PREPARATION OF MAGNETIC Co/Mn/Zn/NANOFERRITE / ALGINATE POLYMER COMPOSITE BEADS FOR THE EFFICIENT REMOVAL OF SAFRANIN DYE FROM AQUEOUS SOLUTION

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This research article presents the synthesis of magnetic material such as Cobalt doped Mn-Zn ferrites (CMZF) by chemical co-precipitation method. Synthesized Cobalt doped Mn-Zn ferrite was immobilized into sodium alginate polymer blend and fabricated into novel polymer CMZF composite beads. The polymer beads were prepared by ionic polymerization route by using Zn^{2+}. The CMZF alginate bead was characterized with FTIR spectroscopy, SEM and XRD. The synthesized CMZF polymer beads were used for the removal of Safranin dye from aqueous solution by using adsorption technique. The dye removal efficiency was assessed by changing the experimental parameters like concentration, temperature, pH, adsorbent dose and contact time. The Langmuir and Freundlich isotherms were used to describe the suitability of adsorption of dye onto polymeric beads. The kinetic mechanism of the dye uptake process was evaluated by using Pseudo first-order and Pseudo second-order equations. The feasibility and spontaneity of the adsorption process were identified by using the thermodynamic parameters like change in free energy, enthalpy and entropy.

Keywords: CMZF, adsorption, kinetics, sodium alginate, safranin

List of abbreviations
CMZF - Cobalt doped Mn-Zn Ferrites

1. Introduction

Major problem encountered in textile and allied industries is the treatment of wastewater (removal of dye and pigments) before it is discharged into water resources. Most of the dyes in the industrial effluents are non-biodegradable nature, having complex aromatic structure [1]. They are considered to be highly toxic and

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even are carcinogenic and cause mutagenic effects to human beings and animals. If the wastewater is discharged into rivers or streams without proper pretreatment may affect the aquatic life, and also lead to destruction of the environment [2]. Safranin is a water-soluble cationic dye as shown in Fig.1. In histology and cytology, it is used as a biological stain. In the staining technique it is employed to detect cartilage, mucin and mast cell granules. This dye is commonly used for dyeing bast fibers, tannin, cotton, leather, wool, silk and paper. Safranin dye in water may affect the skin, digestive and respiratory systems of the humans [3]. The presence of dye color in water bodies reduces transmission of light which affects the biological metabolism process such as photosynthesis [4,5].

Recently the removal of pollutants using nanocomposite materials [6,7] and magnetic nanoparticle as adsorbents is an emerging field of wastewater treatment [8,9]. Several magnetic materials have been used to remove dyes from aqueous solution [10-13]. Oksana et al. [14] studied the removal of various dyes using magnetic nano composite materials.

The magnetic poly (2-hydroxyethylmethacrylate) (mPHEMA) adsorbent tells about the usability for the removal of Al(III) ions from drinking and dialysis water[15]. Jiu-Hua et al [16] investigated the removal of Cd (II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent material. Magnetic adsorbents are mainly used for the removal of heavy metal, oil, dyes, toxic organic compounds, biomolecules and drugs, as well as in a wide variety of catalytic processes. The main advantage of magnetic absorbents in numerous applications is that the adsorbent or catalyst can be easily removed from the reaction medium after adsorption *via* a simple magnet.

In the present work, CMZF nanopowders were synthesized by chemical co-precipitation method and this powder was blended with sodium alginate to form composite beads. The FTIR, SEM and XRD were used for the analytical characterization of alginate beads. Removal of Safranin dye using CMZF alginate composite beads has been studied. The effect of adsorbent dose, solution pH, temperature, initial dye concentration, and equilibrium time were studied, and the results were discussed.

2. Materials and Methods

2.1 Preparation of adsorbent

CMZF were synthesized by chemical co-precipitation method. This method generally depends upon the parameters like temperature of the reaction, pH value of the suspension, initial molar concentration etc. [17]. The ultra-fine particles of $Co_{0.5}Mn_{0.25}Zn_{0.25}Fe_2O_4$ were prepared by co-precipitation method using the aqueous solution containing the mixture of $CoCl_2$, $MnCl_2$, $ZnCl_2$ and $FeCl_3$ respectively in an alkaline medium.

