equal, nitric acid, Hydrochloric acid, Sodium acetate, Sodium chloride and Acetic acid

3. Results and discussion

3.1. Contact time Impact:

In directive to training, the related factors affecting Fe (III), Mn(II) adsorption onto the prepared thermal clay, suitable amount (50 g) of the (B- 8) was treated for this purpose. The prepared (B- 8) quantity was then distributed into seemly servings for performance the balance trainings: contact time, metal concentration, pH, adsorption temperature and adsorbent amount (adsorbent dose).

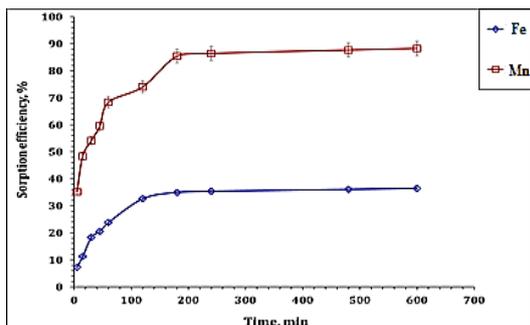


Fig. 1. Influence of the contact time on Fe (III), Mn(II) adsorption efficiency by (B- 8) (0.12 g/15 ml, 100 mg/L at ≈ 25 °C and pH 2.9

3.2. Influence of initial metal application

studying the influence initial metal focus on the sorption effectiveness onto treated bentonite clay (B- 8), sequence of investigates was achieved by communicating a stable mass (0.12 g) for 600 min at temperature (≈ 25 °C) and pH 2.9. The calculated Fe (III), Mn(II) concentrations ranged from 20 up to 500 mg/L by adding standard (1000 ppm) Fe (III), Mn(II) .The obtained results (Fig.2) displayed that Fe (III), Mn(II) adsorption efficiency decreases with increasing its initial concentration. The (theoretical) Fe (III), Mn(II) adsorption capacity of the (B- 8), was determined to be about 18, 40 Fe (III), Mn(II)mg /g respectively.

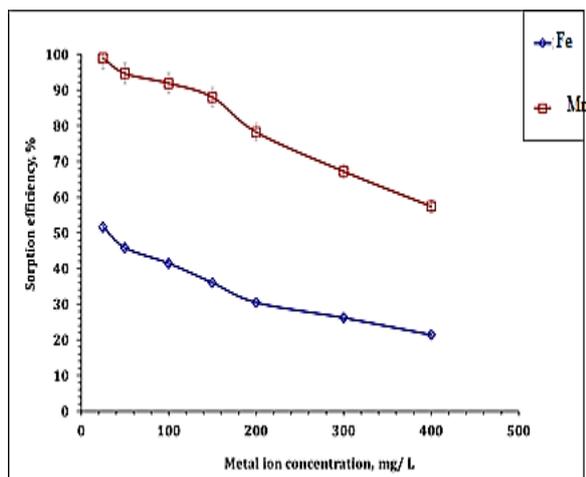


Fig. 2. Effect of initial metal concentration upon Fe (III), Mn(II) adsorption efficiency by (B- 8) (0.12 g/15 ml, 12 h at room temperature and pH 2.9)

3.2.1. Sorption isotherms

Numerous mutual sorption isotherm copies were measured to fit the achieved isotherm documents below

the balance sorption B-8. Models of sorption isotherm as: Langmuir and Freundlich.

3.2.1.1. Langmuir line isotherm

sorption happens equally on lively places of sorbent, when sorbate inhabits a situare, no additional sorption fire income residence at site. Therefore, Langmuir is assumed balance. [17- 22]

