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# Adsorption Isotherm Performance on Direct red 28 dye by Novel Biomass-based Green Composite

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***Abstract*** – The presence of diverse organic compounds, such as dyes, in wastewater may pose potential environmental hazards. Therefore, it is imperative to remove these harmful substances from the various water resources. In this work, superparamagnetic nanoparticles/pomegranate waste biomass derived green magnetic composite (GMC) was fabricated and characterized using SEM, BET, and Vibrating Sample Magnetometer (VSM). The surface area, total pore volume and average pore diameter were evaluated using BET method. The GMC had a specific surface area of 244.43 $m^2/g$ and saturation magnetization value of 1.53 emu/g. The GMC sorbent was utilized for the removal of direct red 28 (DR28) dye from aqueous solution. Adsorption isotherm studies were also conducted to define the adsorption type. Langmuir and Freundlich model isotherms were employed to study the adsorption phenomena. Isotherms studies further show that the DR28 dye sorption follows the Langmuir model. Monolayer adsorption capacity of the sorbent for DR28 dye was 86.96 mg/g at 328 K. In summary, it can be concluded that the developed composite material in this study could be a promising alternative to the traditional DR28 dye removal methods.

*Keywords – Green Magnetic Composite; Characterization; Adsorption; DR28 Dye; Isotherm*

## I. INTRODUCTION

The negative effects of dyestuffs in wastewater on aquatic organisms and humans have attracted great attention recently. Although water has a self-cleaning feature, it is inevitable that this will take time, considering the amount of polluted wastewater discharged into the aquatic environment. In this context, some remediation methods and techniques have been developed to purify contaminated water and increase its reuse. It is possible to group these techniques into three main processes: physical, chemical and biological. Although each of these processes has advantages and disadvantages, the physical process has an advantage over other processes. Considered from this point, the adsorption process is more widely used in the removal of dyestuffs and other pollutants due to its strong benefits such as ease of application and relatively lower cost [1].

Direct red 28 (DR28) dye is generally used for dyeing cellulose, cotton and lignin due to its ease of use in fabric dyeing and its permanence. Since it has an aromatic ring in its structure that is toxic and difficult to decompose in the environment, wastewater must be treated to remove DR28 dye from the environment before being released into the water body [2].

It is possible to come across many studies in which activated carbon, alumina, clay and many other materials are used as sorbents in the removal of dyes from wastewater. However, the high cost of production and sustainable renewal conditions make these adsorbents expensive materials. For these reasons, many approaches to produce low-cost alternatives have been tried in recent years. In recent years, the development of magnetic composite materials has become a striking phenomenon, with increasing application potential in the removal of colored pollutants. At the same time, combining the properties of organic and inorganic components in a single material has aroused great interest. Magnetic-coated biosorbents can be used in aqueous and gas phase pollution removal processes, and after adsorption processes, the composite adsorbent can be separated from the environment using a simple external magnetic field. This separation process of adsorbent in adsorption is advantageous in terms of ease and rapidity of the method. To our knowledge, there is no study so far on the preparation of magnetic composites using water pomegranate pulp and metal chlorides [3, 4].

In this study, we synthesized green magnetic composite (GMC) by easy chemical co-precipitation method. The prepared composite was used to adsorb direct red 28 (DR28) dye from wastewater by adsorption in batch mode. The structure and chemical properties of this magnetic biocomposite were characterized by some spectroscopic techniques. The isothermal aspects of DR28 dye adsorption have been thoroughly studied. This study can be a model for the development of other novel and efficient sorbents based on biomass and superparamagnetic nanoparticles for other environmental remediation and management applications.

## II. MATERIALS AND METHOD

### *2.1.Materials*

Pomegranate waste biomass was collected from the juice factory in Batman, Turkey. All chemicals were analytical grades (AR) used without purification which were ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (Merck, Germany), sodium hydroxide (NaOH) (Merck, Germany), and manganese (II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) (Merck, Germany), and DR28 dye ($C_{32}H_{22}N_6O_6S_2Na_2$) (Sigma-Aldrich, Germany).

### *2.2. GMC synthesis*

The green magnetic composite (GMC) which was used as the support for the development of the sorbent was prepared by incorporating $Mn^{2+}$ and $Fe^{3+}$ into pomegranate waste biomass pretreated with NaOH via the co-precipitation method as reported in the literature [5]. First, 0.025 mol of manganese (II) chloride and 0.05 mol of ferric chloride were dissolved in 200 mL of distilled water in a beaker at 60 $^{o}$C and stirred overnight. Five g of dry pomegranate waste biomass powder was then added, mixed and stirred for 60 min at room temperature. Subsequently, 7 mL of 5 N NaOH were added under 1 min-stirring to reach pH 11, and the resulting suspension was separated using a magnet and washed several times with deionized water. After that, green magnetic composite was dried at 110 $^{o}$C for 12 h, milled, sieved using a sieve with <1 mm diameter and stored for later use.