The solution mixture of $CoCl_2$, $MnCl_2$, $ZnCl_2$ and $FeCl_3$ in their appropriate stoichiometry (100 ml solution of 0.5 M $CoCl_2$, 100 mL solution of 0.25 M $ZnCl_2$, 100 mL solution of 0.25 M $MnCl_2$ and 100mL solution of 2M $FeCl_3$for the case of $Co_{0.5}Mn_{0.25}Zn_{0.25}Fe_2O_4$ was prepared and set aside at 333 K.

Then the solution mixture was added immediately to the boiling solution of NaOH (0.1 M) about 10 seconds with constant stirring. The nano ferrites were formed as the conversion of metal salts into metal hydroxides, which takes place instantaneously, followed by transformation of metal hydroxides into ferrites. The temperature of the solution was maintained at 358K for an hour.

This time was adequate for the transformation takes place between hydroxides into spinel ferrite because the dehydration process followed by an atomic rearrangement was involved in the transformation of intermediate hydroxide stage into ferrite. The magnetic separation method was used for collecting adequate amount of fine nano particles at this stage. These nano particles were washed with distilled water several times followed by acetone and dried under room temperature.

For synthesizing the nano ferrite particles from the pure chemicals the salts of constituent metals were taken as starting materials (shown in Table 1). All the chemicals used were of analytical grade. Sodium hydroxide (NaOH), a reducing agent was used as a base.

Table 1

Specification of the chemicals used

Compound	***Chemical formula***	***Molar mass(g/mol)***	***Purity***	***Supplier***
NaOH Pellets	NaOH	39.997	>99%	Merck India
Cobalt II chloride	$COCl_2.6H_2O$	237.93	>99%	Merck India
Manganese Chloride	$MnCl_2.4H_2O$	197.91	>99%	Merck India
Zinc Chloride	$ZnCl_2$	136.28	>99%	Merck India
Iron (III) Chloride	$FeCl_3.6H_2O$	162.2	>99%	Merck India
Safranin	$C_{20}H_{19}CIN_4$	350.84	>99%	Merck India

2.2 Preparation of CMZF nanocomposite beads

The polymer composite bead was prepared by ionic polymerization route, in which 100 mL of double distilled water was taken in a 500 mL beaker and boiled to 353K. To this hot water, 1.2 g of sodium alginate powder was added and stirred well for 45 minutes till the solution turns clear and viscous. To this 1.2 g of CMZF nanopowder was added and stirred for 30 minutes. This aqueous solution consisting of alginate and CMZF nanopowder was added into 0.2 mol. kg^{-1} of $ZnCl_2$ solution by drop wise manner. The aqueous drops become gelled into polymeric beads on contact with the $ZnCl_2$ solution. Finally, the polymeric beads were washed several times with distilled water for the removal of excess $ZnCl_2$.

2.3 Adsorbate (Safranin)

Safranin (Fig.1 shows the molecular structure of Safranin) is a cationic dye (chemical formula, $C_{20}H_{19}ClN_4$; Molecular weight of 350.84g mol^{-1}; IUPAC name is 3,7-Diamino-2,8-dimethyl-5-phenylphenazinium chloride) which was supplied by Merck, India and it was used as an adsorbate material. Accurately 1.0 g of safranin dye was dissolved in one liter of distilled water to prepare a stock solution of 1000mL. Then all other concentrations were prepared by diluting the stock solution with appropriate quantity of distilled water to maintain the pH of the stock solution at 5.6.

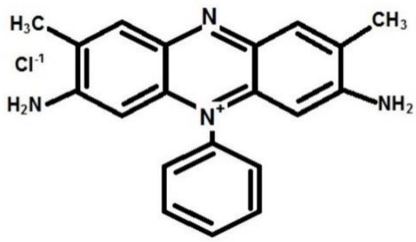


Fig.1. Molecular structure of Safranin

2.4 Analytical Studies

The FTIR analysis was carried out in the frequency range of 4000 to 400cm^{-1} using Perkin Elmer instrument. FTIR study provides information about the surface functional groups that are present in the adsorbent material. The change of physical phase characteristics of adsorption on the adsorbent material was determined using XRD(Shimadzu Japan, XRD Model 6000) analysis. The Scanning Electron Microscope is used to determine the surface porous properties of the adsorbent before and after adsorption of the dye on the CMFZ alginate polymeric bead.

