Preparation and Characterization of a three-component hydrogel composite and study of kinetic and thermodynamic applications of adsorption of some positive and negative dyes from their aqueous solutions

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Abstract. The composite hydrogels (AAC-co-AM)-g-MCC based on microcrystalline cellulose (MCC) and poly(acrylic acid-co-acrylamide) were synthesized by free radical polymerization in an aqueous suspension of (MCC) which use as initiator for the reaction, the structure and surfaces of hydrogels was characterized and analyzed with (FTIR), Xray diffraction spectroscopy (XRD), (FE-SEM) and thermogravimetric analysis (TGA).

The adsorption mechanisms understand the dyes on surface of composite by thermodynamic Study of adsorption process Which include measuring the Enthalpy and Entropy and Gibbs energy, In addition, the dyes adsorption process accorded with pseudo-second-order rate equation, It also showed that adsorption isotherm of the composite Hydrogel is govern by Langmuir and Friendlish equations, The adsorption of dyes is a Physical adsorption, Based on structure analysis and adsorption kinetics of composite, the adsorption process was controlled by the ion-exchange mechanism.

Keyword: Microcrystalline cellulose, Dyes, Adsorption isotherm, Adsorption kinetics Adsorption thermodynamic.

1- Introduction

Pollution control has become an important term in environmental science and management, and without controlling natural pollutants or the pollutants resulting from increased human activities with technological development will lead to environmental degradation, and thus affect human health and living organisms, large quantities of anionic or cationic dyes flow into the environment such as water, and soil [1], consequently, changes occur in the environmental systems as a result of the introduction of these dyes as wastes for industrial and biological activities faster than...
the permissible rate, so the pollution by the dyes has gained a lot of attention due to the damage to the eco-systems, and the dye particles may be highly toxic, allergenic, mutagenic, or carcinogenic to living organisms [2], as they not only pollute the environment but also pass it to food and drink, because some positive dyes interact easily with negative surfaces, or enter through The cell membrane is concentrated in the cytoplasm [3]. Hence, some physical and chemical techniques have contributed to reducing pollution and disposal of dyes, and these techniques include extraction, ion exchange, sedimentation, filtration, reverse osmosis, and fumigation, but these techniques are of limited use due to Its high cost, and adsorption is a technical one the important tasks used in the disposal of pollutants, because it is an effective and fast way to reduce the concentration of dissolved dyes in liquid waste and convert them to the solid phase, adsorption is a surface physiochemical phenomenon used to get rid of pollutants, whether they are heavy metal or dyes with low concentrations that are difficult to remove by other methods [4], the effectiveness of adsorption of adsorbent materials is defined by, a study of thermodynamics, adsorption kinetics and factors affecting adsorption process of dyes on surface composite (AAC-co-AM)-g-MCC, the ability of these adsorbent has been increased On the adsorption by improving the chemical, physical and mechanical properties and the ability to swelling using the graft Polymerization and cross-linking technique[5], microcrystalline cellulose (MCC) were used in the preparation of the adsorbent surface which is pure natural cellulose after being modified by acid decomposition, Cellulose is an available natural source consisting of a polymer Linear β-D-glucose Linked by β-1,4 glycosidic linkages[6].

2- Experimental section

2-1 Chemicals and Materials

It was gotten microcrystalline cellulose (MCC), Acryl amide (AAM), Acrylic acid (AAC), brilliant cresyl blue (BCB), methyl orange (MO) by (Himedia, India), Potassium Persulfate (KPS) by (merck, Germany), N,N'-Methylene-bis-acrylamide (MBA) ware supplied by (Fluka, Germany), Sodium chloride was obtained from (Alpha Chemika), Sodium Hydroxide and Hydrocholric acid were supplied by (Fluka, Germany), The chemical structures of BCB,MO dyes are shown in fig 1:

![Chemical structures of dyes](image)

Fig 1, the chemical structures of dyes, BCB (a), MO (b).

