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Batch Biosorption of Metanil Yellow from Aqueous Solution on Egg Membrane: Kinetics and Mechanism

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Abstract

The removal of metanil yellow (MY), a hazardous azo dye from aqueous solution by batch biosorption on hen egg membrane (HEM) was carried out. The effects of contact time, initial solution concentration, initial solution pH, and biosorbent dosage were evaluated. Experimental data were analyzed with the pseudo-second-order, Elovich, intra-particle diffusion, liquid film diffusion, and Boyd models. Results show that the optimum initial concentration, pH, and biosorbent dosage were 50 mg/L, 3 and 0.01 g per 25 mL solution, respectively at 29ºC. The highest experimental biosorption capacities q_e, obtained were 58.15, 112.30 and 221.65mg/g, respectively for 25, 50 and 100 mg/L MY within the first 60min. The pseudo-second-order and Elovich kinetic models analyzed the experimental data well. However, the pseudo-second-order model fitted better with correlation coefficient values, R^2, 0.9973, 0.9982 and 0.8246, for initial concentrations of 25, 50 and 100mg/L, respectively. This was also confirmed by the sum of square errors (SSE) which were 0.31, 1.41 and 0.81 for C_o 25, 50 and 100 mg/L, respectively. The Boyd model confirmed that the biosorption process was controlled by both the intra-particle diffusion and the liquid film diffusion mechanisms. From the results obtained, HEM has a high potential for the removal of MY from aqueous solution. It might also have the capacity to remove water-soluble anionic organic compounds if well harnessed.

Keywords: Biosorption, kinetics, mechanism, egg membrane, metanil yellow

1. Introduction

The discharge of aqueous dye effluents from textile and dyestuff industries into the aquatic ecosystem has been generating a lot of public concern [1]. These effluents create aesthetic displeasure, hinders light penetration into the water body which is necessary for photosynthesis in aquatic plants, lowers water quality and causes harm generally to aquatic life [2]. Metanil yellow (MY) is a synthetic azo dye applied on wool, nylon, silk, paper, ink, aluminium, detergent, wood, fur, cosmetics, and as a biological stain. It is hazardous when ingested and slightly hazardous when inhaled or contacts the eyes [3]. Toxicity data reveals that oral feeding or intrapertoneal and intratesticular administration of MY in animals produces testicular lesions, causing seminiferous tubules to suffer damage, reducing the rate of spermatogenesis. On oral consumption, it causes met-haemoglobinaemia [4] and cyanosis [5] in humans, while skin contact results into allergic dermatitis [6]. MY also has tu-mour-producing effects and can also create intestinal [7] and enzymic [8] disorders in the human body. It is not mutagenic but can alter the expression of genes [9].

Series of methods have been developed for the removal of synthetic dyes from wastewaters. They include membrane filtration, adsorption, coagulation, advanced oxidation processes and ozonation [10]. Among these processes, adsorption is superior due to its cheapness, flexibility, simplicity of design, ease of operation and lack of sensitivity to toxicants [11, 12].

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Adsorption is a process that takes place at the surface due to the adhesion of particles (atoms, ions or molecules) of one substance (adsorbate) to the surface of the other (adsorbent) [1]. Biosorption is the binding of adsorbate particles on the surface of an adsorbent. The adsorbent is a natural substance of biological origin whether alive or non-living [13].

Due to increased rate of urbanization, there is increase in the number of food manufacturers, hatcheries, hotels, restaurants and homes that use hen eggs. Large quantities of eggshell are discarded as waste. Hen egg membrane (HEM) has good adsorption properties. It contains polysaccharide fibres and collagen which provide hydroxyl, amine and sulphonic functional groups on which the adsorbate particles stick [14]. Pramanpol and Nitayapat [15] used eggshell and eggshell containing the membrane to remove reactive yellow 205. Their result showed a 10-27 fold increase in adsorption capacity due to the presence of the membrane. Moreover, Hassan and Hassan [14] used eggshell containing the membrane to effectively remove methylene blue, a cationic dye, from aqueous solution. Therefore, the batch biosorption of MY, an anionic azo dye, on HEM was investigated in this work with a view to study the kinetics and process mechanism.

2. Materials and Methods

2.1. Preparation of Dye Solution

The MY also called C.I. acid yellow 36, used in this study, was supplied by Merck, Switzerland and used directly without further treatment. The structure of MY is shown in Figure 1. The stock solution was prepared by dissolving 1.0 g MY dye per litre solution in 1 L volumetric flask with distilled water. Different initial MY concentration (25-100 mg/L) used in this work were obtained by dilution of the stock solution. A 0.1 M nitric acid and 0.1 M sodium hydroxide solutions were used for pH adjustments.

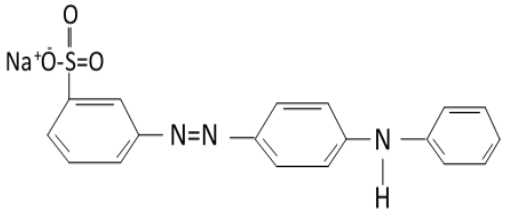

Figure 1. Structure of Metanil Yellow

2.2. Preparation of HEM

Hen eggshells were obtained from restaurants and hatcheries in Owerri, Imo State, Nigeria. The eggshells were washed with hot water and rinsed thrice with hot distilled water to remove odour and dirt. The eggshells were boiled for 30 min and cooled. While soaked, the membranes were peeled off, packed in a lattice and allowed for water to drain off. The membrane biomass was dried at 110°C in a hot air oven for 1 h and cooled. The dried membrane biomass was ground with a blender and sieved to obtain 0.420-0.841 mm particles and packed in an airtight plastic container.