2.5 Kinetic Studies

The adsorption capacity of the adsorbent and the process time are related by the adsorption kinetic studies. The Lagergren's pseudo-first order and second order equations were used to examine the kinetics of Safranin dye adsorption on CMZF alginate polymer beads.

2.5.1 Pseudo first-order model

The pseudo-first order equation of Lagergren is generally expressed as in equation (1).

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303} t \tag{1}$$

where pseudo first order adsorption rate constant is k_1, q_e (mg/g) is the dye solution adsorbed at equilibrium time in total quantity, q_t (mg/g) is the sum of the quantity of dye adsorbed at specific time t. The pseudo-first order rate constant of the process was obtained by plotting a graph between $\log (q_e - q_t)$ vs t (Fig.11). It should be a straight line.

2.5.2 Pseudo second-order model:

The pseudo-second order kinetic rate equation is expressed as equation (2),

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

where q_e (mg/g) is the amount of Safranin adsorbed at equilibrium time, k_2 is the rate constant of the pseudo-second-order adsorption reaction. The plot was drawn between (t/q_t) and t of equation (2) (Fig.12) gives a linear relationship between q_e and k_2.It was determined from the slope and intercept values of the obtained plot.

2.6 Isotherm studies

The adsorption isotherm is a significant arithmetic model in the design of adsorption systems. Adsorption studies explain the adsorption capacity of the adsorbent. This isotherm describes the equilibrium relationships between adsorbent and adsorbate. In this work, the results of the equilibrium isotherms were analyzed using the Langmuir [21] and Freundlich [22] isotherms.

2.6.1 Langmuir Isotherm model

The Langmuir isotherm equation is,

$$\frac{C_e}{q_e} = \frac{1}{q_{m} k_a} + \frac{C_e}{q_m} \tag{3}$$

where C_e is equilibrium concentration, q_e is amount of adsorbate adsorbed per unit mass of CMZF alginate polymer beads at equilibrium, q_m is the theoretical maximum adsorption capacity, and k_a is a Langmuir isotherm constant related to the energy of adsorption.

2.6.2 Freundlich isotherm

The Freundlich isotherm is under the assumption of the relationship between the amounts of solute adsorbed on a given mass of sorbent to the concentration of the solute in the solution at different concentrations. The Freundlich isotherm equation is given by the following expression.

$$q_e = K_F C_e^{1/nF} \tag{4}$$

Here, the adsorption capacity was obtained from the K_F (mg/g) and adsorption intensity was found from *1/n* (L/g). The experimental results were correlated with the linear regression of Langmuir and Freundlich isotherm equations. The results show that Langmuir (Figure. 5c) is the best suited model as compared with Freundlich isotherm equations (Fig.6). This is evident by the correlation coefficient (R^2) value of Langmuir when compared with Freundlich. So the Langmuir isotherm process was the preferred mechanism compared to the Freundlich mechanism [23].

The dimensionless separation factor (R_L) gives the information about the favorability and feasibility of the adsorption process using the equation,

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

Where 'b' is Langmuir constant related to the energy of adsorption (L/mg) and 'C_0' is initial concentration (mg/L).

2.7 Diffusion studies

An intraparticle diffusion parameter K_i was defined by Weber and Morris in 1963 and is given by

$$K_i = \frac{q_t}{t^{0.5}} \tag{6}$$

The intraparticle diffusion-based mechanism was studied for the prediction of the mechanism of adsorption process [25].