### *2.3. Characterization studies*

The characterization studies were carried out using standard protocols. Analytical techniques such as scanning electron microscope (SEM), Brunauer-Emmet-Teller (BET) method and vibrating sample magnetometer (VSM) were used to obtain information about some physicochemical properties of the developed GMC.

### *2.4. Sorption process*

The performance of GMC as sorbent was demonstrated by the adsorption isotherm process of DR28 dye as model in a batch system. 70.00 mg sorbent was added to 50 mL aqueous solution with different initial concentrations (25-340 mg/L) of DR28 dye, different temperatures (298, 308, 318 and 328 K) and at natural solution pH of 6.8. After a certain time, the supernatant was filtered. The concentrations of DR28 were routinely monitored at $\lambda_{max}$= 497 nm using an UV-vis spectrophotometer (Perkin Elmer Lambda 25).

## III. RESULTS AND DISCUSSION

### *3.1. Material characterizations*

The surface morphologies of GMC before and after DR28 dye sorption are given in Fig. 1a and b. As seen in Fig. 1a, the SEM image clearly indicate the flat and irregular shaped structure with porous surface of the synthesized GMC whereas spherically shaped monodispersed $MnFe_2O_4$ nanoparticles are uniformly distributed and finely entrenched in the biowaste network (Fig. 1a). After DR28 sorption process, the surface of GMC is evenly covered with DR28 dye molecules, which confirms its ability to remove this dye [6].

Fig. 2 (a,b) shows the adsorption/desorption isotherms and the results of the analysis of the distribution and pore size. The resulting isotherm corresponds to a combination of type II and type IV according to the I.U.P.A.C. classification. This shape is generally observed in adsorbents with a wide range of pore cracks and pores [7].

Fig. 3 shows the magnetization profile of GMC examined using a magnetometer with a vibrating sample. Since the loops within the limits of measurement accuracy can be considered closed, the obtained the GMC biocomposite can be classified as superparamagnetic material [8].

