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Optimization of Different Parameters of the Adsorptive Study of an Antibiotic Rifabutin onto Synthesized Magnetic Nano Composites (MNC)

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Abstract— Adsorption is one of the most extensively used techniques for environmental remediation. In the present study adsorptive study of an antibiotic Rifabutin onto synthesized Magnetic Nano Composites (MNC) has been done. For this purpose effect of different type of parameters such as effect of MNC dose, pH, initial drug concentration, temperature and contact time were studied using a batch kinetic method. It was found that maximum adsorptive efficiency was achieved with the appropriate dose of MNC (1.66 g/L) in the alkaline medium (10.9) in 100 minutes. Various equilibrium adsorption isotherms such as Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich, Haurkins-Jura, Jovanovic and Redlich-Peterson models were applied to describe the isotherm equilibrium and to analyse the experimental data. In the present investigation Langmuir and Dubinin-Radushkevich models has been reported. Langmuir isotherm model describes maximum efficiency of MNC. The values of mean free energy, E, were obtained within the range of 3-6 kJ mol-1 by Dubinin-Radushkevich isotherm model and it was found that the nature of the present process was likely physisorption. The negative value of Gibbs free energy ΔG° indicated that the adsorption process was spontaneous and the positive value of ΔHo revealed the adsorption process was endothermic. The all finding indicate that MNC are very useful and reproducible for the removal of Rifabutin.

Index Terms— Adsorption; Rifabutin; Magnetic Nano Composites (MNC); Kinetics; Isotherms; Diffusion; Thermodynamics.

I. INTRODUCTION

Pharmaceuticals are painstaking as an up-and-coming ecological difficulty because they nonstop enter and persistence to the marine ecology at low or higher concentrations. They expose to environment and generate colouration of natural water, toxicity, mutagenicity, carcinogenicity and causes pollution, eutrophication, and perturbation in aquatic life in eco-system (1-7). Pharmaceuticals have been detected in many water sources like drinking water [8-10], sediments and soil [11,12], tap water, ocean water, ground and surface water [13,14]. They decrease the dissolved oxygen and increase the BOD level to sustain aquatic life. Pharmaceuticals not only affect the aquatic life but can also cause allergic dermatitis and skin irritation to other organisms and human beings. For this reason, it is very necessary to remove these types of contaminants. There are a batch of physical and chemical techniques has been widely used for the removal of these types of organic contaminants from wastewater such as such as coagulation, ozonization, membrane filtration, electrolysis; oxidation, active sludge biochemical processes, bio-degradation etc. These recognized technologies are frequently not capable to decrease pollutant attentiveness sufficiently to a wanted stage with successfully and inexpensively. Every of them has its own qualities and demerits. Adsorption system is well thought-out to be one of the mainly effectual and established physiochemical processes, with potential applications in both water and wastewater treatment. Many factors influence the adsorption process, including contact time, temperature, drug concentration, pH, and adsorbent dose [15]. In the following adsorptive study of Rifabutin has been studied onto developed nanoparticles. The main objectives of this study are:

(i) To study the viability of synthesized nanoparticles as an adsorbent for the removal of pharmaceuticals.
(ii) To evaluate the various parameters affecting adsorption procedure, such as pH, initial concentration, dose of adsorption, contact time, and temperature
(iii) To examine the value of various kinetic models, viz. pseudo-first-order, second-order and intra-particle diffusion models
(iv) To study the applicability of linear and non-linear forms for different isotherm models (Freundlich, Langmuir, and Tempkin).

After conclusion it was found that the developed method is easy, adaptable, and inexpensive due to its simple process, intend, and low price.

ADSORPTION MECHANISM

The first major challenge for adsorption process is collection of the majority expectant types of adsorbent which have efficiency and low cost. The reaction nature depends upon a few parameters connected to the adsorbent, to the solution, pH, and the complex formed. The adsorption process involves the following steps:

(1) Transfer of adsorbate mass molecules towards the solid particle.
(2) Transportation of adsorbate molecules from the particle surface.
(3) After that Solute molecules adsorption on the active sites take place.

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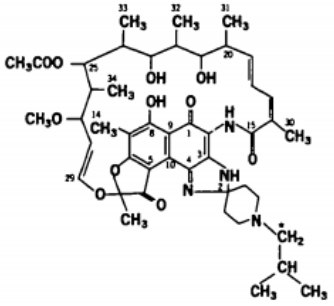
(4) now it may migrate on the pore surface [16].