2.2.1 Analysis of the HEM

Infra-red spectrophotometric analysis of the HEM was carried out by FTIR-8400S spectrophotometer (M/s Shimadzu, Japan). Proximate analysis of the biosorbent was carried out using the Association of Official Analytical Chemists (AOAC) 1990 methods [16].

2.3. Batch Biosorption Process

Batch biosorption of MY from aqueous solution was carried out by agitating 0.01 g portions of the HEM with 25 mL portions of different MY concentrations in 50 mL volumetric flasks. This was done by setting the samples flasks in a water-bath shaker and agitating for 6 h at 29°C and a speed of 175 rpm. Samples were collected each hour, filtered, and the filtrate analyzed using UV-Visible spectrophotometer (Shimadzu, model 752, M/s Shimadzu, Japan) at a wavelength of 440 nm λ_{max} to determine the amount of dye biosorbed on the biosorbent using Equations 1 and 2.

$$q_e = \frac{(C_o - C_e)\mathrm{V}}{1000m} \quad (1)$$

$$\%\,\mathrm{Removal} = \frac{(C_o - C_e)}{C_o} x100 \quad (2)$$

where, V (mL) is the volume of solution, C_e (mg/L), the equilibrium concentration of the dye remaining in the solution, and m (g) is the dry mass of the HEM.

3. Results and Discussion

3.1. Analysis of the Biosorbent

Table 1 shows the protein, carbohydrate, fibre, and lipid contents of the biomass and Figure 2 shows the infra-red spectrum of the biosorbent. The infra-red peaks at 2341.66, 2843.17, 3036.06, 3255.95, and 3618.58 cm^{-1} indicate the presence of –NH- and –OH functional groups, while 1238.34, 1408.08, 1519.96, and1658.84 cm^{-1} show the presence of –CO- functional group. The –NH- and –CO- functional groups exist in protein and protein fibres. Carbohydrates furnish –OH, and esters (lipids) contain –CO and –C-O- functional groups [17, 18, 22].

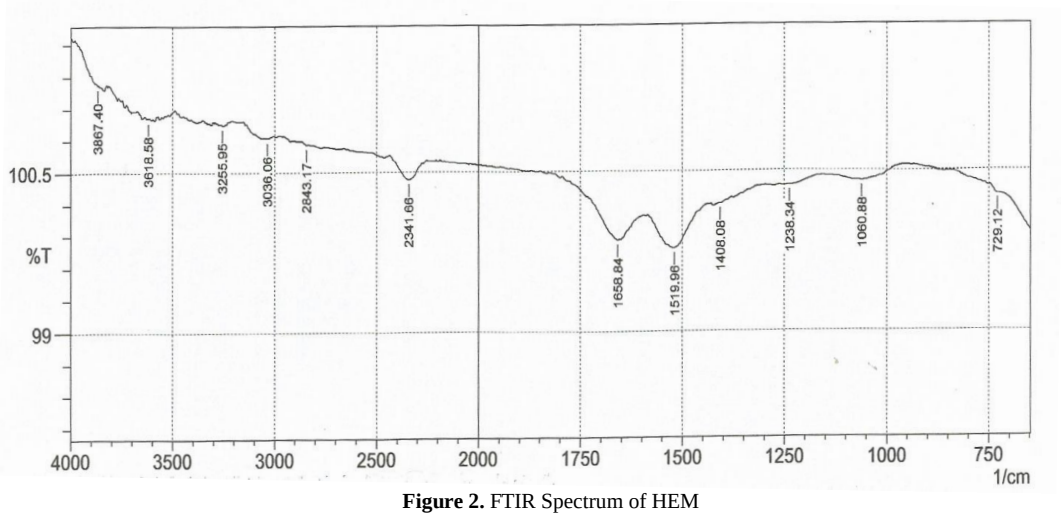

Figure 2. FTIR Spectrum of HEM

Table 1. Proximate Analytical Data for HEM

Parameters	Value (%)
Crude protein	2.1
Carbohydrate	36.57
Fibre	27.59
Lipid	13.65
Moisture	11.7
Ash	8.39

3.2. Effects of Initial Dye Concentration and Contact Time

The effects of initial MY concentration and contact time are shown in Figure 3, for 25, 50 and100 mg/L at 29°C, agitation speed of 175 rpm and pH 3. Maximum biosorption was within the first 60 min for all the concentrations. However, experimental q_e at maximum time of 360 min were 52.83, 99.6 and 74.88 mg/g for 25, 50 and 100 mg/L, respectively. Generally, the biosorption capacities were high for all the MY concentration. However, there was appreciable decline in biosorption with time, especially for 100 mg/L. Results show increase in q_e with increase in initial concentration. This agrees with the work of Njoku and Hameed [19]. The optimum time of biosorption for initial concentration 25 and 50 mg/L was 120 min. For 100mg/L, equilibrium was not reached at 360 min. The appreciable decrease in q_e with time for 100mg/L might be as a result of the competition of the biosorbate anions for the available binding sites [20, 21].