2-2 Preparation of (AAC-co-AM)-g-MCC hydrogels

The hydrogel was prepared by MCC (1.5 g) is dissolved in 30mL deionized water by magnetic stirring (150 rmp) for 15 min in a 250mL three-lines flask equipped with the reflux condenser, and a thermometer, and the nitrogen line With
stirring at 50 °C, KPS (0.3 g) was added into the solution MCC to beget hydroxyl radicals, and AAC (9 mL), AM (0.3 g), MBA (0.05 g) was slowly added into solution MCC with continuous stirring for (5 min). After that mixture put in a water bath at 50°C for 2 h to complete the polymerization reaction as shown in scheme 2, the resulting samples were washed excessively with deionized water To get rid of unreacted parts and unreacted reagents, and then dried in an oven at 60 °C under the reduced pressure For a period of 48 h, The dried samples were grinding and screened to for further analysis.

scheme. 2. Reaction scheme for synthesis of the adsorbent surface (AAC-co-AM)-g-MCC

2-3 Adsorption Isotherm
Batch adsorption experiments of BCB, MO dyes by (AAC-co-AM)-g-MCC were studied at 15°C by adding 10 ml dyes solution to 100 mL conical flasks containing 0.05 mg from hydrogel. The conical flasks were sealed and put it in oscillator (agitation speed 150 rpm) at pH 7, the contact time at adsorption equilibrium is 90 min, the separation of the solutions by the centrifuge for 15 min at 6000 rpm the residual concentration of dyes in the flasks was measured by UV-Visible Spectroscopy (UV-1800, Shimadzu).

The adsorption capacity of the hydrogels (qe, mg/g) and the amount of BCB, MO dyes adsorbed at time t (qt, mg/g) were determined at equilibrium by the following equations [7]:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

(1)

\[
q_t = \frac{(C_0 - C_t)V}{W}
\]

(2)

where qe (mg/g) is the amount adsorbed at equilibrium, qt (mg/g) is the amount adsorbed at specific time, C0 (mg/L) is the initial concentration, Ce(mg/l) is the equilibrium concentration, Ct(mg/l) is the concentrations of dyes solution at the time t (h), V (ml) is the volume of dyes solution, W (mg) is the Weight of hydrogels.

2-4 Effect of pH

The solution preparation were with a pH from (2-12), addition (10ml) of BCB, MO dyes concentration of (200,50) mg/l Respectively, on 0.05g of composite for 90 min, we then separate the solutions by centrifuge and extract the sample by micro syringe and measure amount of dyes adsorbed by using UV-VIS Spectrum.

2-5 Effect of Temperature

To study effect temperature on the adsorption of Poly (AAC-co-AM)-g-MCC, multiple concentrations of BCB dye (10-700) mg/l was prepared, and (5-70) mg/l of MO dye, at same conditions (pressure, dye volume, the adsorption surface) all experiments, the dyes solution was placed in a shaker for 90 min in different temperature (10,15,20,25), after separated the solutions of dyes by centrifuge the concentration was measured by UV-VIS spectrum.

2-6 Effect of Ionic Strength

The effect of some salts (KCl, CaCO3 and NaCl) on adsorption is studied by adding different weights (0.001 - 0.2)g of these salts to 10 ml of dyes solutions, was placed in the shaker for 90 min, and measured the residual concentration of dyes by UV-VIS spectrum, after the solution was extracted by micro syringe and separated by centrifuge (600rpm) for 15 min.

