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Investigation the adsorption properties of the Iraqi Siliceous Rocks composite towards some heavy metal

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Abstract

In this study, ion-exchange resin, capable for coordination with metal ions, is seen synthesis and capacity studies. Siliceous rocks was adding in stoichiometric ratio of 5% to the laboratory prepared melamine -formaldehyde resin and a composite of melamine formaldehyde siliceous rocks (MFSR 5%) was obtained. The possibilities of using the synthesized polymer has been investigated for adsorption of model metal ion solution of Cr+6 and Mn+2. UV spectrophotometric technique was finalized for the production of quantitative adsorption data at various contact time, pH and temperature parameters. Equilibrium isotherms for the adsorption of the two metal ions were measured experimentally. Adsorption isotherms have been analyzed by the Freundlich and Langmuir models. In addition, MFSR 5% was compared according to its percent uptake yields of the heavy metals.

Key words: Heavy metal adsorption, adsorption kinetic, adsorption isotherm, melamine formaldehyde resin, siliceous, rocks.

1. Introduction

Polymers of melamine and formaldehyde form an important class of amino resins, which have been commercially used for more than 60 years. Melamine formaldehyde polymer MF is one of the hardest and stiffest isotropic polymeric systems that exist. A flexural modulus as high as 9Gpa has been reported neat MF. The Presence of contaminates in aquatic environments may cause serious problem to human beings and other organisms. This is one of the most extensive scientific methods because of purification. Adsorption is a prospective process for purifying waste water. This approach requires adsorbents to satisfy the numerous requirements for their operation, stability, accessibility, cheapness. Most importantly, the exchange ions should be harmless and not cause secondary water contamination [1]. Metal ions are so essential because they are not biodegradable and can either be diluted or converted until released into the environment [2,3]. In the aqueous environment, chromium and manganese are often found in the (VI) and (II) states for Cr and Mn, respectively. Cr (VI) is a potent epithelial irritant and known carcinogen in humans [4]. Many plants, marine organisms, and bacteria are also harmful to Cr (VI) and Mn (II). Heavy metals can be removed from wastewater using a variety of physicochemical and biological methods. Filtration membrane, coagulation, and, adsorption [5] flocculation [6], ion exchange [7], as well as (chlorination, ozonation) advanced oxidation [8] are only a few among them. This study reports and for the first time on line the synthesis and characterization of a new composite (KMF 5%), which has a special properties differs from the original materials properties that made from through the development of MF polymer characteristic in the presence of siliceous rocks composite as essential supported material. Batch studies are carried out involving process parameters such as the initial metal ions concentration, solution temperature, and pH effect and contact time. Equilibrium and kinetic analysis were conducted to understand sorption process and optimization of various parameters in metal ions recovery.

2. Physicochemical characteristics of melamine formaldehyde and siliceous rocks.

Melamine Formaldehyde structure:

Melamine polymers and formaldehyde from the major family of amino resins (2, 4, 6-triamino -1, 3, 5-triazine), which have been used commercially for over 60 years. MF is an isotropic polymeric system that is one of the hardest and stiffest on the industry. It has the resistance to scratching and surface gloss is excellent, temperature stability and environmental

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qualities are also beneficial. MF is used as adhesives and in molding compounds. The special characteristics of MF make it an intriguing case as a composite matrix [9].

Siliceous Rocks:

Siliceous rock is a chemical and biochemical sedimentary rock consisting mostly of opal and chalcedony or more rarely of quartz (Tripoli, diatomite, gaize, flint, Jasper and others) Strong products Articles, razor- edge and shelly siliceous rocks usually referred to as “flint” hardness according to most scale 6.5-7) abound among archaeological artefacts [10]. Previous studies [11] shows that the Iraqi rocks consist of more than (50%) from silica and exist in a wide area in (AKASHAT, TRABELE) in Iraq. Table (1) establish the chemical structure for Iraqi siliceous rocks.

This paper reports on work on synthesis characterization of a new (MFSR 5%) composite and its possible use in removal of heavy metal ions Cr+6 and Mn+2 from aqueous solutions. Experiments in batches are carried out, with the operation parameters of the concentration of initial metal ions, solution temperature, pH influence, and contact time, all being taken into consideration. To better understand the sorption mechanism and optimize different parameters in metal ion recovery, equilibrium and kinetic studies were performed.

3. experimental materials and methods

3.1. Preparation of sorbent siliceous rocks:

The siliceous rocks were crushed into small pieces, immersed in distill water for 48 hours, after that, a mixture of diluted nitric acid and hydrochloric acid solutions was added to activate it. For a long time, the liquid was continuously stirred (72 hrs.) and then were dried at 150°c for 24 hours (A laboratory oven thermal (Kamp Gallen Vacuum Oven Drying, HITEC DP6T Yamato, (25-360oC) Japan). The dried rock pieces was ground and sieved by using a test sieve "". The sieved powder was thoroughly washed with double distilled water and dried at (165°C) for 3 hours, then it was allowed to cool to room temperature before being stored in airtight containers.