The increase in q_e with increase in MY initial concentration was as a result of the increase in the driving force from the concentration gradient. The biosorption was enhanced by the protonation of the amino and carboxylate moieties in the protein fibres and the oxo groups in the polysaccharide present in the HEM [22, 23, 24]. At higher biosorbate concentrations the active sites on the membrane were surrounded by many more biosorbate ions, leading to enhanced biosorption [25].

3.3. Effect of Sorbent Dosage

Various masses (0.01-0.32 g) of the HEM were interacted with 25 mL portions of the dye solution (25 mg/L) at pH 3, 29°C and agitation speed of 175 rpm for 6 h in order to evaluate the effect of biosorbent dosage. The results depicted in Figure 4 show that q_e decreased with increase in biosorbent dosage. This is in agreement with the work of Koumanova et al. [26].

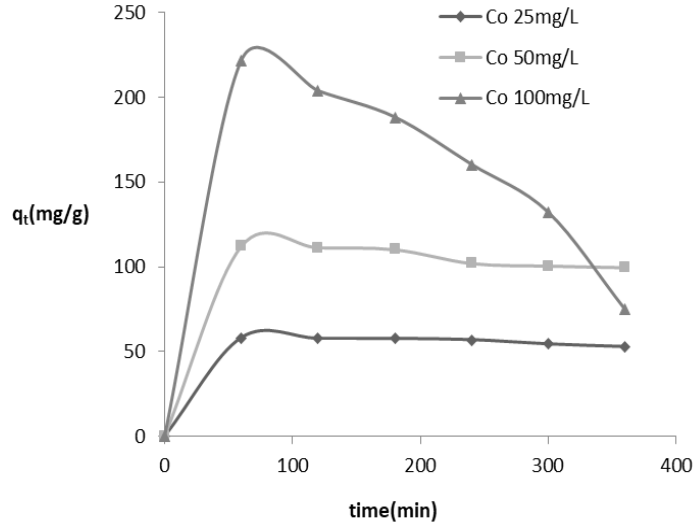

Figure 3. Effect of Initial MY Concentration on the Batch Biosorption of Metanil Yellow on HEM

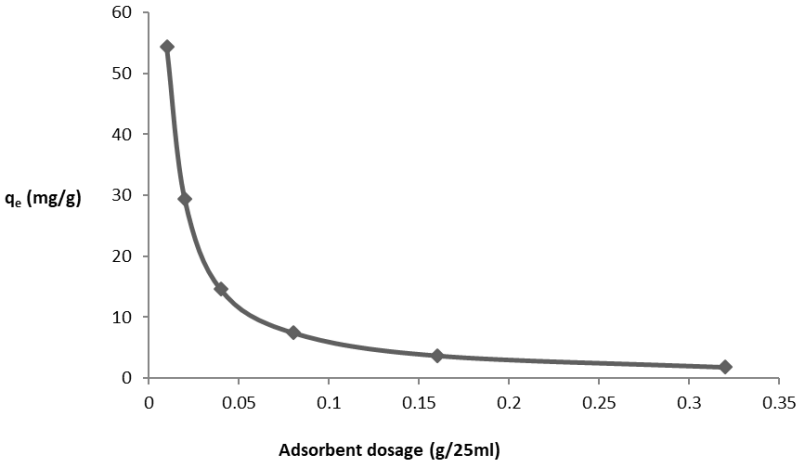

Figure 4. Effect of Biosorbent Dosage on the Batch Biosorption of Metanil Yellow on HEM

At higher biosorbent dosage, there was a very fast superficial biosorption onto the biosorbent surface that produced a lower solute concentration in the solution than when biosorbent dosage was lower. Thus, with increasing biosorbent dosage, the amount of MY biosorbed per unit mass of HEM reduced, hence leading to a decrease in q_e. This is in conformity with the report of Han et al. [25]. Increasing the biosorbent dosage from 0.01 to 0.32 g/25 mL of the solution led to a decrease in q_e, from 54.38 to 1.80 mg/g. The optimum biosorbent dosage was found to be 0.01-0.04 g per 25 mL solution.

3.4. Effect of Initial Biosorbate pH

Solution pH affects the properties of both biosorbate and biosorbent and is therefore a very important parameter that affects biosorption in aqueous solutions [19]. The effect of initial solution pH on the biosorption of MY on HEM was investigated within the pH range 2-7 and the result is shown in Figure 5. The figure shows that the highest q_e was 29.40 mg/g at pH 3, for 25 mg/L initial MY concentration, adsorbent dosage 0.02 g per 25 mL, and temperature of 29^{o}C. There was a decrease in q_e with increase in pH. At pH 7, there was virtually no biosorption. The pH values 2-4 were ideal for the biosorption of MY on HEM. The q_e, decreased from 29.40 mg/g at pH 3 to 26.45 mg/g at pH 2. The reason for the decrease is attributed to the increase in H^+ concentration leading to the formation of aqua complexes thereby retarding the biosorption process. This agrees with the report of Mas Haris and Sathasivam [27].