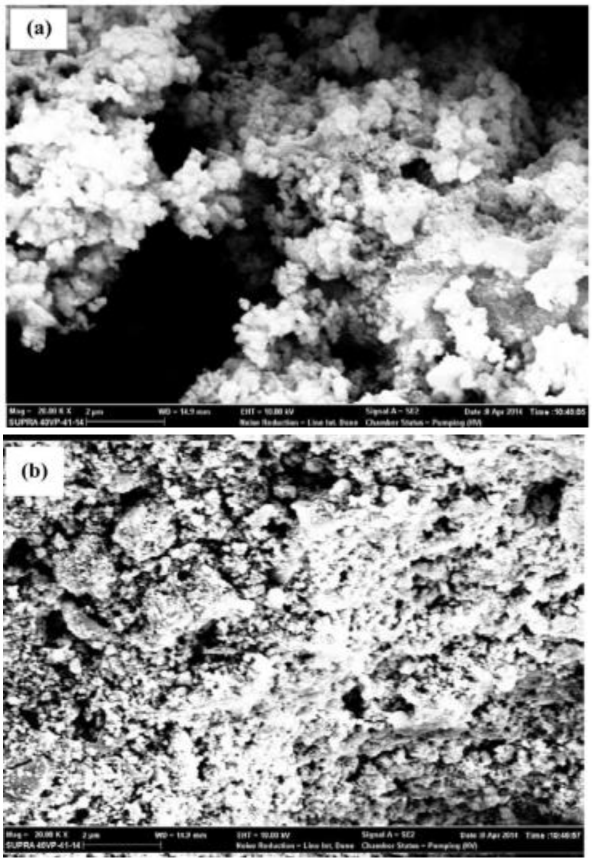



Fig.1. SEM images of (a) GMC, and (b) GMC after DR28 adsorption

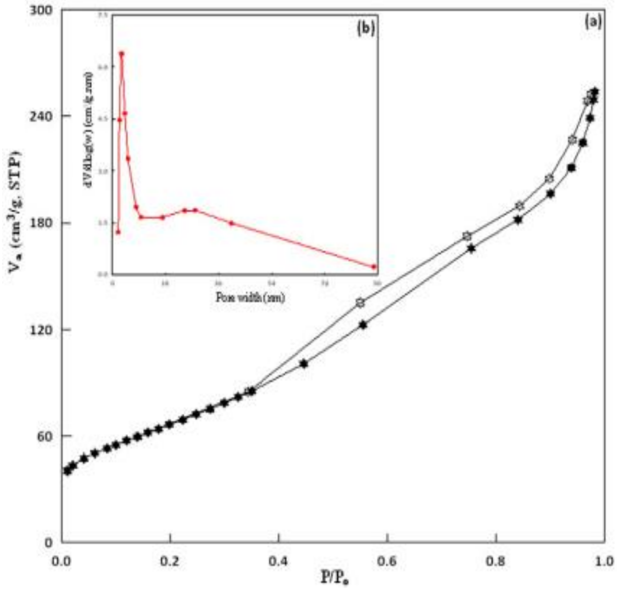



Fig.2. $N_2$ adsorption-desorption isotherm (a) and pore size distribution (b) of GMC sample

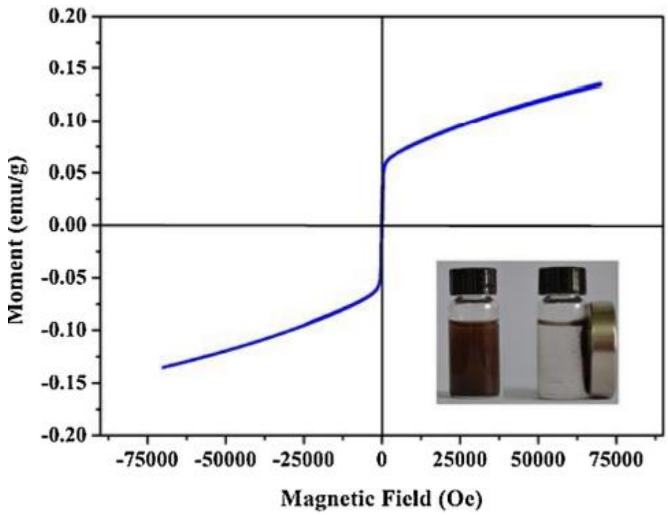
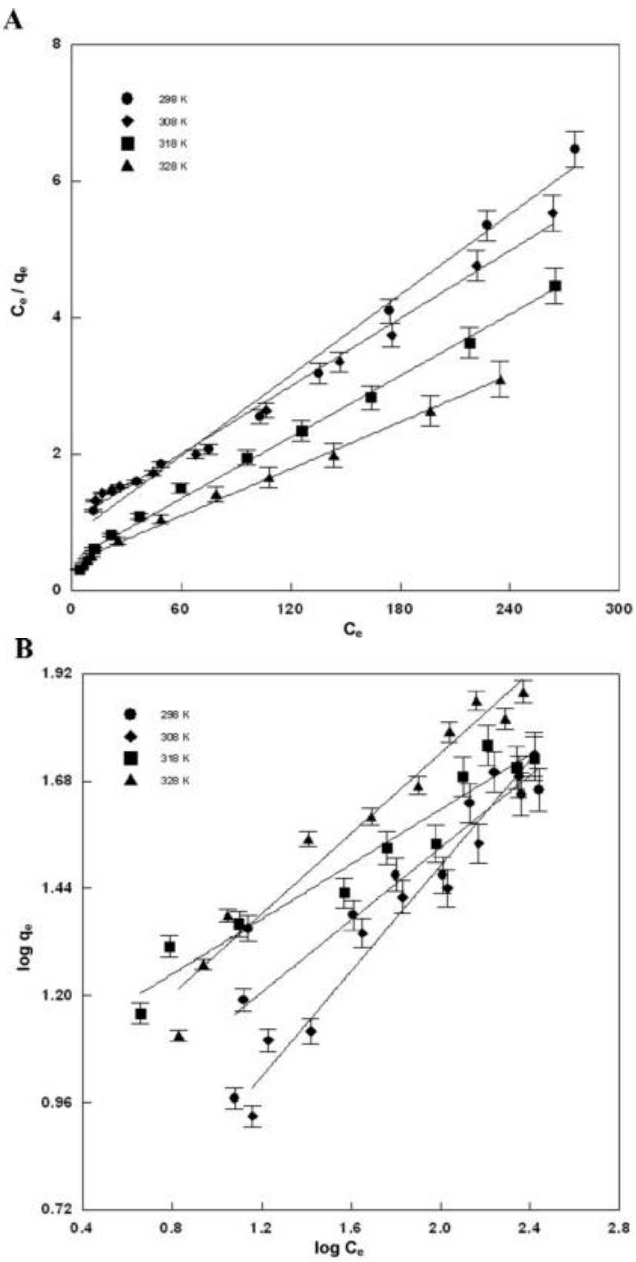