3.2. Synthesis of (MF) polymer:

(MF) polymer is synthesized by aniline, which supports melamine forms (27.75 g) (BDH chemicals, UK) to formaldehyde (37% concentration) after pH equalization to (8) by using NaOH (10%) (MF) after equalization (Research pH meter- pHm 84, Radiometer, Copenhagen, Denmark), Then (31.5 gm.) the melamine was weighed and added with a continuous stirring for (30 min) to formaldehyde boiling solution at (80-100°c) until the melamine had been completely dissolved. After the reaction was finished, a solid precipitate was purified and washed with pure water as a result of the polymerizing reaction. In the oven at (75-100°C), the precipitation was then dried. The formed polymer was cooled then crushed and sieved in a well closed container at room temperature [12].

3.3. Preparation of Composite (MFSR 5%):

A weight of (2,8 g) was well mixed with (92,5 2 g) melamine from purified siliceous rocks and a composite of formaldehyde was added to (60 ml) at (pH 8) a continuous heat at (80-100°C) and stirred at (30 min) until the resulting composite had been formed, the composite was cooled down at room temperature and crushed and a particle size of (75 µm) was obtained using (Retsoh Gmb, electric sieve,Co-KG.

3.4. Chemicals:

•Potassium chromate as Chromium Cr+6) and Manganese Chloride as Manganese (Mn^{+2}) were from (BDH Chemicals, England) were prepared by diluting of stock solutions of metal ions to the desired concentrations. A stock solution was obtained by dissolving (3.73 g) of each of the two metal ions adsorbate in 1000 ml distilled water.

•Melamine has a purity of (97%) and a molecular weight of (126.1 g/mol) was from (chemicals, BDH, England).

•Formaldehyde is equal to (30 g/mol) a molecular weight (Riedel DE Hean. Fluka. Germany).

• Hydrochloric Acid (HCl has a concentration of (37%) and Sodium hydroxide were both from (BDH Chemicals England).

4. Adsorption studies

To check the propensity of the adsorption mechanism, the preliminary investigations were carried out in batches under various pH, concentration, time, and temperature conditions. Solution of each metal ion of concentration range of (10 to 50 ppm) for Cr+6 and (30 to150 ppm) for Mn+2 were chosen. In each 100 ml measuring flasks, (20 ml) of metal ion solutions (is separate way) of known concentrations was poured having a (0.5 g) of (MFSR 5%) composite. A thermostatically shaker was used to shake the flasks by using (Thermostatic water bath shaker (BS.11digital, JE10 TECH, Korea, (20-185) rpm)) at 25°C before it reaches equilibrium. Subsequently the liquid suspension was filtered by a double Whatmann filter NO. 42 paper, with a spectrometrically defined volume of metal adsorbed ion at the value chosen (λmax) per metal ion.

5. Equilibrium Times of Adsorption systems

The amount of time required for the adsorption mechanism to achieve equilibrium at certain conditions of temperature (T=25°C) and PH=2 was by adding an initially fixed concentration of each metal ion solutions (50 ppm) for Cr+6 and (100 ppm) for Mn+2 to (0.5g) of (MFSR 5%). At 5, 15, 30, 45, 60, 75, and 90 minutes, the concentrations of metal ion solutions were measured using spectrophotometry. Table (3) show the time needed for each system to reach equilibrium.

Table 1: Chemical structure of siliceous.

Constituent	SiO_2	Al_2O_3	Fe2O3	P_2O_5	CaO	MgO	Na_2O	L.O.I
%	77.8	3.0	0.6	-	5.3	1.1	2.3	8.5

Table 2: Physical anlysis of siliceous rocks.

Density (gm/cm^3)	Specific gravity	Surface area (m^2/gm)	Pore volume (cm3/gm)	Ava. Pore diameter µm
1.323	1.301	39.688	0.338	0.030

Table 3: Equilibrium times for each adsorption system.

Adsorbate	Adsorbent	Equilibrium time(min)
MFSR 5%	Cr^{+6}	90
	Mn^{+2}	60

The amount of metal ions adsorbed on the adsorbent was calculated according to equation (1) [13].

Qe = (C0 –Ce) V/m ……. (1)

Where Qe (mg/g) and Ce (mg/l) are the concentration equilibrium adsorbate in solid phase and liquid respectively, C0 (mg/l) is the initial concentrations of adsorbate, V is the volume of metal ion solution (L) and m (g) is the weight of adsorbent. The efficiency of metal ions removal (R) defined by equation (2) [14].

Removal efficiency (R) =(C0-Ce)/C0 X100……. (2)

6. Result and Discussion

6.1. Kinetic studies:

Figures (1) display the quantity of metal ions removed by synthesis (MFSR 5%) as a function of contact time (1). As we see in these figure, Cr+6 and Mn+2 adsorption systems approached equilibrium within (90min) and (60min) respectively of contact time.