II. MATERIALS AND METHODS

CHEMICALS AND REAGENTS

The Rifabutin was purchased from local market. The chemical structure of Rifabutin is presented in Table 1. The distilled water was used to prepare the stock solution of Rifabutin other chemicals used in this study were prepared. All chemicals applied in this study were of analytical grade or higher. Sulphuric acid, acetic acid and boric acid were obtained from Merck, Germany.

Table 1: Physical and Chemical properties of Rifabutin

Name	Rifabutin
Chemical formula	$C_{46}H_{62}N_4O_{11}$
Molecular weight	874 G/MOL
Molecular structure	
Synonyms	Mycobutin, Rifabutine, Ansatipine
CAS	72559-06-9
Complexity	2110
Solubility	0.19 mg/mL (Minimally soluble)
λ max	370 nm

APPARATUS

SEM was performed using a Zeiss EVO 50 instrument. Powder X-ray diffraction (XRD) studies were carried out on Diffractometer system XPERT-PRO X-ray powder diffract meter using a graphite monochromatic with Cu Ka radiation (k = 1.5406 Å). For pH measurements decibel DB 1011 digital pH meter was used. A spectrophotometer (systronics spectrophotometer 166 over the wavelength range 325 – 900 nm) with a 1.0 cm light path quartz cells was used for examination at λ max of 370 nm.

PREPARATION OF ANALYTICAL SOLUTIONS

The stock solution is prepared by dissolving 0.35 mg of Rifabutin in 50 mL of methanol. Further required dilution is made by stock solution with double distilled water. All solutions were prepared in double distilled water. All chemicals were of analytical grade and used without any further purification. Britton- Robinson buffers in the pH range 2.48 to 12.3 were prepared by adding suitable amount of 0.4 M NaOH solution to the stock solution of 2.14 sulphuric acid, 2.3 acetic acid and 2.472 g of boric acid. Solution was left over night to attain equilibrium.

SIMPLE COLORIMETRIC METHOD FOR RIFABUTIN

This method is on the basis of colour formation. Operational solution of rifabutin is prepared with the NaOH and F-C reagent. A blank solution was prepared in the same way but not having drug. The blank was measured against water. 370 nm was the optimum wavelength for maximum absorbance.

PREPARATION OF MAGNETIC NANO COMPOSITE

In this method activated alumina, ferric chloride (FeCl3), ferrous sulphate (FeSO4·H2O) and sodium hydroxide (NaOH) materials were used to manufacture magnetic nano composite (MNC) adsorbent. In the suspension of activated alumina (400 mL) solution of FeCl3 (7.8 g, 28 mmol) and FeSO4·H2O (3.9 g, 14 mol) was mixed followed by the addition of NaOH (100 mL, 5 mol·L−1) solution drop wise for the precipitation of iron oxides. The amount of activated alumina was adjusted to obtain the activated alumina/iron oxide with weight ratio of 3:1. The 3:1 weight ratio of activated alumina to Fe oxide was maintained to avoid a decrease in adsorption capacity of the composites due the high content of iron oxide. The obtained materials were dried in an oven at 373 K for 3 hours.

ADSORPTION ISOTHERM STUDIES

Adsorption study was done by a continuous batch process to study the appropriate assessment of parameters that control the adsorption procedure. Adsorption isotherm procedure were performed in a 30 mL of conical flask. The conical flasks were potted and agitated in a water bath shaker at different temperatures (30, 40, and 50 °C) until symmetry reach. After that the samples was split from the adsorbent using Whatmann filter paper (No. 42). The drug removal was determined spectrophotometrically at maximum absorbance λmax370 nm.