3. Results and Discussion

3.1 FTIR studies

FTIR was recorded in the range of 4000–400 cm^{-1} for the prediction of various functional groups that are present in the adsorbent material. The Fig.2 shows the FTIR spectrum safranin dye and Fig.3 shows the FTIR spectrum of CMFZ/alginate beads and CMZF/alginate/Safranin dye beads. For the dotted line of CMFZ/alginate beads shows, the peaks are at 3426.39 cm^{-1}, 2927.2 cm^{-1}, 2365.6

cm^{-1}, 1597.1 cm^{-1},1405.06 cm^{-1}, 1118.15 cm^{-1}, 1033.23 cm^{-1}, 929.03 cm^{-1}, 827.10 cm^{-1}, 617.12 cm^{-1}indicates the presence of N-H group, O-H group, C=C group, C-H and C=O group. The peak obtained at 3426cm^{-1} reveals the presence of symmetric and asymmetric stretching vibration of O-H group [18] and the peaks 2924cm^{-1} and 2855 cm^{-1} show the presence of C-H symmetric or asymmetric stretching vibrations [19].

In the case of dye loaded CMFZ/sodium alginate beads (solid line)indicates the deviations or shifting or reduction in the peak position at 3973.66cm^{-1},3879.45cm^{-1},3759.60 cm^{-1},3691.15 cm^{-1},3426.94 cm^{-1},2924.89cm^{-1},2855.13cm^{-1}, 2373.35cm^{-1}, 2339.45cm^{-1}, 2202.36cm^{-1}, 2144.27cm^{-1}, 1597.27cm^{-1}, 1405.10cm^{-1}, 1338.02cm^{-1}, 1118.65cm^{-1}, 1025.90cm^{-1}, 927.92cm^{-1}, 829.57cm^{-1}, 701.58cm^{-1}, 615.90 cm^{-1}, 466.55cm^{-1}. The deviation in the peaks of Safranin, confirms the adsorption of safranin dye on the surface functional groups of the CMZF/alginate polymer beads.

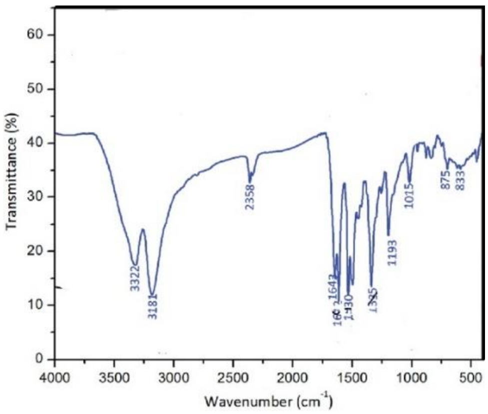


Fig.2. FTIR spectrum of Safranin dye

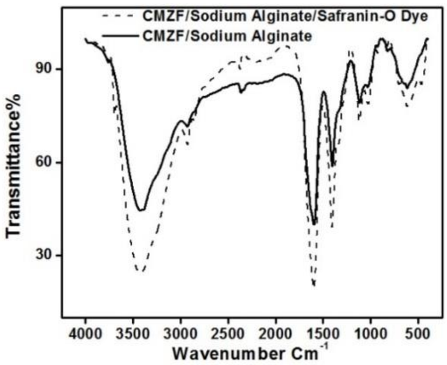


Fig.3. FTIR spectrum of CMZF/ alginate and CMZF/alginate/Safranin dye

3.2 XRD studies

Fig.4. shows the XRD pattern image for CMZF/alginate and CMZF/alginate/Safranin dye. On comparing both the peaks, there is no remarkable or additional peaks were seen.

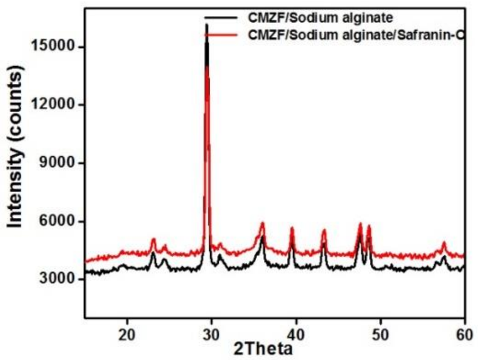


Fig.4. XRD of CMZF/ Sodium alginate and CMZF/ alginate/Safranin dye

The broadening of peaks shows that the polymer beads are amorphous in nature, which indicates the good absorption of dye molecule as compared with the crystalline substance.