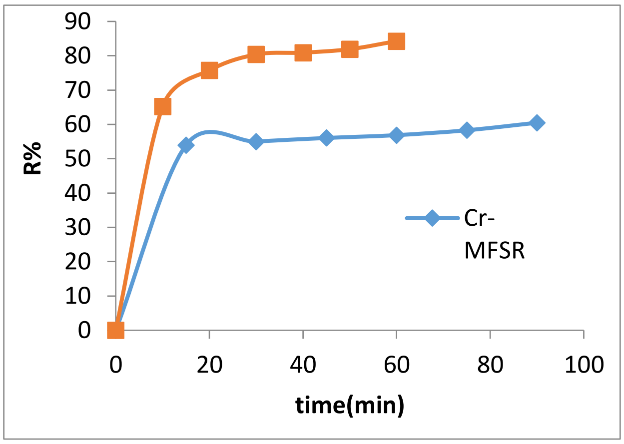


Fig. 1: kinetics of Cr+6 and Mn+2 removal by (MFSR 5%).

The rate constant of adsorption for each metal ions Cr+6 and Mn+2 were determined at 250C using equations of Lagergreen [15],[16]and second order reaction which are as follows:

log (qe –qt) = log qe – t ……(3)

Where K1 (min-1) is the first-order sorption Lagergreen constant evaluated from the plot log slope (qe-qt) versus t.

$$\frac{t}{qt} = \frac{1}{K2\ qe^2} + \frac{1}{qe}\ t \ldots\ldots\ldots\ldots (4)$$

Where K2 is the rate of second-order sorption constant (L/mg .min) and qe is the rate of equilibrium sorption (mg/L).

6.2. Adsorption Rate constant study

The validity of these models can be interpreted by the linear plots of log (qe-qt) vs (t) for Lagergreen equation, and platting (t/qt) vs (t) for pseudo second order. (Fig. (2), (3)). The equations which gave the best fit for the experimental kinetics data was the pseudo second-order model. The (R) values and the rate constant for the adsorption systems under study was calculated form the slopes of the respective plots was showed in table (4).

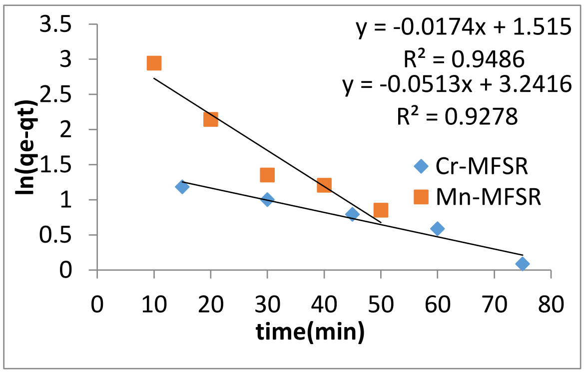


Fig. 2: Kinetics of Cr+6 and Mn+2at 25°C and PH=2, adsorption was calculated using the Lagergreen equation.

6.3. Isotherm Analysis

The isotherm data must be analyzed in order to create an equation that correctly describes the effects and can be used for design purposes [17]. Different isotherms have been established theoretically or empirically, but two of them have been selected in this study, as they are considered the most applicable isotherms in adsorption from Solution Langmuir and Freundlich isotherms[18],[19].

$$\frac{Ce}{Qe} = \frac{1}{Qm\,K} + \frac{Ce}{Qm} \quad \text{Langmuir equation........ (5)}$$

Where, Qe (mg/g) and Ce (mg/L) are the concentration equilibrium adsorbate in solid phase and liquid respectively. Qm is the monolayer capacity of the adsorbent (mol/g) and K is the adsorption constant Fig. (4) Present the Langmuir isotherm of the adsorption of the two metal ions under study.

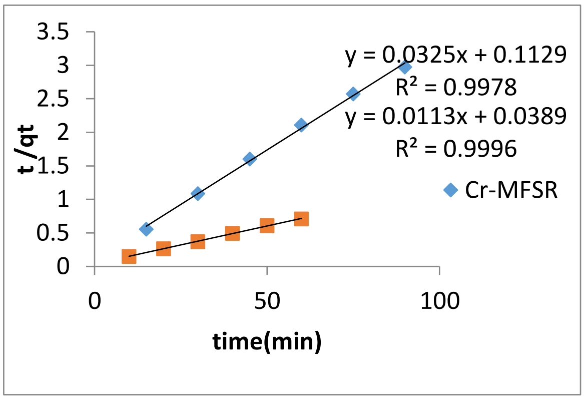


Fig. 3: Kinetics of Cr+6 and Mn+2 at 25 0C and PH=2, adsorption was calculate using the pseudo second- order equation.