The effect of pH is attributed to the electrostatic interaction between the biosorbate particles and biosorbent surface. At low pH, the carboxylate anion of the protein fibre present in the membrane as part of the amino acid functional group is protonated and the amino acid exists primarily as the ammonium ion; the oxo functional group present in the polysaccharide is also protonated. These conditions create positively charged surface on the biosorbent, hence a high biosorption; if the pH is raised, the ammonium ion site in the protein is deprotonated, and the molecule exists as the carboxylate anion; the

oxo functional group is hydrated generating hydroxyl ions which repel the MY anions [22, 23]. These conditions were responsible for poor biosorption at higher pH values.

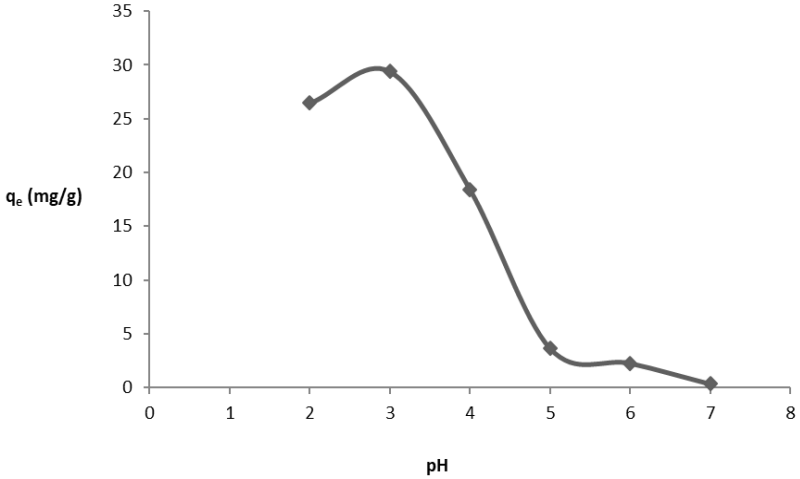

Figure 5. Effect of Initial Solution pH on the Batch Biosorption of Metanil Yellow on HEM

3.5. Biosorption Kinetics

Isotherms are obtained under equilibrium conditions, whereas in most biosorption treatment applications the retention time is too short for equilibrium to be attained. Hence, information must be obtained on the time dependence of biosorption processes by carrying out process-orientated kinetic studies [24]. The time dependent experimental data in this study were analyzed using five kinetic models.

3.5.1. Pseudo-second-order Kinetic Model

The linearized form of the pseudo-second-order model [28] is expressed as Equation 3;

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{t}{q_e} \quad (3)$$

where, q_t (mg/g) is the biosorption capacity at time t, h_o (mg/g/min) the initial biosorption rate and t (min) is time. h_o is expressed as Equation 4.

$$h_o = k_2 q_e^2 \quad (4)$$

where, k_2 (g/mg/min) is the second-order rate constant. A plot of t/q_t against t, yields a straight line with slope $1/q_e$ and intercept $1/h_o$ (Figure 6). The R^2 values show that the pseudo-second-order model simulated the experimental results well. The calculated rate constants, experimental and predicted q_e with corresponding R^2 values are shown in Table 2.

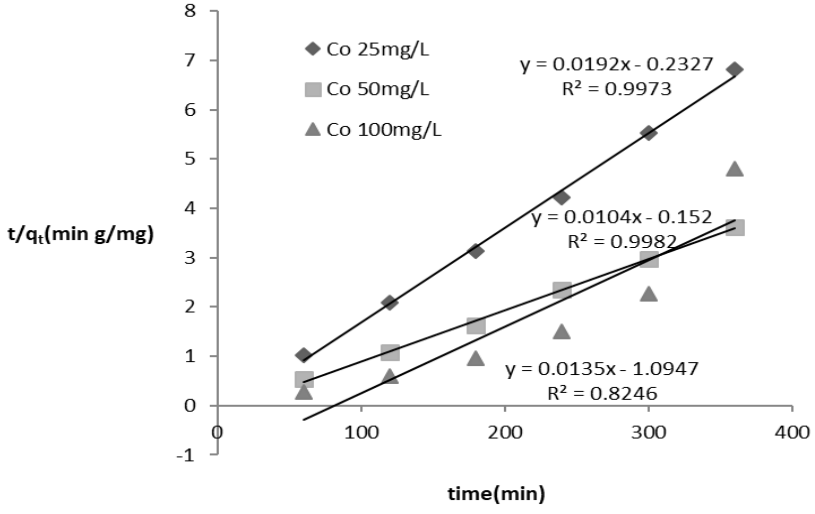

Figure 6. Pseudo-second Order Kinetic Plots for the Batch Biosorption of Metanil Yellow on HEM

Table 2. Kinetic Models Parameters for the Biosorption of MY on HEM at 29°C and pH 3

	C_o (mg/L)		
Model/Parameter	25	50	100
Pseudo-second-order			
q_e exp. (mg/g)	52.83	99.6	74.88
q_o (mg/g)	52.08	96.15	74.07
k_2 (g/mg/min)	0.0016	0.0007	0.0002
R^2	0.9973	0.9982	0.8246
SSE	0.31	1.4	0.081
Elovich			
A	392.289	51.78	212.937
B	0.379	0.129	0.014
R^2	0.6675	0.8024	0.794
Liquid film diffusion			
K_{id}	0.0008	0.0109	0.0017
R^2	0.5977	0.8319	0.9006
Boyd			
B	0.0076	0.0122	0.0012
R^2	0.7326	0.9038	0.9307

3.5.2. Elovich Kinetic Model

The linearized form of the Elovich model is mainly applicable to chemisorptions kinetics. The equation expressed in Equation 5 is often valid for systems in which the biosorbing surface is heterogeneous [29].