$$C_e/q_e = 1/bq_0 + C_e/q_0 \quad (1)$$

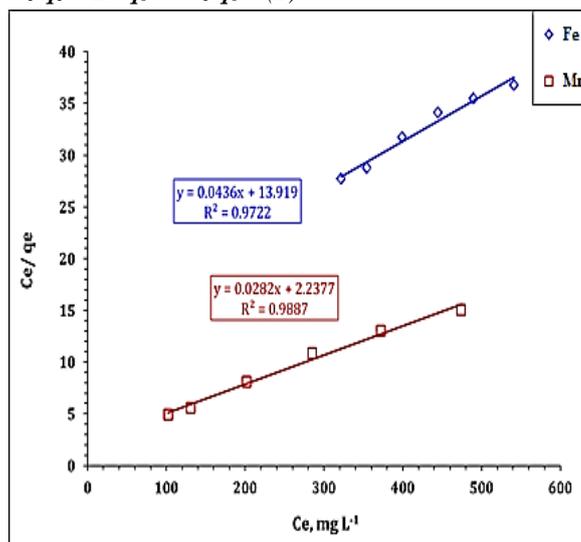


Fig. 3. Langmuir line plans aimed at sorption of Fe (III), Mn(II) onto B- 8.

3.2.1.2. Freundlich line isotherm

Freundlich ideal instructs that solute adsorbed to solute application is purpose the result. [17- 22]:

$$q_e = K_F C_e^{1/n} \quad (3)$$

$$\log Q_e = \log K_F + 1/n \log C_e \quad (4)$$

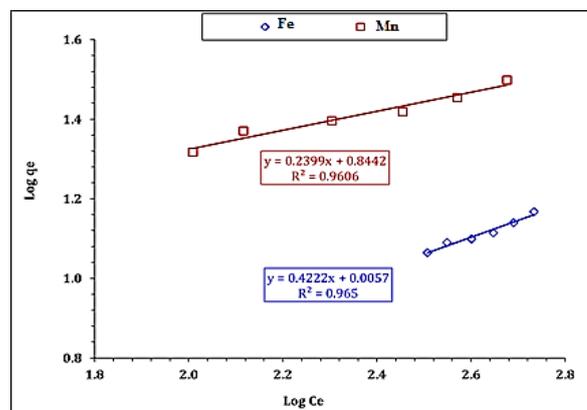


Fig. 4. Freundlich line plans for sorption of Fe (III), Mn(II) onto B-8.

Table 4: Adsorption isotherms

		Fe	Mn
Freundlich isotherm model	n	2.37	4.17
	K_f (mg/g)	1.01	6.99
	R^2	0.96	0.96
Langmuir isotherm model	Q_m (mg/g)	22.94	35.46
	b (L/mg)	0.003	0.013
	R_L	0.347	0.117
	R^2	0.97	0.98

3.3. Influence of sorption temperature

Training influence of temperature on Fe (III), Mn(II) sorption on clay bentonite (B- 8) sections, sequences sorption investigates was achieved by changed temperatures going 20 to 50 °C. In these trials new factors were saved continuous, i.e., primary Fe (III), Mn(II) concentration of 100 ppm, pH 2.9 and 10 h as contact time. achieved grades (Fig.4) showed clearly that Fe (III), Mn(II) adsorption efficiency decreased from 35 up to 33% and from 90 up to 85% for Fe (III), Mn(II) respectively, by increasing the temperature. This designates that the sorption response is an exothermic method. Hence, we container determine that temperature (≈ 25 °C) is most right temperature at investigational Fe (III), Mn(II) sorption trainings.

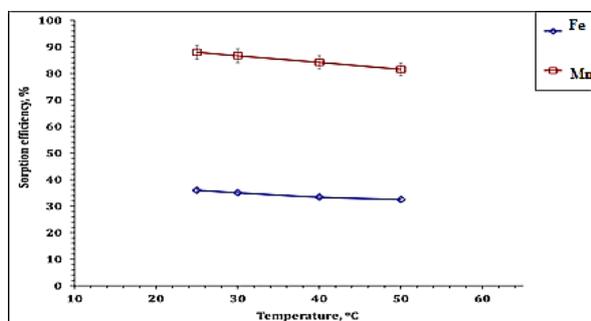


Fig.4. Effect of temperature upon Fe (III), Mn(II) adsorption efficiency onto B- 8 (0.12 g/15 ml, 12 h. and pH 2.9)

3.4. Influence of pH

Influence of pH is unique best essential features which mechanism the sorption capability of impurities on clay shells. Variation of pH shakes the adsorptive procedure concluded severance of efficient collections ob adsorbent surface-active places. influence pH on Fe (III), Mn(II) sorption by B- 8 was planned pH series among (0.51 / 7.61). investigates were done below continuous primary Fe (III), Mn(II) concentration of 100 ppm at temperature (≈ 25 °C) , 10 h quaking time. Fig. 5. For determination, sorption of Fe (III) rises around (10 - 36%)by rise pH (0.51 - 0.3) and then faintly improved (36% - pH 7.55). sorption of Mn(II) rises since around (50.3 - 88.6%) by rise pH (0.51 - 3.00) and formerly faintly improved (89.5% - pH 7.61) for Mn(II) . Thus, determine pH 3 is the greatest appropriate pH rate.