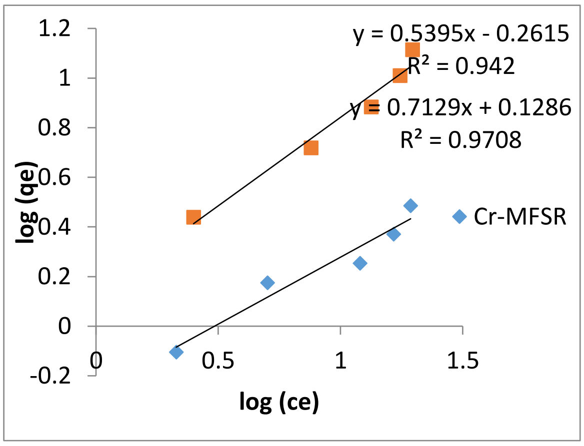


Fig. 4: liner form of Langmuir isotherm of Cr+6 and Mn+2 on (MFSR5%).

The logarithmic form of Freundlich equation is given as follows [20]

$$\log Qe = \log K + \frac{1}{n}\log Ce \quad \text{Freundlich equation...... (6)}$$

Where (K), and (n) are the Freundlich constants and represents the measures of adsorption capacity and intensity of adsorption respectively [21] Fig. (5) Gives isotherm Freundlich for the removal of Cr+6 and Mn+2 from Solution by (SRMF 5%) composite. The application of the two parameters of isothermal models for the current data is seen in Table (5) as follows: Freundlich (Fig. 4)>Langmuir (Fig. 5)

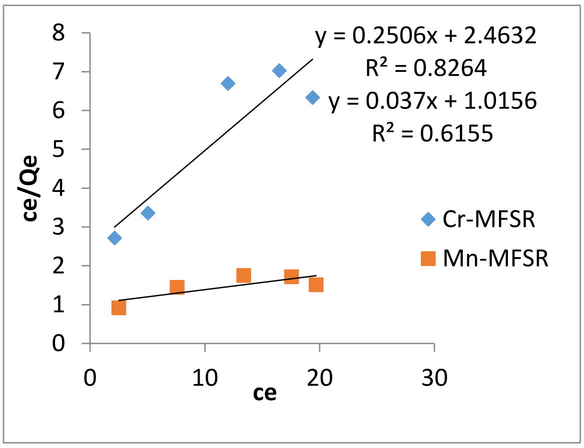


Fig. 5: linearized Freundlich adsorption isotherms of Cr+6 and Mn+2on (MFSR5%).

6.4. Effect of pH

The solution pH values ranged between (2) and (7). From Figure (6) it is clear that the PH plays a significant part in the adsorption of Cr+6 and Mn+2 from aqueous solution using 0.5g (MFSR 5%) composite and 50,100 ppm Metal ions solution at 25°C. The result showed the maximal adsorption of (Cr+6) and (Mu+2) occurred at (pH=2) and decreased as pH increased. The pH of prepared Cr+6 and Mn+2 solutions was standardized to pH=2 in this study. Due to the electrostatic attraction between negative ions, the adsorption of metal ions Cr+6 and Mn+ 2 on the surface of the (MFSR 5%) composite material was studied. This is because the negative ions exist in the form of (Cr2O7-2) and (MnO2-2) in the solution. Each has positive charges of functional amino groups, these charges are present on the surface of the adsorbent in protonated form, and the result has been approved and a few researchers [22],[23], structure (1).

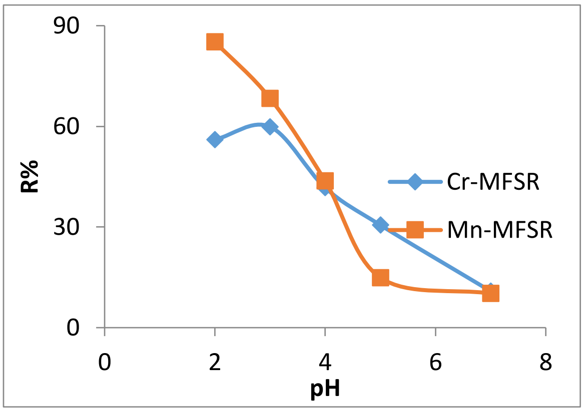
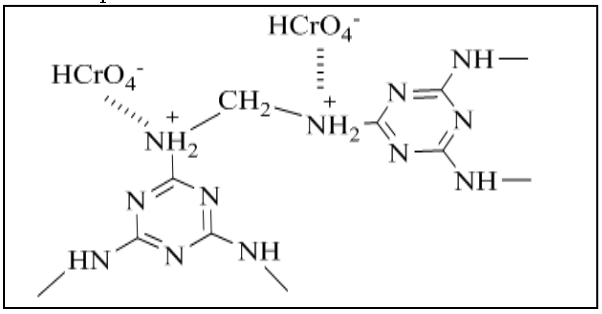


Fig.6: Effect of pH in adsorption uptake of Cr+6 and Mu+2on (MFSR 5%) composite at 25°C.