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln\ t \qquad 5$$

A plot of q_t against In t gives a straight line with slope 1/β and intercept (1/β)*ln*(αβ), where α is the initial biosorption rate (mg/g/min) and β is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg) (Figure 7). The R^2 values portray the Elovich model good for analyzing the experimental data. However, the pseudo-second-order model was a better model for the analysis than the Elovich model. Table 2 shows the R^2, α and β values.

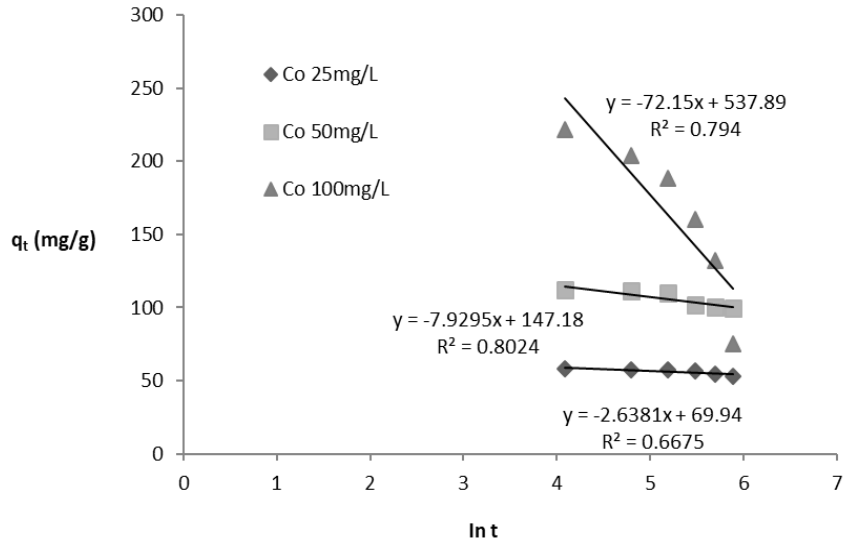

Figure 7. Elovich Kinetic Plots for the Batch Biosorption of Metanil Yellow on HEM

3.5.3. Liquid Film Diffusion Model

When the transport of the biosorbate molecules from the liquid phase up to the solid phase boundary plays a major role in biosorption, the liquid film diffusion model equation is used which is expressed as Equation 6.

$$\ln(1-F) = -K_{id}\,t \qquad 6$$

where, F is the fractional attainment of equilibrium ($F = q_t/q_e$), K_{id}, the biosorption rate constant and t, the time (min). A linear plot of –*In*(1-F) against t with zero intercept suggests that the kinetics of the biosorption process is controlled by

diffusion through the liquid surrounding the biosorbent [29]. Figure 8 shows the R^2 values and intercepts for initial MY concentrations 25, 50 and 100mg/L. None of the intercepts is zero though the model fits the experimental data well. Hence the liquid film diffusion biosorption mechanism was not the only rate-determining step in the biosorption process.

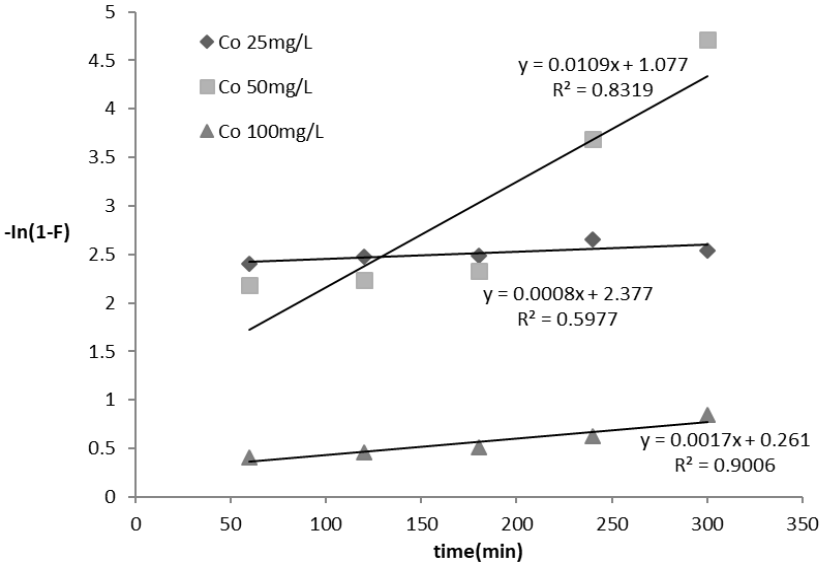

Figure 8. Liquid Film Diffusion Plots for the Batch Biosorption of Metanil Yellow on HEM

3.5.4. Intra-particle Diffusion Model

The possibility of intra-particle diffusion being the rate determining step in the biosorption process can be ascertained using the intra-particle diffusion model [30]. Involved in the process are the transport of the biosorbate to the surface of the sorbent which is usually a slow process. Based on this theory;

$$q_t = \mathrm{K}_{id}\, t^{0.5} + C \qquad 7$$

where, K_{id} is the intra-particle diffusion rate constant (mg/g/min $^{0.5}$) and C is a constant that gives idea about the thickness of the boundary layer, i.e., the larger the value of C the greater is the boundary layer effect [31]. If a plot of q_t against $t^{0.5}$ gives a straight line, then the biosorption process is controlled by intra-particle diffusion only and the slope gives the rate constant, K_{id}. However, if the data show multi-layer plots, two or more steps controlled the biosorption process. Figure 9 shows the analysis of experimental data with this model.