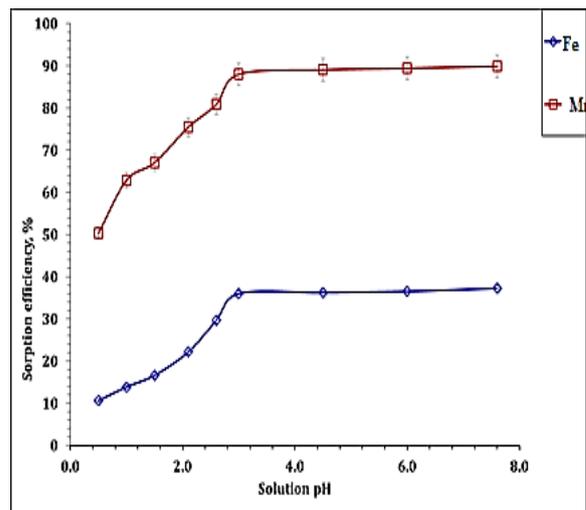


Fig. 5. Effect of pH upon Fe (III), Mn(II) adsorption efficiency onto B- 8 (0.12 g/15 ml, 12 h and Room temperature)

3.5. Effect of adsorbent amount

Elimination Fe (III), Mn(II) from aqueous clarification, the total of the organized B- 8 charity in the development is essential for financial requests. The worse volume adsorbent recycled the worse total development. influence of adsorbent contented on the acceptance of Fe (III), Mn(II) was established (Fig. 6). sequences of adsorption trials was achieved by changed adsorbent

amounts going (2 – 10) g B- 8 /L. Experimentations stayed achieved below continuous first Fe (III), Mn(II) concentration of 100 ppm at temperature ($\approx 25\text{ }^\circ\text{C}$), 10 h quaking time and pH of 2.9. sorption percentages of manganese (II) rises with growing adsorbent volume. in treated bentonite clay adsorbent (2 to 12) g/L (24 - 89%) and guileless growth (92% - 12g/L). this is owing to the rises of the lively places on adsorbent, fixity the quantity of existence Fe (III), Mn(II) in the clarification. Thus, efficient idea opinion 8 g/L adsorbent amount was designated as the best amount.

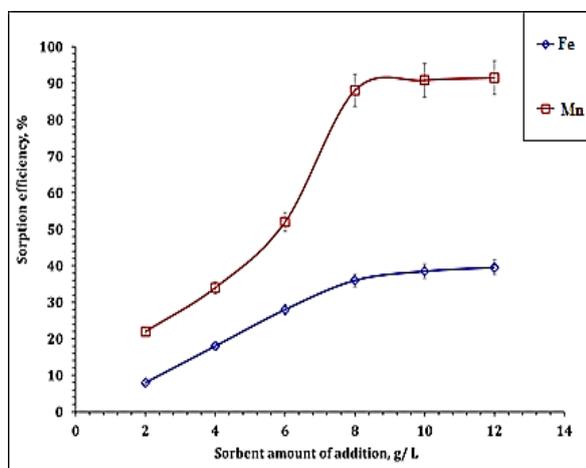


Fig. 6. Effect of adsorbent amount upon Fe (III), Mn(II) adsorption efficiency onto B- 8 (PH 3, 12 h, and room temperature)