Table (6) shows the data concerning the amount of the removal efficiencies (R) of (Cr+6) and (Mn+2) according to equation (2) on (MFSR 5%) composite at different pH values.



Structure 1: Adsorption suggested Mechanism of metal ions on (MFSR5%) Composite.

6.4. Effect of temperature.

Both the Cr and Mn metal ions were adsorbed in the range of concentrations (10-50 ppm) to Cr+6 ion and (30-150 ppm) Mn+2 ions respectively, at a fixed pH of 2.0, and the temperatures 25, 35, 45°C Figure (7) and (8). The results showed an increase in the amount of metal ions adsorbed (MFSR5%) with decreasing temperature [24], hence the adsorption process appeared exothermic process. This could be interpreted as result due to an increase with temperature will increase in the kinetic energy of the adsorbed ions and thus their separation from the surface [25].

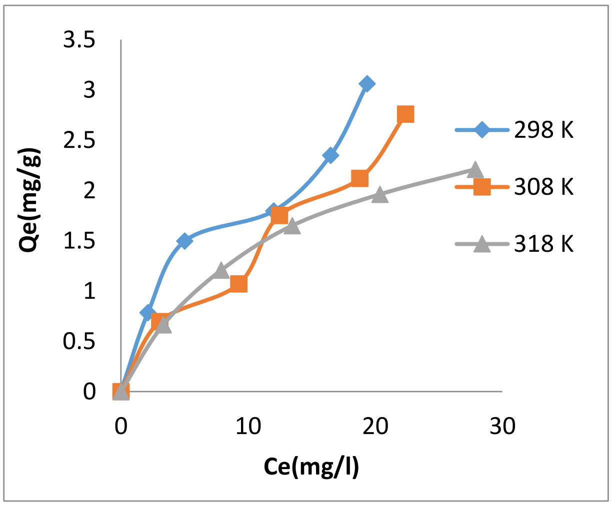


Fig.1: Adsorption isotherms of Cr^{+6}on (MFSR5%) at pH=2 and different temperature (K).

Temperature helps assess the thermodynamic functions of adsorption mechanism (Δ H, ΔS, ΔG) on the basis of the equations given in the following literature (Eq 7-9)[26][27].

ΔG=-RT ln k……….. (7)

lnK=(-ΔH)/RT + constant… (8)

ΔG=ΔH-TΔS ………. (9)

(K) Is the equilibrium constant of adsorption at a certain value of concentration equilibrium (Qe/Ce) and C0 =30 ppm (Cr+6) and 60 ppm (Mn+2) that was fixed for all temperatures of study, (R) is 8.314 the constant gas.

Figure (9) and Table (7) shows the thermodynamic fundamental values of removal of (Cr+6) and (Mn+2) on the new syntheses surface. The exothermic adsorption of Mn+2 on (MFSR 5%) is followed by a change in enthalpy. The fact that the entropy change (ΔS) of the ordered constrained adsorption layer has always been less than that of the dissolve solute explains this result, on the other hand the adsorption of the (ΔG) change in free energy of adsorption of the systems under study possess negative values indicating spontaneous adsorption processes. While the positive value of entropy indicates that the adsorbed ions are less regular and more random when they are adsorbed on the adsorbent surface [28].

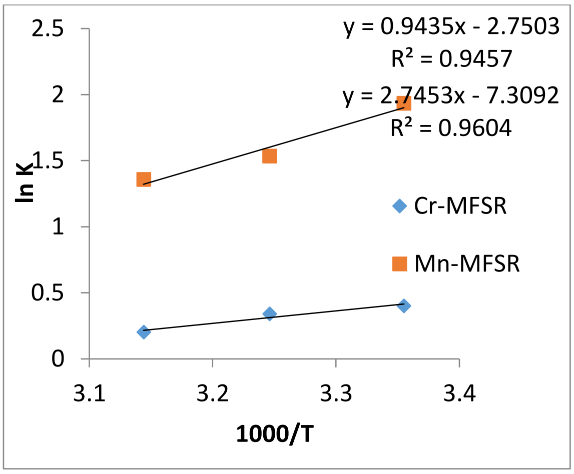


Fig.2: Plot of ln K against corresponding absolute temperature for removal of (Cr^{+6}) and (Mn^{+2}) on (MFSR 5%).

Table 4: The kinetics parameters of adsorption process of Cr^{+6} and Mn^{+2} on (MFSR 5%) composite surface.

Metal ion adsorbed	R^2	q_e (mg/l)	K_1 (min^{-1})	R^2	q_e (mg/l)	$K_{1(}$ l/mg .min)
Cr^{+6}	0.9486	4.549	0.0174	0.9978	30.769	0.00936
Mn^{+2}	0.9278	25.570	0.0513	0.9996	88.495	0.00328

Table 5: gives the values of Langmuir and Freundlich constants.