3. Results and discussion

3.1. Characterization

The several functional groups in the composite hydrogel were measured with FTIR as shown in Fig 3, The FTIR spectrum of composite showed typical characteristic peaks, the absorption Broad band around 3353-2700 cm\(^{-1}\) were attributed to O-H groups overlapped with N-H groups, and peak at 2901 cm\(^{-1}\) was
related to C-H stretching vibrations, Additional peaks at 1431 cm\(^{-1}\) and 1060 cm\(^{-1}\) correspond to the bending vibrations of -CH\(_2\) groups and C-O-C stretching vibration in the structure MCC [8], additionally a peak at 1563 cm\(^{-1}\) was related stretching of C-N bonds, and peak at 1705 cm\(^{-1}\) was attributed to the stretching of carbonyl group (C=O) from acrylic acid and polyacrylamide and crosslink agent (MBA), and the weakened band at 1230 cm\(^{-1}\) of C-O groups [9].

fig 3, also shows the FT-IR spectroscopy of composite after the adsorption of BCB dye and shows the shifted of some distinct peaks and appear strong peak at 1000 cm\(^{-1}\) due to the overlapped stretching vibrations of the C-N and C-O bonds, and the peaks in range 1400-1600 cm\(^{-1}\) related to the C = C bond in the aromatic ring of the dye, the carbonyl group (C=O) peaks of the compounds are weak due to the hydrogenic bond between the functional groups of surface and dye Molecules, and this indicates adsorption of the dye on surface of composite [10].

The FT-IR spectrum of MO dye adsorbed on the prepared surface is shown in fig 3, absorption peaks at 1475-1600 cm\(^{-1}\) related to C = C in Aromatics ring in MO dye, and peak at 1115 cm\(^{-1}\) attributed to S = O group in MO dye, and the broad band in a range of 2700-3600 cm\(^{-1}\) which is due to overlapped of the stretching vibrations of the N-H, O-H bonds from the composite with C-H aromatic of the MO dye [11].

Fig 3, FT-IR spectrum of composite before and after adsorbed BCB, MO dyes.

The crystalline properties of composite (AAC-co-AM)-g-MCC were studied by XRD analysis and the XRD spectra showed diffraction peaks at (20.2, 21.11, 19.52) \(\text{A}^0\). The broad beam in Fig 4 which falls within the range (10-25) deg indicates The crosslinked chemical structure of the hydrogel is of amorphous nature, and the broad beam of the composite which is at \(\theta_0 = 21.11\) at the interface distance \(d = 4.2 \text{ A}^0\) indicates that the graft polymerization has increased amorphous nature of the composite by grafting microcrystalline cellulose with AAC, AM and this increases the distance between polymeric chain [12].
Thermogravimetric analysis technique was used to study the thermal stability of the prepared composite, the sample were heated under atmosphere with a rate of 10 °C min⁻¹ from 40-900 °C, where heating the (AAC-co-AM)-g-MCC composite a weight loss of up to 3.75 % in the range of 80-220 °C due to the presence of moisture. However heating the composite in the range of 220-351 °C causes 43.59% mass loss which can be due to the pyrolysis That causes the breaking of the chemical bonds inside the polymeric chains consequently a decrease in the degree of polymerization and remove the groups of hydroxyl and carboxyl in the form of CO₂, CO as well as remove the groups of amine and amide, after that, the composite loses 18.14% of its weight within the thermal range (351-640) °C which is due to the thermal breakage of the interlocking polymeric chains of the hydrogel composite [13].

AFM was used to determine the surface topography of the hydrogel, fig 6 shows a three-dimensional image of surface composite (AAC-co-AM)-g-MCC, Table 1 shows that the mean roughness (Ra) and the root mean square roughness (Rq) of the surface. The composite is greater than the coarse coefficients of the gel poly(AAC-co-AM) and this is due to the apparent effect of the microcrystalline cellulose (MCC) that increased the surface roughness [14].

The value is negative of surface skewness (Rsk) it indicates that the dips are more than heights thus the surface is more planar, and the surface kurtosis value.
(Rku) indicates that the surface is bumpy in nature, because of the peak leveling value which is <3 Rku, and the surface is thorny when Rku> 3 [15].