The adsorption amount at predetermined time t (qt, mg/g) and equilibrium adsorption amount (qe, mg/g) of Rifabutin on materials and removal efficiency (R, %) were calculated via:

$$qt = \frac{(C0-CT)V}{m} \quad (1)$$

$$qe = \frac{(C0-Ce)V}{m} \quad (2)$$

$$R = \frac{(C0-Ce)}{Co} \times 100\ \% \quad (3)$$

Where Ct (mg/L) is the remaining extract concentration at sampling time t (min); C0 (mg/L) are the initial and equilibrium concentrations of Rifabutin, respectively; V (L) is the total volume of the working solution; and m (g) is the mass of adsorbent. Rifabutin concentration (Cd, mg/L) was determined upon centrifugation and filtration, and the percent of Rifabutin desorbed was calculated via:

$$D = \frac{Cd}{(C0-Ce)} \times 100\% \quad (4)$$

III. RESULTS AND DISCUSSION

ADSORBENT CHARACTERIZATION

SEM was used for the determination of morphologies using H-7500 (JEM-1230 HC, JPN). X-ray diffraction measurements were performed on Shimadzu X-ray JPN. The magnetic nano composite was investigated using a scanning

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electron microscope (SEM). According to the SEM picture of MNC employed in this study, the generated compound has a rough surface and is porous. The measurement shows that the magnetic nano composite adsorbent (MNC) has a surface area of 740 m2/g. The surface elemental compositions of the adsorbent were determined by X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific, K-alpha 1063, UK) (Figure 1).

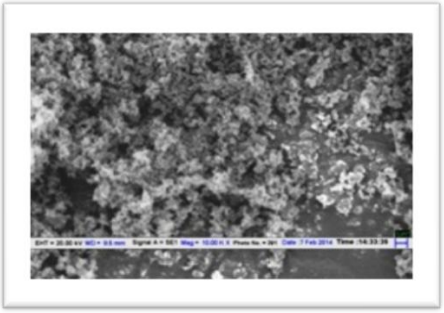

Figure 1: Scanning Electron Microscope of MNC

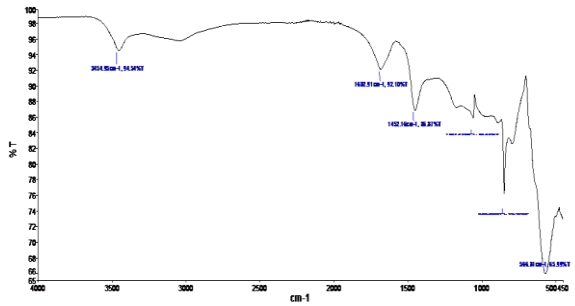

Figure 2: X-Ray diffraction pattern of MNC

Optimization of parameters has to be carried out to determine the optimal conditions showing maximum response and affect the overall process of adsorption. Different types of parameters such as effect of adsorbent dose, drug concentration, contact time, pH and temperature were examined in this study. Adsorbent dosage has physically powerful consequence on the capability of an adsorbent at given initial concentration of the adsorbate therefore it is considered as an important parameter in the adsorption process. In the present study, Rifabutin adsorption onto the dose was studied by changeable the amount of MNC, and constant other parameters (pH, initial concentration, and contact time). Figure 2 shows that the increase in adsorbent dosage resulted in a decrease of uptake capacity. The adsorption capacity was found to be high at low dosages (91.4%). The rate of adsorption is increased with the increased amount of adsorbent to 1.66 g/L, further increase in adsorbent doses results a sudden decreased in adsorption rate. Therefore, optimum amount of adsorbent dose was taken 1.66 g/L for all the subsequent studies.

Another parameter which also plays an important role in the adsorption procedure is effect of pH. Hydrogen and hydroxyl ions present in pH of the solution have an effect on the chemical characteristics of both adsorbate and adsorbent. Functional groups attached to the adsorbate, dissociate on the adsorbent surface active sites consequently it change the pH of the solution. The parameter initial pH effect was studied by varying pH from 6.5 to 12.5 at 30◦C, dose of MNC 1.66 g/L

S. No.	Parameter	Range	Other conditions	Optimum value
1.	Effect of dose	0.4 to 2.4 g/L	Initial concentration of drug:0.35mg/mL Initial pH: 10.9 Temperature: 30°C Contact time: 100 min	1.66 g/L
2.	Effect of drug concentration	0.1 to 0.55 mg/mL	Optimum dose of adsorbent: 1.66 g/L Initial pH: 10.9 Temperature: 30oC Contact time: 100 min	0.35mg/mL
3.	Effect of temperature	30oC to 50oC	Initial concentration of drug: 0.35mg/mL Optimum dose of adsorbent: 1.66 g/L Initial pH: 10.9 Contact time: 100 min	30oC
4.	Effect of pH	6.5 to 12	Initial concentration of drug: 0.35mg/mL Optimum dose of adsorbent: 1.66 g/L Temperature: 30oC Contact time: 100 min	10.9
5.	Effect of contact time	20 to 140 minutes	Initial concentration of drug: 0.35mg/mL Optimum dose of adsorbent: 1.66 g/L Initial pH: 10.9 Temperature: 30oC	100 minutes