Metal ion adsorbed	Langmuir isotherm			Freundlich isotherm		
	K	Q_m (mol/g)	R^2	K_f	n	R^2
Cr^{+6}	0.10173	3.9904	0.8264	1.8535	0.5476	0.9420
Mn^{+2}	0.03643	27.027	0.6155	1.344	1.4027	0.9708

Table 6: Amounts of removal efficiency values (Cr) and (Mn) by (MFSR 5%) surface at 250C from solutions of different pH values.

pH	R% Cr^{+6}	R% Mn^{+2}
2	56.05	85.17
3	59.87	68.36
4	41.71	43.72
6	30.58	14.91
7	10.87	10.19

Table 7: Values of thermodynamic functions of adsorption process of (Cr+6) and (Mn+2) ions on (MFSR 5%) at 25 0C.

Metal ions	ΔH KJ.mol^{-1}	ΔG KJ.mol^{-1}	ΔS J.mol^{-1}.K^{-1}
Cr^{+6}	-7.844	-0.996	22.979
Mn^{+2}	-22.82	-4.7916	-60.511

7. Characterization of Adsorbent:

FTIR of the SR and MFSR 5 % specimen characterization reveals many different peaks. In the area of 3412cm-1, the N-H band was seen along with other peaks in the region (1545cm-1) and -NH Sections (1560 cm-1) as seen in Figures (1) and (2). (N-H bend). At 1618 cm-1 there is a band for C = N. The C-N stretching of bands in the region 1338-1137 cm-1. And the creation of a new high peak at 2360 cm-1 is consistent with the extended vibration of the bridged CH2 group which provided a clear evidence of the formation of methylene bridges. The intensity of the peaks, in comparison with the spectrum, also decreases, which coincides with the vibration of methylene bending from 1560 cm-1 and 1487 cm-1 to 1557 cm-1 and 1475 cm-1 (SR) The intensity decrease may be attributed to the extent of crosslinking. The triazine ring bending vibration at 812 cm-1 was found. Figure 2 also illustrates the MFSR FTIR spectrum for comparison. However, even though the load on clay is increased, all peaks (MFSR- 5 %) have the same characteristics as pure MF-polymers. This shows that due to agglomeration or lower dispersion of clay weak bonds exist between clay and polymer matrix. The melamine responded and crossed through during the thermal curing process was confirmed by this FTIR interpretation.

XRD siliceous rock and MFSR composite spectra as seen in Figures (3) and (4), 2 digits = 21,5 , 37,6 and 21,9 in the siliceous composite with very low splitting are shown in Figures (3) and (4). This may be attributed to the resin binding, which indicates that there has been a slight pronounced alteration of its composite formation peak structure and confirmation that siliceous crystal structure has been maintained in composite.

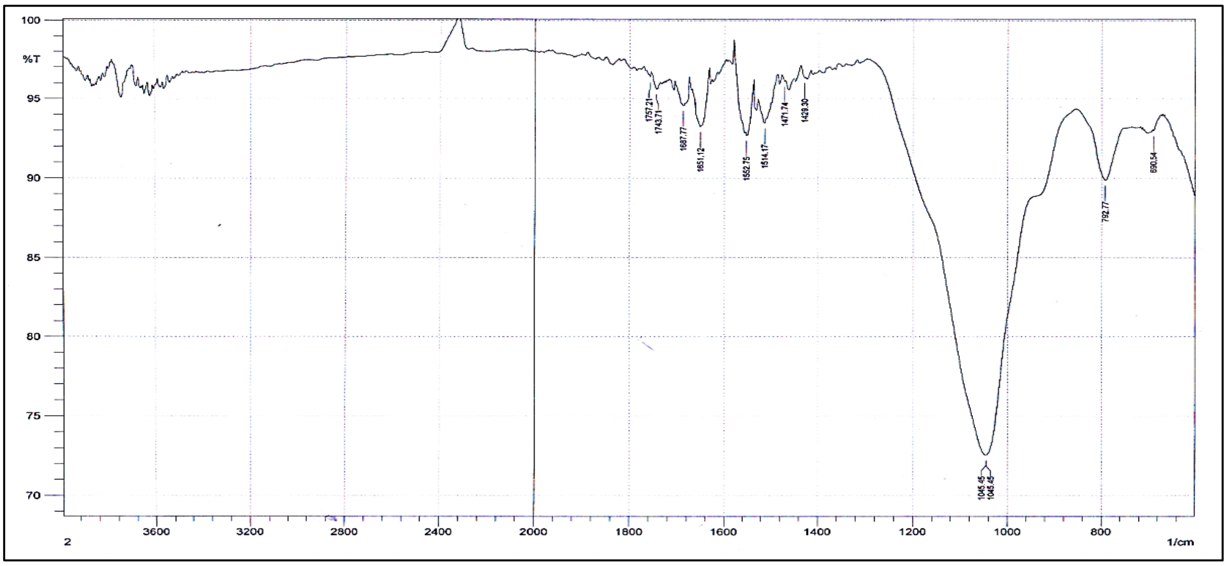


Fig. 3: FT-IR Spectrum of Siliceous Rocks.