3.3 SEM studies

Distribution of the dye on the polymer bead and the shape and size of the particle can be determined using SEM analysis. Scanning electron micrograph of magnetic nanoparticle before and after adsorption of dye is shown in Fig.5 and 6. It shows that before adsorption there are more number of pores and rough surface was seen. After adsorption this was altered to smooth and the surface was uniform without any pores. This indicates that dye molecule completely occupied the entire surface of CMZF alginate polymer beads. This was an evident for the adsorption of dye on the beads.

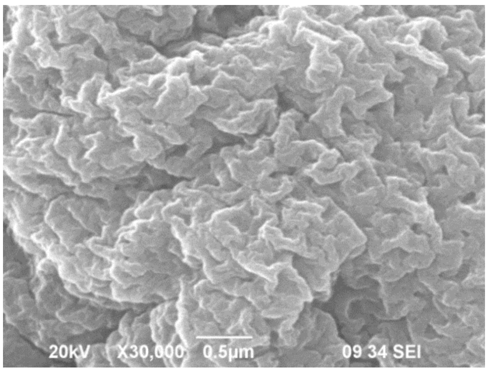
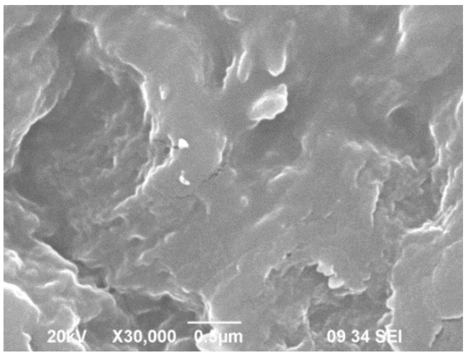


Fig. 5. SEM images of CMZF/alginate
``````````(before absorption of dye)``````




```````````````` Fig. 6. CMZF/alginate/Safranin dye
`(after absorption of dye)

### 3.4 Effect of operational parameters on the dye removal

#### 3.4.1 Effect of pH on dye absorption process

The impact of pH on the experimental solution plays a vital role in the adsorption process. The effect of different pH values for the removal of Safranin is shown in Fig.7. The absorption capacity of safranin dye on CMZF alginate beads was found to increase from pH 2 to pH 5 then decreases up to pH 11. The maximum dye removal efficiency (98%) was obtained at the pH of 5, so it was chosen as the optimum pH for the removal of Safranin dye by CMZF alginate polymer beads. The dye removal efficacy was very high at optimum pH value, this is due to the positively charged dye ions in the aqueous solution might show an enhanced electrostatic force of attraction to CMZF alginate polymer beads, therefore the surface charges on the adsorbents are negative at about the optimum pH values.

At lower pH values the CMZF alginate bead surface may attain positive charge owing to the creation of $H_3O^+$ ions. This offering a competition among the positive ions and positively charged surface sitethat is likely to reduce the dye adsorption proficiency of the CMZF alginate beads. With increase in pH value the alginate bead surface is found to attain negatively charged surface sites due to the ionization of the functional groups and electrostatic forces of attraction, thereby increasing its dye uptake capacity.

At higher pH values, the dye undergoes protonation, thus encouraging an electrostatic force of repulsion between the protonated safranin and positively charged CMZF alginate beads sites resulting in diminished adsorption ability was found then the optimum value.