Table 2: Adsorption operational parameters with their range and optimum values

and drug concentration 0.35 mg/mL (Fig. 3). It was observed that the rate of adsorption increases in the neutral to alkaline range from 6.5 to 12.5. With increasing pH values the adsorption of tends to increase up to pH 10.9. Other parameters were also investigated and the statistics with series and finest value of all the parameters is given in table 2. Table 2 shows all the circumstances set to decide the overall attractiveness purpose.

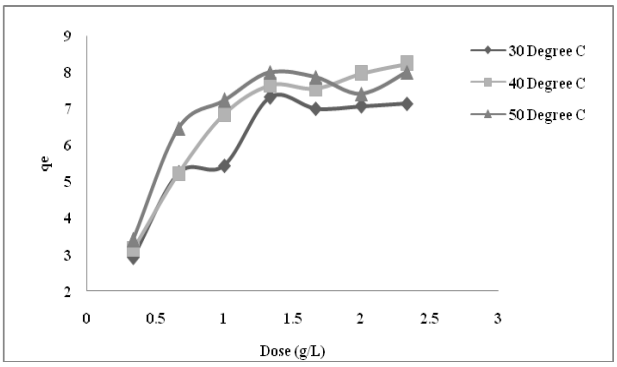

Figure 3: Amount of adsorbent effect for the removal of rifabutin at constant pH 10.9 and different temperatures

IV. ADSORPTION ISOTHERMS

Adsorption isotherms studies were helpful to predict the interaction between the surface of the adsorbent material. Though several types of adsorption isotherms are available for the determination of the adsorption process, and useful for predicting the adsorption parameters and optimizing the design of an adsorption system, adsorption equilibrium isotherm data were studied using the Langmuir, Freundlich, Tempkin and D-R isotherms models.

DUBININ- RADUSHKEVICH ISOTHERM

The Dubinin–Radushkevich (DR) [16,17] isotherm is extensively applied for adsorption in microporous resources. This equation gives a macroscopic behaviour of adsorption loading for a given pressure. The sorption curve involved in it is plotted between qe and E2 can be computed by the relationship [18,19]:

$E=1/(2B)0.5$ (vii)

Where B is denoted as the isotherm constant. Meanwhile, the parameter can be calculated as:

$\varepsilon=RTln(1+1/Ce)$ (viii)

Where R, T and Ce represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively.

Figure 4 represents the Dubinin- Radushkevich plots for the removal of rifabutin over MNC, and R2 values and constants for the model are given in Table-3. Dubinin- Radushkevich isotherm gives a good description for the adsorption process. Value of qD is high enough to indicate the adsorption capacity while the values of the apparent energy of adsorption depict the physical adsorption process.

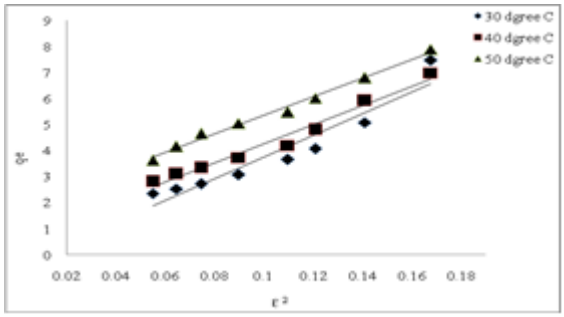

Figure 4: Dubinin- Radushkevich (D-R) isotherm for rifabutin adsorption

Table 3: D-R constants for rifabutin over MNC

Temp. (°C)	B_D	E	q_D	R^2
30 °C	14.8	22.02	24.35	0.919
40 °C	21.6	35.33	29.21	0.989
50 °C	39.12	59.41	19.56	0.953

V. CONCLUSION

This study investigated the symmetry and the dynamics of the adsorption of rifabutin. The adsorption was found to be strongly dependent on pH, dose and temperature. It was found through the experiments that the adsorption of rifabutin onto MNC was endothermic in nature with the drug removal capacity increasing with increasing temperature due to increasing mobility of the drug molecules. The pseudo-first-order kinetic model is in agreement with the dynamic behaviour for the adsorption of rifabutin onto MNC under different temperatures. The equilibrium data have been analyzed using adsorption isotherm models. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The values of mean free energy, E, were obtained within the range of 3-6 kJ mol-1 by Dubinin-Radushkevich isotherm model and it was found that the nature of the present process was likely physisorption.