![Fig 6: 3D image of AFM poly(AAC-co-AM) hydrogel(a), and (AAC-co-AM)-g-MCC composite(b).](image)

Table (1): the statistical roughness coefficients of prepared samples

| Amplitude Factors                 | P(AAC-co-AM) | (AAC-co-AM)-g-MCC |
|----------------------------------|--------------|-------------------|
| Mean roughness (Ra)              | 2.3100       | 3.4339            |
| Root mean square roughness (Rq)  | 2.7209       | 3.5000            |
| surface Skewness (Rsk)           | -3.8044      | -2.9663           |
| surface Kurtosis (Rku)           | 7.2268       | 4.9719            |

The field Emission-Scanning Electron Microscopy use to Surface morphology analysis, a Smooth surface was observed of composite as presented in Fig 7(a) with continuous phase but possessing pores Meanwhile [16], Fig 7 (b,c) is the FE-SEM image for composite after adsorption BCB, MO dyes. Compared to Fig 7(a) rougher surface was observed for composite after adsorption, several structures which indicate the BCB,MO particles are observed to be attached on the surface composite due to electrostatic attraction between the oppositely charged for active sites of surface and BCB,MO dyes. The smooth surface of composite could no longer be observed in fig 7(b,c) as it was saturated with BCB,MO particles [17].
Fig 7, FE-SEM image for composite before adsorption(a), after adsorption BCB dye(b), after adsorption MO dye(c).

3.2. Adsorption Experiments

3.2.1. Effect of contact time and initial ion concentration

fig 8(a,b) shwo the effect of contact time on adsorption of BCB,MO dyes by hydrogels. The amount of dyes adsorbed increase quickly and noticeable during the first 20min, then the amount of dyes adsorbed increase gradually until the equilibrium time is reached, was found that the best time for adsorption of MO,BCB dyes is 90 min, the reason rapid increase in the amount of dyes adsorbed at the beginning of the adsorption process is due to There are sufficient effective sites to dyes adsorb at the beginning of the adsorption , then adsorption decreases gradually and becomes more difficult with the decrease in the number of unoccupied active sites, as well due to the repulsive forces between the dyes molecules on the solid phase [18].
3.2.2. Effect of pH on adsorption

Fig 9(a) which shows the amount of BCB dye adsorbed decreases at PH = 2. The reason for the decrease in the amount of BCB dye adsorbed is due to the competition of the positive hydrogen ions with dye molecules to bond with the active site of the absorbent. The functional groups of the absorbent -OH, -COO, are proteinized at low PH, likewise an electrostatic repulsion occurs between the groups of the absorbent (-COOH, -OH, –NH3) and the positive charge of the BCB dye, thus the adsorption decreases, fig 9(a) shows an increase in the amount of BCB dye adsorbed with an increase in PH the solution, this increase in PH leads to the loss of active sites of the proton and its transformation into groups with a negative charge( – COO, -OH), thus the electrostatic attraction between the negative charge of absorbent and positive charge of BCB dye increases[19].

Fig 9(b) shown that the amount of MO dye adsorbed increases with the decrease of PH, betinization process of the groups -NH2, -OH, -COO occurs at low PH and turns into positive groups, therefore, electrostatic attraction increases between these groups and the negative charge of the dye on the sulfonate group (-SO3Na), then the amount of MO adsorbed starts to decrease with increasing pH due to betinization process of functional groups of the adsorbent gradually and turns them into negative groups –COO, -OH, thus electrostatic repulsion occurs between the negative charges of the active sites and the MO dye molecules [120].

Fig 9, Effect of pH on adsorption BCB dye(a), Effect of pH on adsorption MO dye (b)
3.2.3 Effect of temperature and thermodynamic functions

Fig 10(a) shows a decrease the amount of BCB dye adsorbed As temperatures rise, this indicates that adsorption process is exothermic [21], this decrease is due to increase in the solubility of the dye with increasing temperatures, which leads to an increase in the affinity of dissolved dye molecules towards the solvent More than that is the direction the active sites of the adsorbent, thus leads to reduce and dissociatel of the strong correlation between dye molecules adsorbed and the effective sites, then affect negatively on adsorption dye [22].