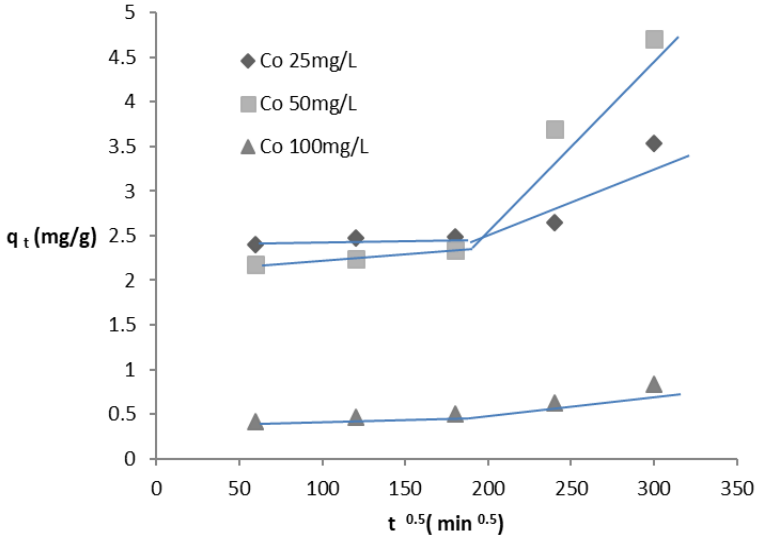

Figure 9. Intra-particle Diffusion Plot for the Biosorption of Metanil Yellow on HEM

The figure shows that the biosorption process was governed by the intra-particle diffusion for initial MY concentration 25 mg/L.

3.5.5. The Boyd Model

The Boyd kinetic equation [19, 32] was applied to distinguish between film diffusion and intra-particle diffusion and to determine the rate determining step in the biosorption. The equation is expressed as Equation 8.

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2 B_t) \quad (8)$$

where, B_t is a mathematical function of F, the fractional attainment of equilibrium at time t. F is given by Equation 9.

$$F = \frac{q_t}{q_e} \quad (9)$$

Equation 8 can be simplified with approximations to give Equations 10 and 11.

$$B_t = -0.4977 - \ln(1-F) \quad (for \quad F > 0.85) \quad (10)$$

$$B_t = \left[\sqrt{\pi} - \sqrt{\pi}\left(\frac{\pi^2 F}{3}\right)\right]^2 \quad (for \quad F < 0.85) \quad (11)$$

A plot of B_t against t yields a straight line which can be used to determine the rate-determining step in the biosorption process. A straight line which passes through the origin for a given initial concentration shows that intra-particle or pore diffusion is the rate-determining step in the biosorption process. If the plot is nonlinear or linear but does not pass through the origin then the biosorption process is controlled by liquid film diffusion. Figure 10 shows that the biosorption process was controlled by intra-particle diffusion for 100 mg/L. For initial concentration 25 and 50 mg/L, the biosorption process was controlled by liquid film diffusion. The R^2 values 0.7326, 0.9038 and 0.9307 for 25, 50 and 100 mg/L, respectively show that the Boyd model is a good fit for the experimental data.

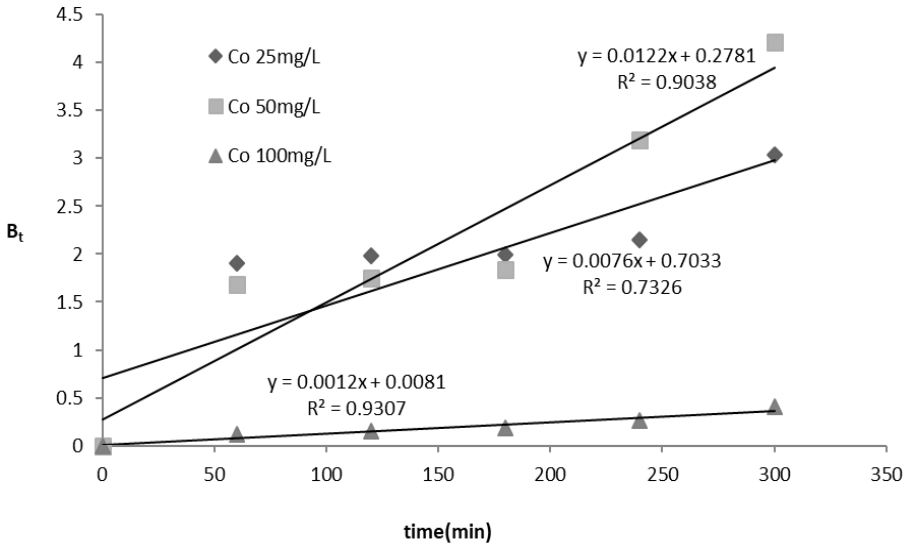

Figure 10. Boyd Model Plots for the Batch Biosorption of Metanil Yellow on HEM

Table 3. Comparison of Maximum Biosorption Capacity of HEM for MY with other Biosorbents