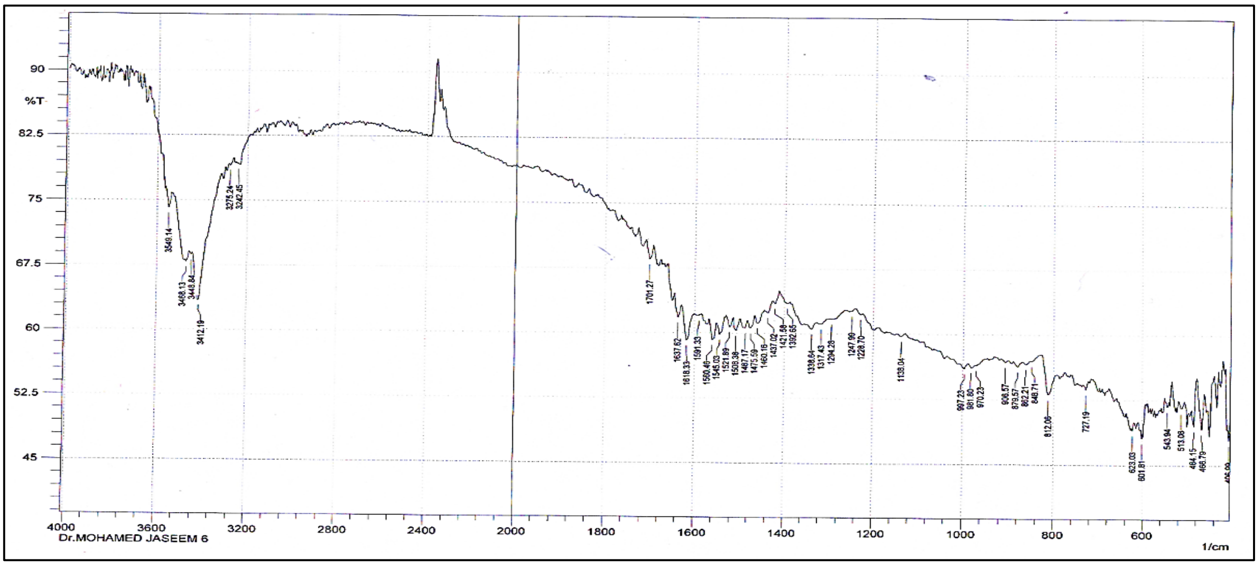


Fig. 4: FT-IR Spectrum of MF- Siliceous Rocks Composite.

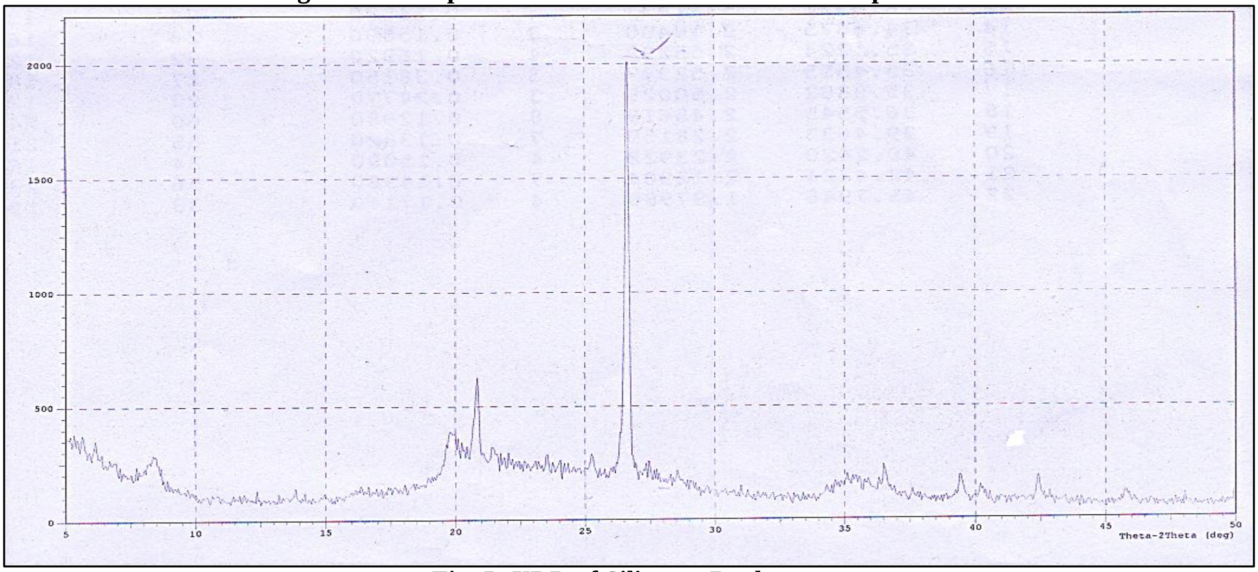


Fig. 5: XRD of Siliceous Rocks.