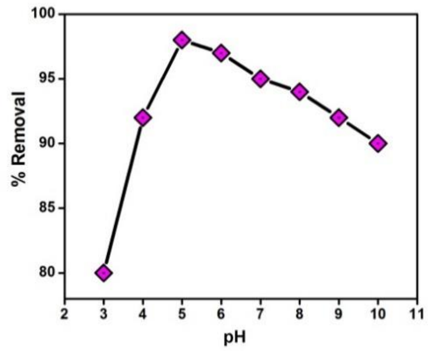



Fig. 7. Effect of pH on the removal of Safranin dye

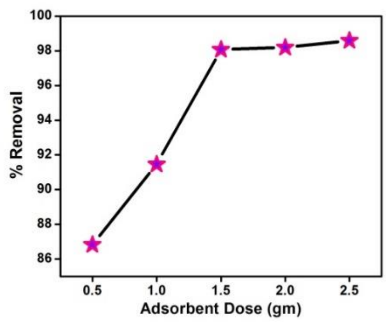



Fig. 8. Effect of dosage on the removal of Safranin dye

#### 3.4.2 Effect of adsorbent dose

The dosage of the adsorbent in the removal of Safranin is shown in Fig.8. The dosage of the adsorbent increases, the rate of adsorption also increases, this is due to the availability of adsorbent sites that enhances better adsorption of the dye molecules. The removal of dye was evaluated using various quantities of adsorbent from 0.5g to 2.0 g with the variation of 0.25 g. From the figure it is evident that 1.5g of absorbent dose gives 98% removal of Safranin dye compared to other dosages. This phenomenon can be described on the basis of the larger surface area of the adsorbent as well as availability of large number of active sites on the CMZF alginate surface. The higher adsorbent dosage with lower rate of adsorption indicates, the accumulation of adsorbent cites or overlapping with other sites.

### 3.4.3 Effect of contact time of an absorbent dose with dye solution

Figure 9, shows the contact time intervals on the adsorption of Safranin dye on CMZF alginate polymer beads. The contact time is increased from 10 minutes to 90 minutes. From the figure, it is seen that as contact time increases the equilibrium adsorption percent also increases and approaches the equilibrium time after 50 minutes. Thus 60 minutes (1 hour) was acknowledged as optimal time for adsorption of Safranin on CMZF alginate polymer beads. This indicates the monolayer formation of the adsorbate molecules at the adsorbent surface. At equilibrium condition the entire surface sites are fully occupied by the dye molecule which leads to maximum adsorption. Further increase in contact time did not show any increase in absorption. This indicates that as contact time increases the active sites are unavailable in the adsorbent surface.

### 3.4.4 Effect of temperature on absorbent

The effect of temperature is an important operational parameter in the adsorption studies. Hence the effect of temperature on the removal of Safranin was investigated and it is shown in Fig.10 at various temperatures ranges from 30$^{o}$C to 70$^{o}$C with the increment of 10$^{o}$C range. The figure shows that 30$^{o}$C is the optimum temperature for the effective adsorption. The adsorption decreases with increase in temperature indicates high temperature enhances the desorption process between the adsorbate and adsorbent rather than adsorption.

Al-qodah Z [20] reported that any alteration in the temperature will vary the equilibrium ability of the adsorbent at the adsorption process and the enhanced rate of intraparticle diffusion of the sorbate. The decrease in adsorption process with increase in temperature shows that it is exothermic adsorption.

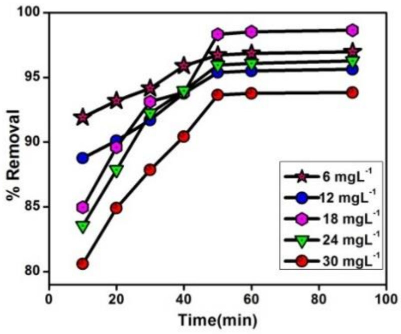



Fig. 9. Effect of contact time on the removal removal of of Safranin dye

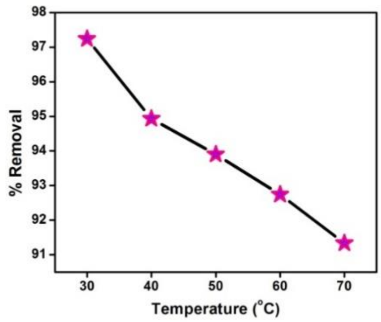



Fig. 10. Effect of temperature on the Safranin dye

### 3.5 Pseudo first-order and second order models

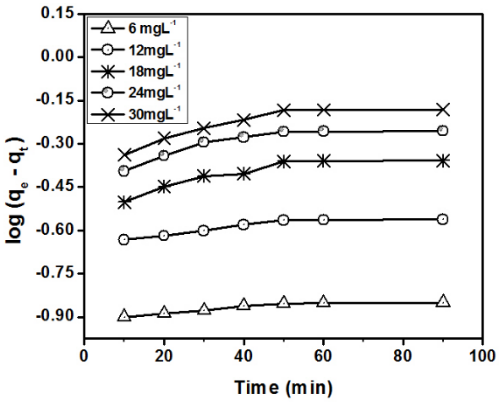



Fig. 11. Pseudo-first order plot for the removal of for the Safranin dye.