Sorbent	Sorbate	% Removal	References
Hen egg membrane	Metanil yellow	79.69	This work
Immobilized aquatic weed	Metanil yellow	98.8	Sivashankar et al. [35]
H_3PO_4-activated carbon	Metanil yellow	12.04	Isiuku et al. [36]
NaOH-activated carbon	Metanil yellow	12.90	
Egg membrane	2, 4-DCP	48.2; 71.2	Koumanova et al. [24]

A comparison of the biosorption capacity of HEM for MY with other biosorbents in literature is presented in Table 3. Sivashankar et al. [35] used immobilized aquatic weed to remove MY from aqueous solution and obtained 98.8% total removal. Isiuku et al. [36] used H_3PO_4- and NaOH-activated carbons to remove the same dye and obtained 12.04 and 12.90%

total removal, respectively. Koumanova et al. [24] used HEM to remove 2, 4-Dichlorophenol under varying conditions and obtained 48.2 and 71.2% total removal, respectively. The total removal of MY from aqueous solution with HEM of 79.69% obtained in this work is comparatively high.

3.6. Spontaneity of the of the Biosorption

The spontaneity of the biosorption process was determined by evaluating the Gibb's free energy of biosorption ΔG_{ads} [33, 34] expressed as Equation 12.

$$\Delta G_{ads} = -RT \ln K_D \quad 12$$

where, R (8.314J/mol/K) is the universal gas constant, T (K) the absolute temperature and K_D the equilibrium distribution constant. K_D is determined from Equation 13.

$$K_D = \frac{(C_o - C_e)_e}{C_e} \quad 13$$

The ΔG_{ads} values were -4.261, -3.43 and 2.132 kJ/mol for initial MY concentrations 25, 50 and 100 mg/L, respectively. The values show that the biosorption was spontaneous for 25 and 50 mg/L but non-spontaneous for 100 mg/L.

4. Conclusion

The highest experimental equilibrium biosorption capacities of 58.15, 112.30 and 221.65 mg/g for initial MY concentration 25, 50 and 100 mg/L, respectively were obtained within the first 60 min at pH 3, sorbent dosage 0.01 g/25 mL solution and 29ºC. Ho's pseudo-second-order kinetic model simulated experimental data best. The Boyd model confirmed that for initial MY concentration 100 mg/L, the biosorption process was controlled by intra-particle diffusion while for 25 and 50 mg/L, the biosorption was controlled by the liquid film diffusion. The study shows that HEM is a good biosorbent for MY removal from wastewater.

REFERENCES

[1] Isiuku B.O., Nwosu C.N., 2017. Fixed-bed adsorption of metanil yellow from aqueous solution on HNO_3-treated-H_3PO_4-activated carbon from *G. aborea* bark. Asian J. Chem., 29 (3), 475-479.

[2] Isiuku B.O., Horsfall Jnr. M., Spiff A.I., 2014. Colour removal from a simulated methyl red wastewater by adsorption on carbon in a fixed bed. Res. J. Appl. Sci., 9 (4), 201-207.

[3] Isiuku B.O., 2015. Adsorption of metanil yellow and methyl red from aqueous solutions using cassava (*Manihot esculenta*) peels activated carbon in a fixed-bed column. Ph D. Dissertation, University of PortHarcourt, PortHarcourt, Nigeria.

[4] Sachdeva S.M., Mani K.V., Adval S.K., Jolpota V.P., Rasela K.C., Chadha D.S., 1992. Acquired toxic methaemoglobinaemia. J. Assoc. Physcians Ind., 40, 239-240.

[5] Chandro S.S., Nagaraja T., 1987. A food poisoning out-break with chemical dye: An investigation report. Medical J. Armed Forces Ind., 43, 291-300.

[6] Hausen B.M., 1994. A case of allergic contact dermatitis due to metanil yellow. Contact Dermatitis, 31, 117-118.

[7] Ramachandani S., Das M., Joshi A., Khanna S.K., 1997. Effect of oral and parental administration of metanil yellow on some hepatic and intestinal biochemical parameters. J. Appl. Toxicol., 17, 85-91.

[8] Das M., Ramachandani S., Upreti R.K., Khanna S.K., 1997. Metanil yellow: a bifunctional inducer of hepatic phase I and phase II xenoblastic-metabolizing enzymes. Food Chem. Toxicol., 35, 835-838.

[9] Gupta S., Sundarrajan M., Rao K.V.K., 2003. Tumor promotion by metanil yellow and malachite green during rat hepatocarcinogenesis associated with disregulated expression of cell cycle regulatory proteins. Tertogen. Carcin. Mut. (Suppl. 1), 301-312.

[10] Turhan K., Durukan I., Ozturcan S.A., Turgut Z., 2012. Decolorization of textile Basic Dye in aqueous solution by ozone. Dyes Pigm., 92, 897-901.

[11] Tong Z., Zheng P., Bai B., 2016. Adsorption performance of Methyl Violet via α – Fe_2O_3 @ porous hollow carbonaceous microspheres and its effective regeneration through a Fenton-like reaction. Catalysts, 6(4), p 58.

[12] Wang L., Zhang J., Zhao R., Li C., Li Y., Zhang C., 2010. Adsorption of Basic Dyes on activated carbon prepared from *Polygonum orientale* Linn: Equilibrium, kinetic and thermodynamic studies. Desalination, 254, 68-74.

