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Magnetic Bagasse Pith as an Efficient Adsorbent for Toxic Dyestuffs (Preparation, Characterization, and Application)

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ABSTRACT

An increasing awareness about environmental and economic issues is acting as the poetical force behind the use of waste products from industry and agriculture as valuable materials. Bagasse pith, an agricultural waste produced from pulp industry, was successfully converted into a novel magnetic adsorbent via a simple method using iron salt. Bagasse pith and the modified one were characterized through analytical methods: scanning electron microscopy (SEM) and FTIR while, the adsorption characteristics was examined using Methylene Blue. The equilibrium isotherm for the two types of pith ware studied for different temperatures, 25:75ºC; where Langmuir, Freundlich, and Dubinin-Radushkevich models ware used to investigate the equilibrium data, to judge which one simulates the process and determines the adsorption capacity. The results showed that the Langmuir model provided a good description of adsorption behavior. as well as adsorption capacity was slightly improved due to magnetization of pith. In particular, the adsorption rate was so fast that the equilibrium was achieved within 100 min for magnetic pith compared with 140 min for the unmodified one, in addition the maximum capacities were 149.2, 156.3, 166.7 and 175.4 mg.g^{-1} for magnetic pith at 25, 40, 60 and 75ºC processes temperature respectively.

Keywords: Pollution control, Agricultural wastes, Bagasse pith, Magnetic adsorbent.

1. INTRODUCTION

In order to meet the demands of the rapidly expanding human population, development in all sides of our life, including agriculture, medicine, energy, and industry, is required. Water contamination is a primarily caused by industrial waste, which contains a variety of dyes and other contaminants [1]. Large amounts of synthetic dyes have been excreted in wastewater from different activities. Numerous industries, including those that manufacture dyes, paper and pulp, tanneries, electroplating plants, distilleries, cosmetic, pharmaceutical, food, and many others, release colored effluent [2]. The majority of dyeing-related byproducts are poisonous, mutagenic, and carcinogenic, and they even raise the chemical and biological oxygen demands (COD and BOD) of aquatic sources. They also hinder photosynthesis, stunt plant growth, enter the food chain, cause recalcitrance and bioaccumulation, and endanger human health [3]. Consequently, the presence of very low concentrations of dyes in effluent is clearly visible. Approximately 10,000 different commercially available dyes and pigments are in use today, and more than 70 million tons of synthetic dyes are manufactured globally each year. According to estimates, during the dyeing procedures, 10 to 15 percent of the dyes are lost in the effluent [4].

Various technologies have been developed to eliminate dyes from wastewater such as membrane processes, electrochemical methods, chemical coagulation, and adsorption [5&6]. Due to its effectiveness, high selectivity, cheap cost, simplicity, flexibility of use, and availability in a variety of experimental settings, adsorption could be seen as a promising alternative for removing dyes from aqueous environments. Adsorbent materials are obtained from various recourses. These resources are composed of natural materials [7], agricultural waste and by-products [8] and industrial waste [9]. The major by-product of the sugar cane industry is sugarcane bagasse (SCB); it is one of the largest agriculture residues. The global production of dry SCB is approximately 54 million tons per year [10]. The main use of SCB in the pulp and paper industries after separating pith in a separate process named de-pithing. Bagasse pith, the primary byproduct of the sugarcane industry in Egypt, is thus widely accessible and cost-free. Thus, using of this waste as an inexpensive adsorbent might provide two-fold benefits with respect to environmental pollution, the by-product volume could be partially reduced, and wastewater pollution could be reduced at a fair price.

Due to presence of magnetic material loaded in the adsorbents, which can facilitate separation phase by application of an external magnetic field, magnetic adsorption technique offers promising and successful outcomes for wastewater treatment [11]. The main objective of this work is to introduce a useless and environmentally friendly material, bagasse pith, as an adsorbent for dyestuffs from wastewater. The aim extended for modifying the pith by magnetite to enhance adsorption dynamics and facilitate the separation process.

2. EXPERIMENTAL WORK

2.1 Materials and Reagents

Bagasse pith, a main solid waste from sugar and pulp industry, was provided from Edfo Pulp Mill, Aswan governorate, Egypt. The approximate constituents of BP are: α- cellulose (53.7%), alcohol- benzene (7.5%), pentosans (27.9%), lignin (20.2%) and ash content (6.6%). The adsorbate used in this study was the Methylene Blue (MB). The dyestuff was used as a commercial salt and all chemicals were of analytical reagent grade available from Al-Nasr Company, Cairo-Egypt. The chemical structures of MB as well as other physical properties are presented in a previous work [6]. A stock solution (1g/L) was prepared where other initial concentrations of dye was obtained by dilution using double-distilled water (DDW), which is used through all experimental phases. After each test, samples were allowed to settle for 5 min, centrifuge and then then analyzed using UV–Visible Spectrophotometer (8700 series Unican UV/V) at its maximum absorbance wavelength of 665nm.