REFERENCES

1. A.Mehra, M. Mandal, P. Narang, and V. Chamola, "Reviewnet: A fast and resource optimized network for enabling safe autonomous driving in hazy weather conditions," IEEE Transactions on Intelligent Transportation Systems, pp. 1–11, 2020.
2. Zolllinger H, Color chemistry-synthesis, projects and applications of orange dyes and pigments, VCH publisher, New York, 92-102, 1987.
3. Robinson T., McMullan G., Marchant R., Nigam P., Remediation of dyes in textiles effluent: a critical review on current treatment technologies with a proposed alternative, Biresour Technol; 77:247–255, 2001.
4. Banat I. M., Nigam P., Singh, Marchant R., Microbial decolourization of textile- D. dye containing effluents: a review, Bioresour Technol; 58:217–227, 1996.
5. Milani A., Ciammella A.M., Degen C., Siciliano M., Rossi L, Ascites dynamics in Cirrhosis proposal and validation of methylene blue dilution test, J hepatol; 16:369-375, 1992.
6. Belaz-David N., Decosterd L. A, Appenzeller M.,. Ruetsch Y.A, Choilero R., Buclin T., Biollaz J., Spectrophotometric determination of methylene blue in biological fluids after ion-pair extraction and evidence of its adsorption on plastic, Eur J Pharm Sci; 5: 335-345, 1997.
7. Nubbe M.E, Adams V.D., Moore W.M, The direct and sensitized photo-oxidation of hexa-chloro-cyclopentadiene, Water Res; 29: 1287-1293, 1995.
8. Sarioglu M., Atay U.A., Removal of Methylene Blue by using Biosolid, Global NEST Journal; 8; 113-120, 2006.
9. Bozlur R.M., Shibata S., Diba C.S.F., Uono M., Low Cost Biodegradable Adsorbent Material for the Removal of Dissolved Dyes from Aqueous Solutions: An Economical Process, IACSIT Int J Eng Technology; 2: 468-477, 2010.
10. Ghosh D., Bhattacharyya K.G., Adsorption of methylene blue on kaolinite, Appl Clay Sci; 20: 295–300, 2002.
11. Tan I.AW., Ahmad A.L., Hameed B.H., Adsorption of basic dye on high-surfacearea activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, J Hazard Mater; 154:337–346, 2008.
12. Tan I.A.W., Ahmad A.L., Hameed B.H., Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, Desalination; 225:13–28, 2008.

13. Ghoreishi S.M., Haghighi R., Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent, Chem Eng J; 95: 163–169, 2003.
14. Jain A.K., Gupta V.K., Bhatnagar A., Suhas, Utilization of industrial waste products as adsorbents for the removal of dyes, J Hazard Mater B; 01;31–42, 2003.
15. Ho Y. S., G. McKay, "Sorption of dyes and copper ions onto biosorbents, Process Biochem; 38:1047–1061, 2003.
16. Derbyshire F, Jagtoyen M, Andrews R, Rao A, Martin-Gullon I, Grulke E, Radovic L.R. (Ed.), Carbon materials in environmental applications, in: Chemistry and Physics of Carbon, Marcel Dekker, New York, vol. 27:1–66, 2001.
17. Radushkevich L.V., Potential Theory of Sorption and Structures Of Carbons, Zhurnal Fizicheskoi Khimii; 23: 1410-1420, 1949.
18. Dubinin M.M., Modern State of the theory of Volume filing of Microscope Adsorbents during Adsorption of Gases and Steams on Carbon Adsorbents, Zhurnal Fizicheskoi Khimii; 39: 1305-1317, 1965.
19. Dubinin M.M., The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Nonuniform Surfaces, Chem Rev; 60: 235-241, 1960.
20. Hobson J.P., Physical Adsorption Isotherms Extending from Ultrahigh vacuum to Vapor Pressure, J Phys Chem; 73: 2720-2727, 1960.