3.6. Influence of (rpm) speed

Rpm exercise main factor in sorption wonders, inducing supply clay bentonite in substance result and development of outside edge movie. result of exercise on sorption of Fe (III), Mn(II) on clays bentonite stayed observed at numerous exercise rpm (100, 200,300,400, 500, 600, 700, 800,.... rpm) at 10 min. The effects planned Figure 7 as a relative among Fe (III), Mn(II) sorption effectiveness %, agitation rpm. Since the effects it pure that, Fe (III), Mn(II) elimination ratio is unclearly improved as agitation rpm better. High agitation rpm shows a dangerous part, wherever it bases reduction the edge sheet and drops conflict of moving. Lastly, develops

removal grade Fe (III), Mn(II) seeming the adsorbent, which is named diffusion-controlled appliance

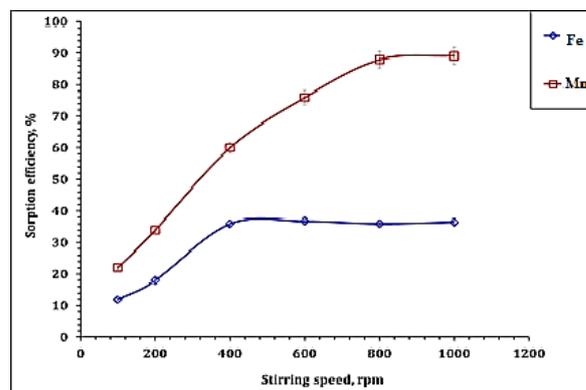


Fig. 7. Influence of agitation moving rpm on Fe (III), Mn(II) sorption effectiveness % (10 h, 0.12 / 15 g/ mL, $\approx 25\text{ }^\circ\text{C}$).

3.2. Metal elution

resulting answers HCl, NaCl, CH₃COONa, acetic acid and HNO₃ remained tried aimed at metal elution since full B- 8 clay. elution trials remained accepted ready by quaking loaded B- 8 example (0.52g) by eluent slices (25.00 ml). Design the eluted metallic quantities remained approved out later its examination in the together models. Fig.8 reviews found documents, obviously evident that Sodium acetate elution result is the greatest answer experienced as eluant for Fe (III), Mn(II) since loaded B- 8.

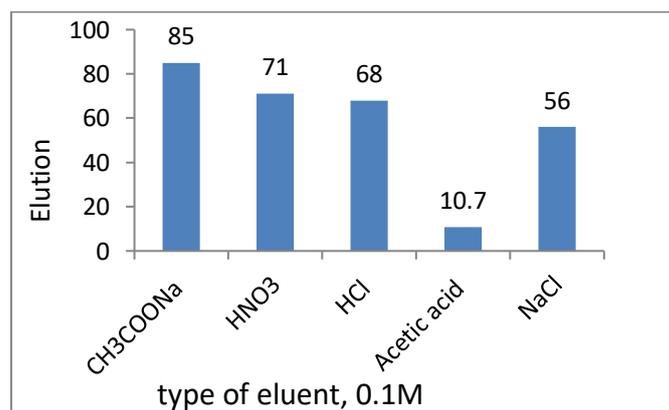


Fig.8: Elution yields using different eluent reagents

4. Characterization of the adsorbent

4.1. FTIR Study

FTIR spectra of clay thermal activated Bentonite B- 8 clays were presented (Fig. 8). B and B- 8 depends on its functional groups reactivity. IR spectra of B (7 before, 9 after sorption) and B- 8 (8 before, 10 later sorption) complexed through Mn(II) remained revealed Fig. 9. Associate FTIR groups formerly and later sorption, numbers revealed that around supplementary group 3800, 3692, 3622 cm^{-1} after sorption at thermal activated stage. but in case of bentonite, the band at 1186 cm^{-1} disappeared and 605, 1042 and 3412 cm^{-1} appear after sorption due to the increased substitution of metal by Fe (III), Mn(II)

4.3. morphology educations

SEM pictures surface B-8 before and after Fe (III), Mn(II) sorption (Fig. 9), indicated basic B-8 external which shaped owing to instability, elements decay through living action. Afterward sorption, these holes, gaps remained busy by Fe(III),Mn(II)