2.2 Preparation of Adsorbents

Bagasse pith (BP) was washed several times with a warm distilled water to remove all dirt and solvable particles, dried in sunlight and for 3 hours at 60ºC, then grind. It was sieved for different particle size ranges, all fractions are kept in closed plastic packages where the 250-180 µm was used in all experiments. The magnetic bagasse pith (MBP) was prepared by dissolving 11.68 g of $FeCl_3.6H_2O$ and 4.30 g of $FeCl_2.4H_2O$ in 200 mL DW with strong stirring at 85ºC. Following the addition of 5g of BP and 30 minutes of stirring, 20 mL of NH_3-solution (30%) was slowly added and then stirred for 2h with keeping temperature constant at 85ºC. The MBP was washed with DW and twice with 0.02M sodium chloride, then after drying it was tested with magnet as illustrated in Figure1. All of particles were obviously attracted to the magnet, indicating that the prepared materials have a magnetic activity. The affinity of prepared adsorbent was investigated using methylene blue dye and compared with natural pith.

Figure 1: Photographs of (A) sugarcane bagasse, (B) bagasse pith (BP), (C) magnetic bagasse pith (MBP), (D) MBP attracted to magnet.

2.3 Method and Measurements

Adsorption studies were carried out in a batch manner by adding 0.1g (dp = 250:180 µm) of BP or MBP to the 50mL of dye solution at different concentrations in 100mL brown flasks. A controlled temperature rotary shaker at 300 rpm was used to achieve mixing of solution at constant temperature. For each experiment, the dye-adsorbent system was conducted for 3h and 2h in order to reach equilibrium state for BP and MBP respectively. A set of experiments were done at a particle size range of 180-100µm for different process temperature 25, 40, 60 and 75ºC while initial dye concentrations are varied between 20 to 300ppm. After the dye solution and adsorbent were separated by centrifugation at 15000 rpm for 15 min, a spectrophotometer was used to measure residual concentration at a wavelength that corresponded to its maximum absorbance (λ_{max} = 665 nm) in order to calculate the amount of dye adsorbed. Three different of two parameters models, Langmuir, Freundlich, and Dubinin-Radushkevich, were used to analyze the equilibrium data obtained in this study. The solid phase dye concentration at any time q_t (mg/g), and that at equilibrium q_e (mg/g) as well as the removal efficiency (R%) were calculated according to the following expressions:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

$$R\% = \frac{100(C_0 - C_t)}{C_0} \quad (3)$$

Where, V is the solution volume (50 mL), C_0, C_t and C_e are dye concentration at initial, at any time and at equilibrium respectively (mg/L), m is the mass of adsorbent (g).

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characteristics

The surface of the BP waste was enhanced with magnetite particles, giving it magnetic characteristics, as indicated by the SEM picture of the BP and MBP, as shown in Figure 2. A heterogeneous surface characteristic is observed with various particles shape and size. The presence of fibrous (high aspect ratio) particles in pith image is another notable aspect; this may be due to the known limitation of sieve to hold fibrous particles that pass sieve longitudinally [12].

The FTIR is a useful tool to identify the existence of certain functional groups in a molecule. In order to confirm functional groups changing for the modified pith (MBP) compared with the unmodified one (BP); the spectral analysis was employed, Figure 3. The band at 581 cm^{-1}, which appears only in the spectrum of the modified pith, is related to the Fe-O bending vibration. It is noteworthy mentioning that the Fe-O corresponding peak is broad and having high intensity which reflects high oxide content in the analyzed sample. This result further proves the successful incorporation of iron oxide within the pith matrix. Other peaks observed approximately the same for both materials indicated a presence of –OH and –CHO groups at 3410 cm^{-1} and 1733 cm^{-1} respectively.