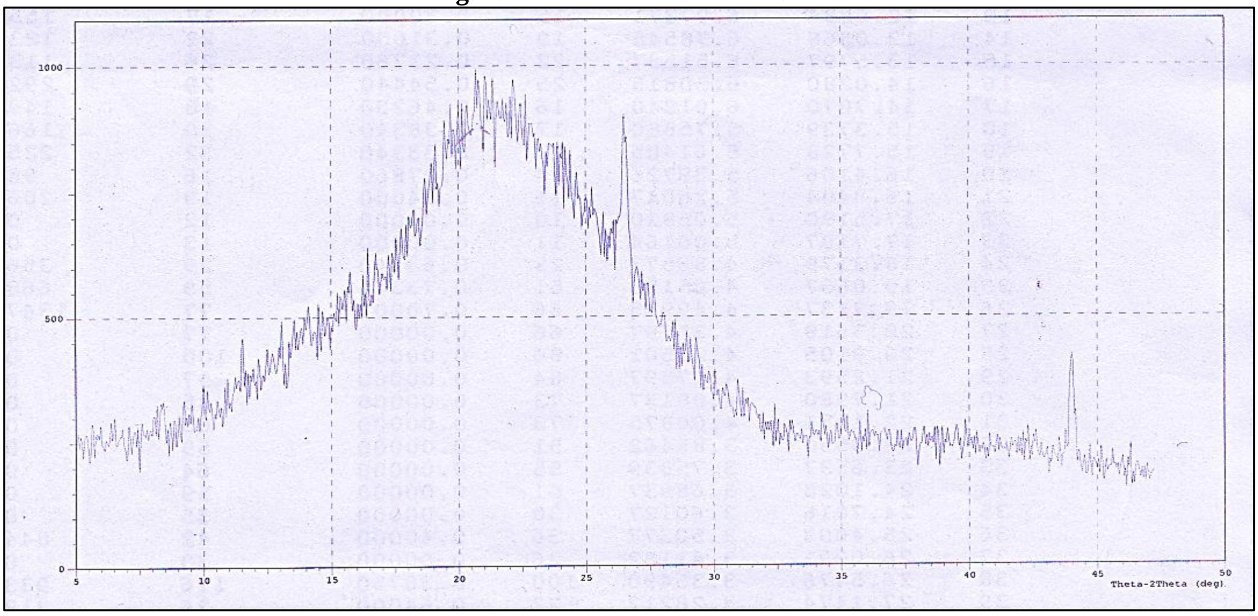


Fig. 6: XRD Spectra of MF- Siliceous Rocks Composite.

8. Comparison of adsorption results synthesized composite with the Natural siliceous rocks.

Additional siliceous rocks in melamine formaldehyde have to be evaluated and checked for adsorption and compared with results on the only natural siliceous rocks in previous research, comparable to melamine formaldehyde, in order to form a new composite (MFSR 5%)[16],[27]. Table (8) shows the related results by the fixed initial concentration (in a separate way) (50ppm) and (100ppm) of each metal ion, and using 0.5g of each adsorbent at affixed temperature, pH, for each metal ion adsorption, a fixed time equilibrium is needed.

Table 7: Comparison of adsorption results synthesized composite with the Natural siliceous rocks.

Adsorbate	R% from the natural siliceous rocks alone	R% from the synthesized (MFSR 5%) composite	R% from the new synthesized composite (KMF 5%)	R% from the new synthesized composite (AMF 5%)
Cr^{+6}	5.06	56.05	61.20	62.020
Mn^{+2}	19.36	85.17	78.22	98.146

As can be seen from the table (8) the removed efficiency of the two metal ions under study from solution are higher by the new (MFSR 5%) than that for the siliceous rocks alone and that result clearly suggest that (MFSR %) as surface is much qualified and more effective. It is possible to do so effectively use to remove heavy metal from solution. Furthermore, the sequence of heavy metal ions for adsorption on siliceous rocks (MFSR 5%) has the sequence Mn+2 > Cr+6.

9. Conclusions

This study clearly suggest the use of (MFSR 5%) composite as a new synthesis adsorbent is much influential, qualified surface. It can be efficiently used to remove heavy metal ions from its aqueous solutions. The various operating parameters during the investigation process show that adsorption processes overall are governed by the contact time, temperature, the pH-adsorbent and the adsorbate concentrations. The experimental data were a good fit in the linear form of Freundlich isotherm. The process of adsorption of the two metal ion under study (MFSR 5%) is spontaneous and exothermic in nature. From the experimental date it is observed that the qualification of the adsorption process for Mn+2 and Cr+6 on (MESR 5%) increased with decreasing pH Values.

10. Conflicts of interest

There are no conflicts to declare.

11. Acknowledgments

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