Fig 10(b) shows a increases the amount of MO dye adsorbed with height temperature this indicates that adsorption process is endothermic, the kinetic energy of the MO dye molecules increases with the high temperature, thus facilitating the diffusion of dye molecules adsorbed within the pores of the hydrogel and this It indicates that the rate of adsorption prevalence in surface pores would contribute to adsorption of the MO dye at high temperatures[23], the endothermic process indicates that the adsorption process is accompanied by action Of absorption [24].

Table 2 shows the values of thermodynamic functions for the adsorption process of BCB ,MO dyes by surface (AAC-co-AM)-g-MCC, the negative value of the Gibbs free energy (ΔG) indicates that adsorption process the dyes is (spontaneous) [25], the value The positive for entropy (ΔS) of BCB,MO dyes indicates that increased degrees freedom of dyes molecules adsorbed on the surface adsorbent than in the liquid phase because the process is accompanied by diffusion [26], the negative enthalpy value (ΔH) indicates that the BCB adsorption process is exothermic, It is a small value that falls within the values of physical adsorption (40 KJ.mol-1)[27], the positive value of enthalpy (ΔH) of the adsorption MO dye this indicates it is The endothermic process, and the value of the (ΔH) indicates that the adsorption process is accompanied by the absorption process this phenomenon is called sorption [28].

Table 2; thermodynamic functions of BCB,MO dyes adsorbed on (AAC-co-AM)-g-MCC

| Composite       | Dyes   | ΔH (kJ.mol⁻¹) | ΔG (kJ.mol⁻¹) | ΔS (J.mol⁻¹.K⁻¹) | Equilibrium Constant (K) |
|-----------------|--------|---------------|---------------|------------------|--------------------------|
| (AAC-co-AM)-g-  | BCB    | -9.2618       | -12.4796      | 10.9821          | 41.95804196             |
3-2-4 Effect ionic strength

Fig 11(a) show decrease in the amount of BCB dye adsorbed with an increase in the concentration of salts, this decrease is due to the effect of competition between The positive BCB dye molecules and positive ions of salts on the active sites, the presence of the electrolyte in the solution causes neutralization of the surface charge of the adsorbent while competing with the dye molecules on surface adsorbent and with increasing ionic strength the adsorption capacity decreases due to the isolation of the surface charges (screening of surface charge) for dye molecules, also, increased concentration of salts increases the solubility of the BCB dye in their aqueous solution[29].

Fig 11(b) shows an increase in the amount of MO dye adsorbed with an increase in the concentration of NaCl, KCl salt, increase concentration of salts lead to a decrease in its solubility MO dye, as amount of dye adsorbed increases as result of the double electric layer formed by the positive ions of salts during contact the solid phase with the liquid phase through the compatibility of charges and this layer reduces the electrostatic repulsion that occurs between the negative charges of the dye and the surface adsorbent [30], Fig 11(b) shows decrease amount of the MO dye adsorbed with an increased concentration of CaCO3 salt this is due to increase in the positive charge Ca+2 lead to a complex formation that unable adsorption with the negative part of the dye [31].

![Fig 11 Effect ionic strength of BCB dye(a), MO dye(b) adsorbed on (AAC-co-AM)-g-MCC.](image)

3.2.5. Adsorption kinetics

The study of adsorption kinetics is important in determining the time of adsorption and its effect on the adsorption efficiency, Fig 12(a,b,c,d) show variation of the adsorption capacity of MO, BCB dyes as a function of time on the surface (AAC-co-AM)-g-MCC, the dynamic model was applied to match the experimental data through the using of liquid-solid interference, in order to determine the kinetic model that is most appropriate for a BCB,MO dyes on the surface (AAC-co-AM)-g-
MCC, The correlation coefficient $R^2$ is indicates in Table 3, the adsorption of BCB,MO dyes Subject to pseudo-second-order Model [32].