Fig.3. VSM curve of GMC

### *3.2. Adsorption isotherm studies*

Finally, sorption isotherms of DR28 dye removal were investigated. Three isotherm models, i.e., the Langmuir [9], Freundlich [10], and Temkin [11] equations, which are widely used to describe adsorption results at equilibrium, have been tested, and their fitting results obtained using GMC are listed in Table 1 and visualized in Fig. 4 (a-c), respectively. The Freundlich and Temkin models are demonstrated to have lower $R^2$ values than the Langmuir model, demonstrating that the Langmuir model is a superior fit for describing the adsorption behavior of DR28 dye. This finding shows that DR28 dye were adsorbed in monolayer form on the homogenous surface. The GMC possesses a maximum adsorption capability of 86.96 mg/g for

DR28 dye. The current work indicates that the synthesized GMC with a distinct structure and excellent adsorptive characteristics could be employed to remove hazardous anionic dyes from industrial wastewater.



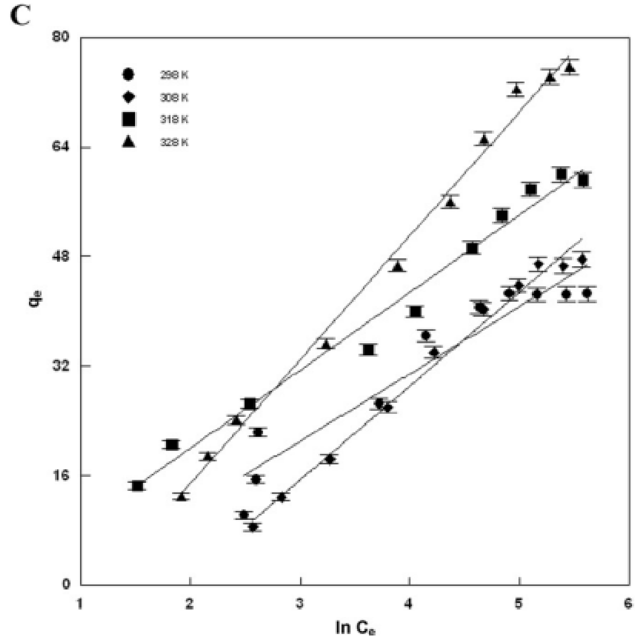




Fig.4. The plots of (a) Langmuir, (b) Freundlich and (c) Temkin isotherm models for DR28 sorption onto GMC

Table.1. Langmuir, Freundlich, and Temkin isotherm models for DR28 adsorption on GMC

| | Temperatures (K) | | | |
|---|---|---|---|---|
| | 298 | 308 | 318 | 328 |
| *Langmuir model* | | | | |
| $q_m$ | 50.76 | 60.61 | 66.67 | 86.96 |
| $b$ | 0.0163 | 0.0247 | 0.0284 | 0.0335 |
| $R_L$ | 0.2347 | 0.2024 | 0.1761 | 0.1493 |
| $R^2$ | 0.9872 | 0.9929 | 0.9944 | 0.9960 |
| *Freundlich model* | | | | |
| $K_F$ | 2.04 | 5.26 | 6.96 | 10.03 |
| $1/n$ | 0.71 | 0.59 | 0.45 | 0.31 |
| $R^2$ | 0.8399 | 0.9645 | 0.9382 | 0.9556 |
| *Temkin model* | | | | |
| $B$ | 9.8175 | 11.351 | 13.714 | 18.089 |
| $A$ | 0.3080 | 0.4241 | 0.7905 | 3.5491 |
| $R^2$ | 0.9118 | 0.9874 | 0.9815 | 0.9927 |

## IV. CONCLUSION

A new magnetic green composite of GMC was successfully designed and applied for the highly efficient removal of DR28 dye from an aquatic environment. The GMC was easily separated and collected from the aqueous solution after adsorption process by external magnetic field. Isotherm data clarified that the monolayer chemisorption was primarily responsible for the adsorption behavior of DR28 dye. The maximal uptake capacity of DR28 was estimated by the Langmuir model to be 86.96 mg/g. The results of the current study reveal that the GMC, which has a distinctive structure and good adsorptive properties, could be utilized to decontaminate water polluted with organic dyes.

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