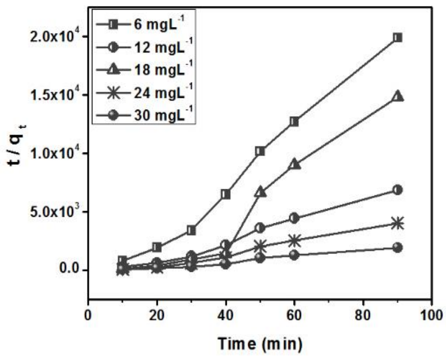



Fig. 12. Pseudo-second order plot removal of Safranin dye.

From the experimental and correlation results it is concluded that the reaction rate of the entire process depends on the concentration factor (pseudo-first order) (Fig. 11) and also the rate of the process governed on both concentration and time (pseudo-second order) (Fig. 12). Therefore, the rate-determining step specifies the adsorption of dyes was chemisorption rather than physisorption, which involves attractive forces of electrons between the adsorbent and adsorbate molecules.

### 3.5.2 Langmuir and Freundlich isotherm

The Langmuir isotherm for the saffranin dye gives a correlation co-efficient ($r^2$) value of 0.9981 (Table 2 & Fig. 13) at 30 mg/L. The Freundlich isotherm (Table 2 and Fig. 14) indicates a correlation coefficient ($r^2$) value of 0.9785 and by comparing the values it is accept that the Langmuir shows a better correlation coefficient value than other.

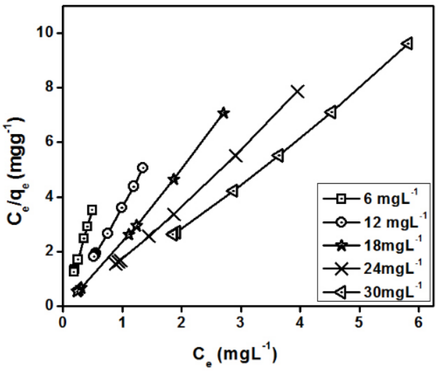



Fig.13. Langmuir isotherm for the adsorption adsorption of Safranin dye.

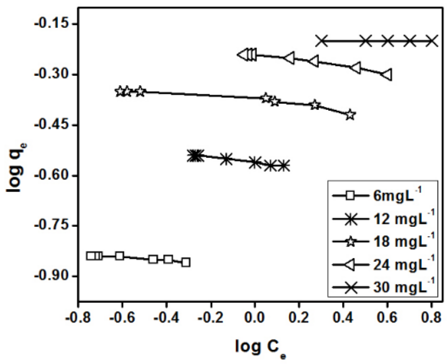



Fig.14. Freundlich isotherm for the Safranin dye.

This means that the monolayer adsorption as proposed by Langmuir was the most suitable isotherm for the removal of Saffranin dye than the multilayer adsorption. The experimentally calculated values of Freundlich and Langmuir isotherm parameters were presented in Table 2.

If the value of dimensionless factor, $R_L$ =0; the isotherm is irreversible. The isotherm is favorable for ($0 < R_L < 1$), linear for ($R_L$=1) and unfavorable for ($R_L$>1) [24]. Fig.15 reveals that the obtained experimental results of $R_L$ values lie in the range of 0–1 for CMZF /alginate adsorbents.

Thereby the adsorption of Safranin dye onto adsorbent material was considered to be a favorable adsorption process. Further the lower values of $R_L$ indicate that there is a strong molecular force of attraction exists between the adsorbent material for the adsorption of Safranin and adsorbate.

*Table 2*

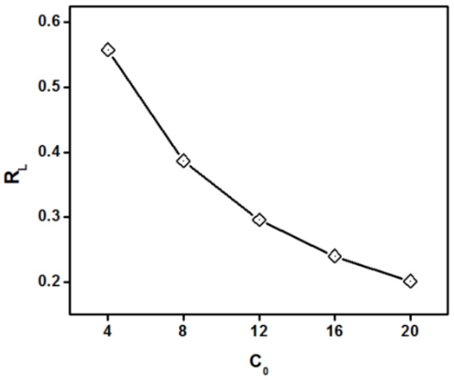
**Isotherm parameters for the adsorption of Safranin dye**