Table 3
Kinetic parameters for the adsorption of BCB , MO dyes.

|          | pseudo-first-order | pseudo-second-order |
|----------|--------------------|---------------------|
|          | k1         | qe     | R2       | k2         | qe       |
| BCB      | 0.0291     | 2.381  | 0.6704   | 0.0484     | 39.84    |
| MO       | 0.0084     | 0.111  | 0.4039   | 2.4192     | 7.9744   |

![Graphs](a.png) ![Graphs](b.png) ![Graphs](c.png) ![Graphs](d.png)
3.2.6. Adsorption isotherm

Adsorption isotherms Describe the relationship between the amount of MO, BCB dyes adsorbed on surface of composite (AAC-co-AM)-g-MCC and its concentration in the liquid phase at equilibrium, adsorption isotherm gives important information to understand the mechanism of interference between adsorbate and adsorbent[33], tabl 4 show and according to Gels classification, the adsorption process of the BCB dye is covered Stay with class (L), In this class the dye particles adsorbed are oriented horizontally parallel to the surface layer adsorbent, fig 13(a,b,c) the results in Table 4 showed that Langmuir Isotherm corresponds to the adsorption of BCB dye on the adsorbent better, and this indicates that the surface is a Monolayer of the dye adsorbed on the surface adsorbent and that the active sites are have the same equivalent energy [34], analyzing the results of adsorption the MO dye and according to Giles' classification, it was found that the adsorption of this dye corresponds to the class (S), In this class the direction of dye particles adsorbed is perpendicular to the surface adsorbent, solvent is subjected to intense adsorption on the surface adsorbent, the dye can suffer from a severe diffusion on the surface adsorbent, through correlation coefficient $R^2$ it was found that Freundlish isotherm in fig 14(a,b,c), is more closely matched with the adsorption MO dye on surface adsorbent[35].

### Adsorption isotherms for the adsorption of BCB, MO dyes

| Dye | Langmuir | Freundlich | Temkin |
|-----|----------|------------|--------|
|     | KL | qm | R2 | KF | n | R2 |
| BCB | 0.4827 | 142.8571 | 0.974 | 28.8735 | 1.4958 | 0.865 |
|     | 5.3062 | 27.897 | 0.96 | | | |
| MO  | 0.0340 | 31.1526 | 0.9022 | 2.1252 | 1.9040 | 0.9233 |
|     | 1.8749 | 2.6577 | 0.8409 | | | |

Fig 12, pseudo-first-order (a). pseudo-second-order (b) of BCB, pseudo-first-order(c), pseudo-second-order of MO(d).
CONCLUSIONS:

Fig 13 Langmuir Isotherm (a), Freundlich Isotherm(b), Temkin Isotherm(c), of BCB dye.

Fig 14 Langmuir Isotherm(a), Freundlish Isotherm(b), Temkin Isotherm(c), of MO dye.

1-The composite MCC-g-(AA-co-AM) were prepared by cross-linking and grafting with acrylamide and acrylic acid, and adsorbed BCB, MO dyes from solutions, under a different conditions.

2- physicochemical characterization of the composite, show confirmed that the grafting of the acrylamide and acrylic acid monomers had occurred efficiently with microcrystalline cellulose.

3- FE-SEM indicated prepared composite surface was smooth, and porous, and that these composite hydrogel displayed high thermal stability.

4- The value of the change in free energy ΔG shows that the adsorption of both dyes is a Spontaneous process.

5- The kinetics and isotherm of adsorption indicate that the carboxylic acid and amide groups attached with the dyes molecules.

6- Adsorption of the dyes on the composite is affected by the pH value.

7- Hydrogel can be used to treat water pollution with dyes.

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