[13] Njoku V.O., Ayuk A.A., Oguzie E.E., Ejike E.N., 2012. Biosorption of Cd(II) from aqueous solution by cocoa pod husk biomass: Equilibrium, kinetic and thermodynamic studies. Sep. Sci. Technol., 47, 753-761.

[14] Hassan A.A., Salih Z.A.H., 2013. Methylene blue removal from aqueous solution by adsorption on eggshell bed. Euphrates J, Agric. Sci., 5(2), 11- 23.

[15] Pramanpol N., Nitayapat N., 2006. Adsorption of reactive dye 205 by eggshell and its membrane. Kasetsart J. (Nat. Sci.), 40(Suppl.), 192-197.

[16] Association of Official Analytical Chemists (AOAC), 1990. Official Methods of Analysis, 15th ed., Arlington, VA, p 331.

[17] Williams D.H., Fleming I., 1980. Spectroscopic Methods in Organic Chemistry, 3rd ed., McGraw-Hill Book Company (UK) Ltd., pp 49-58.

[18] Finar I.L., 1975. Organic Chemistry, Vol. 2, 5th ed., ELBS, Longman Group Ltd., pp 651-660.

[19] Njoku V.O., Hameed B.H., 2011. Preparation and characterization of activated carbon from corncob by chemical activation with H_3PO_4 for 2-4-dichlorophenoxyacetic acid adsorption. Chem. Eng. J., 173, 391-399.

[20] Ekpete O.A., Horsfall Jnr. M., Tarawou T., 2010. Potentials of fluted pumpkin and commercial activated carbons for phenol removal in aqueous systems. ARPN J. Eng. Appl. Sci., 5(9), 39-47.

[21] Mahvi A., Maleki A., Eslami A., 2004. Potentials of rice husk and rice husk ash for phenol removal in aqueous systems. Amer. J. Appl. Sci., 14, 321-326.

[22] Finar I.L., 1973. Organic Chemistry, Vol. 1: The Fundamental Principles, 6th ed., Longman Group Ltd, p 207.

[23] Jones Jr. M., 2000. Organic Chemistry", 2nd ed., W. W. Norton and Company, p 715.

[24] Koumanova B., Peeva P., Allen S.J., Gallagher K.A., Healy M.G., 2002. Biosorption from aqueous solutions by eggshell membrane and *Rhizopus oryzae*: Equilibrium and kinetic studies. J. Chem. Technol. Biotechnol., 77, 539-545.

[25] Han R., Zou W., Yu W., Cheng S., Wang Y., Shi J., 2007. Biosorption of methylene blue from aqueous solution by fallen phoenix tree leaves. J. Hazard. Mater., 141, 156-162.

[26] Koumanova B., Peeva-Antova P., Yaneva Z., 2005. Adsorption of 4-chlorophenol from aqueous solutions on activated carbon – Kinetic study. J. University Chem. Technol. Metallurg., 40 (3), 213-218.

[27] Mas Haris M.R.H., Sathasivam K., 2009. The removal of Methyl Red from aqueous solution using banana pseudo fibres. Amer. J. Appl. Sci., 6(9), 1690-1700.

[28] Ho Y.S., John W.D., Foster C.F., 1995. Batch nickel removal from aqueous solution by *Sphagnum moss* peat. Water Res., 29(5), 1327-1332.

[29] Ekpete O.A., Horsfall Jnr. M., Spiff A.I., 2012. Kinetics of chlorophenol adsorption onto commercial and fluted pumpkin activated carbons in aqueous systems. Asian J. Nat. Appl. Sci., 1(1), 106-117.

[30] Srivastava V.C., Swammy M.M., Mall I.D., Prasad B., Mishra I.M., 2006. Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics. Colloid Surf. A. Physicochemical Eng. Aspects, 272, 89-104.

[31] Kannam N., Sundaram S., 2001. Kinetics and mechanism of removal of methyl blue by adsorption on various carbons: Comparative study. Dyes Pigments, 5, 25-40.

[32] Boyd G.E., Adamson A.W., Myers L.S., 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites: II. Kinetics. J. Am. Chem. Soc., 69, 2836-2848.

[33] Depci T., Kul A.L., Onal Y., Disli E., Alkan S., Turkmenoglu Z.F., 2012. Adsorption of crystal violet from aqueous solution on activated carbon derived from Gölbasi Llignite. Probl. Miner. Process, 48 (1), 253-270.

[34] Bello O.S., Fatona T.A., Falaye F.S., Osuolale O.M., Njoku V.O., 2012. Adsorption of eosin dye from aqueous solution using groundnut hull-based activated carbon: Kinetic, equilibrium and thermodynamic studies. Environ. Eng. Sci., 29(3), 186-194.

[35] Isiuku B.O., Horsfall Jnr. M., Spiff A.I., 2013. Adsorption of metanil yellow on chemically-activated carbon in a packed-bed column: Effect of activation reagent. J. Eng. Appl. Sci., 8(9-12), 282-289.

[36] Sivashankar R., Sivasubramanian V., Sathya A.B., Pallipad S., 2013. Biosorption of hazrdous azo dye, metanil yellow using im-mobilized aquatic weed. In Proceedings of the International Conference on Future Trends in Structural, Civil, Environmental and Mechanical Engineering, Institute of Research Engineers and Doctors, SEEK Digital Library, India, 153-157.