| Isotherm | | Concentration (mg/L) | | | | |
|---|---|---|---|---|---|---|
| | | 6 | 12 | 18 | 24 | 30 |
| Langmuir | $q_m$ (mgg$^{-1}$) | 0.0469 | 0.1063 | 0.1889 | 0.2853 | 0.3635 |
| | $K_a$ (Lmg$^{-1}$) | -3.0121 | -2.1762 | -3.008 | -4.5963 | -2.7748 |
| | $R^2$ | 0.991 | 0.9879 | 0.9899 | 0.9938 | 0.9981 |
| Freundlich | 1/n(L/g) | -0.4128 | -0.3167 | -0.1995 | -0.1309 | -0.1556 |
| | $K_F$(mgg$^{-1}$) | 6.9084 | 6.6743 | 7.2341 | 7.7332 | 8.7832 |
| | $R^2$ | 0.9761 | 0.9597 | 0.939 | 0.9244 | 0.9785 |

### 3.5.3 Intra Particle Diffusion Modeling Studies

The kinetic model delivers inadequate information about the diffusion mechanism in the adsorption process. Therefore the theory of intra particle diffusion model considered as the best approach for the adsorption processes, which shapes that the dye acceptance ability varies correspondingly with $t_{1/2}$ rather than the contact time t and consequently given that an empirically well-designed relationship. The experimental values thus correlated using the plot of $t_{1/2}$ vs $q_t$ .

From the graph (Fig. 16) it is inferred that there are two portions of straight lines are obtained. The first portion indicates that diffusion of Safranin dye onto the CMZF/alginate polymer beads takes place through the external surface of the beads. Here the intraparticle diffusion was rate limiting one, therefore the diffusion of dye molecules on the boundary layer occurs gradually. Whereas the other portion of straight line shows that the intraparticle diffusion process starts in a slow manner because of the lower concentration of dye molecules available in the solution or adsorption process attained equilibrium in the end stage.



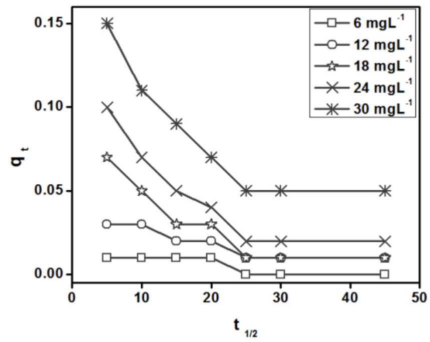




Fig.15. Dimensionless separation factor ($R_L$) for the removal of Safranin dye.

Fig.16. Intra particle diffusion plot for the removal of Safranin dye.

## 4. Conclusion

The magnetic adsorbent material Cobalt doped Mn-Zn ferrite was synthesized by chemical co-precipitation method. Then it was immobilized into sodium alginate polymer blend to fabricate novel polymer composite beads (CMZF). The polymer beads were prepared by ionic polymerization route by using $Zn^{2+}$solution. The FTIR study shows that a change in peak heights and shifted position of peaks confirms that the safranin dye intensely adsorbed on CMZF beads. SEM images display characterized morphological images before and after adsorption that are obvious for the adsorption of the dye molecule on the surface of the polymeric beads. The XRD pattern indicates an amorphous nature of the adsorbent material, which can effectively adsorb the dye. The various adsorption studies were concluded that the optimum dye adsorption found at pH value of 5, dose of adsorbent 1.5 g, agitation time 60 min, and temperature 30°C. From the Freundlich isotherm and Langmuir isotherm correlation results, the Langmuir isotherm process was the applicable mechanism as compared to the Freundlich isotherm. The dimensionless separation factor ($R_L$) values were in between $0 < R_L < 1$, this confirms that the isotherm process was feasible. The analysis of kinetic equations, the pseudo-second order correlation coefficient ($r^2$) results fit well with the experimental values as compared to the pseudo-first order equation. It specifies that the adsorption process follow pseudo second order kinetic equation rather than pseudo-first order equation. Therefore, the synthesized CMZF-alginate polymeric beads are more suitable adsorbent material for the proficient removal of the Safranin dye from an aqueous solution.

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