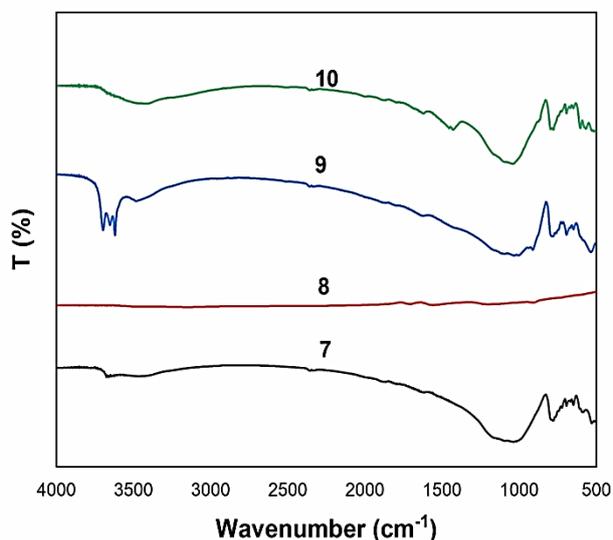


Fig. 9. FTIR bands occupied clay examples earlier and later sorption, B-8 Fe (III), Mn(II) (7, 9), B (8, 10)

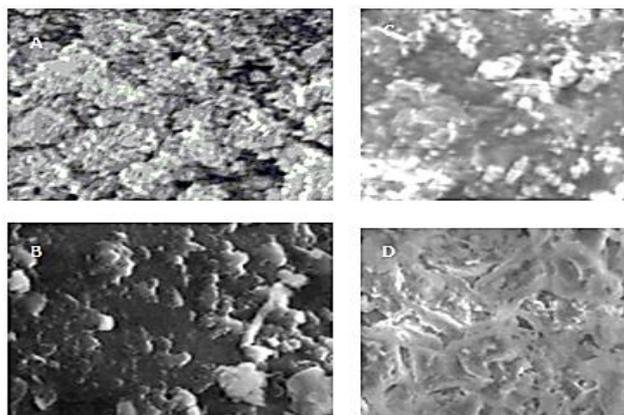


Fig. 10. SEM images of B-8 (a, b), B (c, d) before and after Fe (III), Mn(II) sorption Fe (III), Mn(II) .

7. Case training

Example training, sorption consequences remained approved out, by 500 mL since contaminated liquid water Fe (III), Mn(II) concentration of 151.56, 272.3 ppm communicated by 5 g since B- 8, 600 min. (25±2) °C and pH 3. Later balance, the result remained clarified and examined for Fe (III), Mn(II) application then it is originate that, whole sorption ability B- 8 attained 71, 93% for Fe (III), Mn(II) respectively.

8. Conclusion

sorption Fe (III), Mn(II) from contaminated aquatic water, by treated bentonite clay stayed examined. Outcomes show that Fe (III), Mn(II) sorption elimination happening treated bentonite clay was significantly pretentious by changed influences: temperature, application metal ppm, time, agitation speed rpm and solid liquied ratio. sorption procedure bigger with growing time, solid liquied ratio, temperature and rpm remained reduced with growth concentration of Fe (III), Mn(II) .

8. References

- [1] Ashutosh Tripathi and Manju Rawat Ranjan, Heavy Metal Removal from Wastewater Using Low Cost Adsorbents Tripathi and Ranjan, *J Bioremed Biodeg* 2015, 6:6 DOI: 10.4172/2155-6199.1000315
- [2] Al-Degs Y.S., El-Barghouthi M.I., Issa A.A., Khraisheh M.A. and Walker G.M. (2006), Sorption of Zn(II), Pb(II), and Co(II) using natural sorbents: equilibrium and kinetic studies, *Water Research*, 40, 2645–2658.
- [3] Ijagbemi C.O., Baek M.H. and Kim D.S. (2009), Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions, *Journal of Hazardous Materials*, 166, 538–546
- [4] Fu F. and Wang Q., (2011), Removal of heavy metal ions from wastewaters: A review, *Journal of Environmental Management*, 92(3), 407–418.
- [5] Ahmed M. Masoud; Walid M. Youssef and Mostafa I. Amin, “applicable technique for decreasing the content of iron, cadmium, copper, zinc and manganese from wet process phosphoric acid using synergistic organic mixture of methyl isobutyl ketone (mibk) and butanol”, *Nuclear Sciences Scientific Journal*, 8A, 243- 256, 2019.
- [6] A. A. Abdel-Samad, M. M. Abdel Aal, E. A. Haggag, W. M. Youssef (2020) Synthesis and Characterization of Functionalized activated Carbon for Removal of Uranium and Iron from Phosphoric Acid. *Journal of Basic and Environmental Sciences*, 7 (2020) 140-153
- [7] W. M. Youssef , Solid–liquid extraction of uranium from aqueous solution using Marathon C as a strong cation exchanger resin: kinetic, and isotherm studies. *INTERNATIONAL JOURNAL OF ENVIRONMENTAL ANALYTICAL CHEMISTRY*, <https://doi.org/10.1080/03067319.2022.2134995> , (2022).
- [8] Mostafa Ibrahim Amin· Hady S. Gado · Walid M. Youssef · Ahmed M. Masoud “Precipitation of iron from wet process phosphoric acid using oxalic acid and potassium hexyl xanthate (PHX)”, *Chemical Papers* <https://doi.org/10.1007/s11696-019-00735-8> (2019)
- [9] Sherien Hussein Ahmed, Entesar Mohamed El Gammal, Mostafa Ibrahim Amin, Walid Mohamed Youssef (2021). Studying the Effect of Potassium Amyl Xanthate Surfactant on Fe, Cu and U Ions for the Pretreatment of Abu Zeneima Sulphate Leach Liquor. *Journal of Periodica Polytechnica Chemical Engineering* 65(3), pp. 408–415., <https://doi.org/10.3311/PPch.15795>
- [10] W.M. Youssef, M.S. Hagag and A. H. Ali, “Synthesis, Characterization and Application of Composite Derived from Rice Husk Ash with Aluminum Oxide for Sorption of Uranium” *Adsorption Science & Technology*, 36(5–6), 1274–1293 (2018)
- [11] W. M. Youssef, A. E. M. Hussein, M. H. Taha, and M. M. El-Maadawya(2022.). Uranium(VI) Sorption from Liquid Waste Solution Using Functionalized Polyurethane Polymer: Kinetic and Isotherm Characterizations. *Russian Journal of Inorganic Chemistry*, 67, pages 1058–1068
- [12] Manjot Kaur Toor, “Enhancing adsorption capacity of bentonite for dye removal: physicochemical modification and characterization”, *Clays Clay Miner* 77-120 (2010)
- [13] Prathiksha P. Prabhu1, and Balakrishna Prabhu1 A Review on Removal of Heavy Metal Ions from Waste Water using Natural/ Modified Bentonite *MATEC Web of Conferences* 144, 02021 (2018) *RiMES* 2017 <https://doi.org/10.1051/mateconf/201814402021>
- [14]- G. E. Christidis, P. W. Scott, A. C. (1997). Dunham Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Aegean, Greece *Applied Clay Science*, Vol. 12, 4:329-347
- [15] Stella Triantafyllou, E. Irini Christodoulou, and Paraskevi Neou-Syngouna, “Removal Of Nickel And Cobalt From Aqueous Solutions By Na-Activated Bentonite”, *Clays Clay Miner.* 5 567-572 (1999)
- [16] A. Mellah and S. Chegrouche, “The Removal of Zinc from Aqueous Solutions by Natural Bentonite”, *War. Res.* 3 621-629 (1997)
- [17]- Chegrouche. S., Mellah. A., Telmoune. S., *Water Res.* 31 (7) (1997) 1733–1737.
- [18]- Mellah. A., Chegrouche. S., *Water Res.* 31 (3) (1997) 621–629.
- [19]- Bhatnagar. A., Jain. A.K., *J. Colloid Interface Sci.* 28 (1) (2005) 49–55.
- [20]- Ho. Y.S., McKay. G., *Water Res.* 33 (2) (1999) 578–584.
- [21]- Worku. N., Feleke. Z., Chandravanshi. B.S., Removal of excess fluoride from water using waste residue from alum manufacturing process, *J. Hazard. Mater.* 147 (2007) 954–963.
- [22]- Arami. M., N.Y. Limaee, Mahmoodi. N.M., Tabrizi. N.S., Removal of dyes from colored textile waste water by orange peel adsorbent: equilibrium and kinetic studies, *J. Colloid Interface Sci.* 288 (2005) 371–376.