3.2 Effect of Contact Time

Preliminary tests were conducted to determine the contact time required for the MB-pith system to reach equilibrium; this data may be used to forecast the operating conditions needed to conduct adsorption isotherms later. For each adsorbent, the test was done at two distinct initial dye concentrations of 70.9 and 138.7

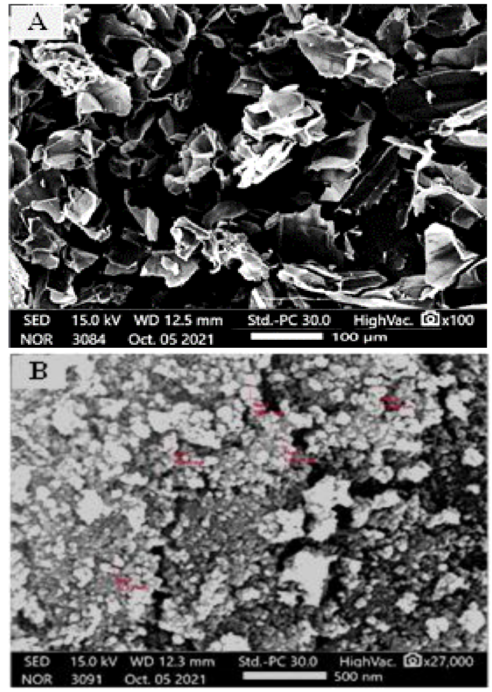

Figure 2: SEM image for: (A) BP and (B) MBP.

$mg.L^{-1}$. A decrease in dye concentration indicates that the amount of dye adsorbed rises with contact time, and attains equilibrium at about 140 and 100 minutes for BP and MBP respectively, Figure 4. In the beginning, dye uptake was rapid; later, it slowed down as it approached equilibrium. The concentration gradient between the dye molecules in the solution and the dye on the adsorbent surface is very significant in the initial stage. The process will occur at a high rate in the early stages as a result of this concentration gradient's driving force. After some time has passed, both the gradient of the dye concentration and the rate of adsorption are decreased until they reach equilibrium. All experiments for both equilibrium and kinetic study must be run for 150 and 120 min for BP and MBP respectively to assuring the equilibrium condition.

3.3 Equilibrium Isotherm

The adsorption isotherm, which is the most popular way to display adsorption data and shows how the adsorbate spreads between the liquid and solid phases in equilibrium (Ce & qe), is essential for adsorption system design. Figure 5 shows the isotherms (spreading) of dye onto BP and MBP for different temperatures, 25, 40, 60 and 75ºC for 0.18mm pith mean particle size. As it is appears from the plots, isotherm's shape is L-behavior in accordance with Giles classification [13]. The adsorption of MB is clearly temperature-dependent, showing that the process is endothermic. The improvement in dye uptake with temperature rise may be caused by a decrease in viscosity and an increase in molecular mobility at higher temperatures, which facilitates easier molecule uptake into holes that is borne out by the present result.

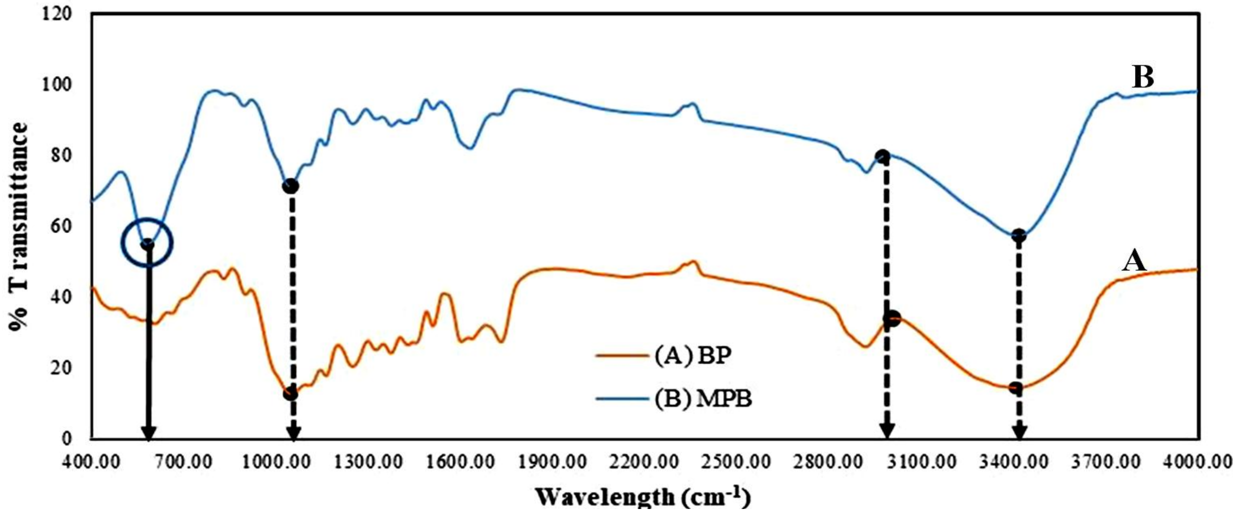

Figure 3: FT-IR spectra for: (A) (BP) and (B) magnetic bagasse pith (MBP).

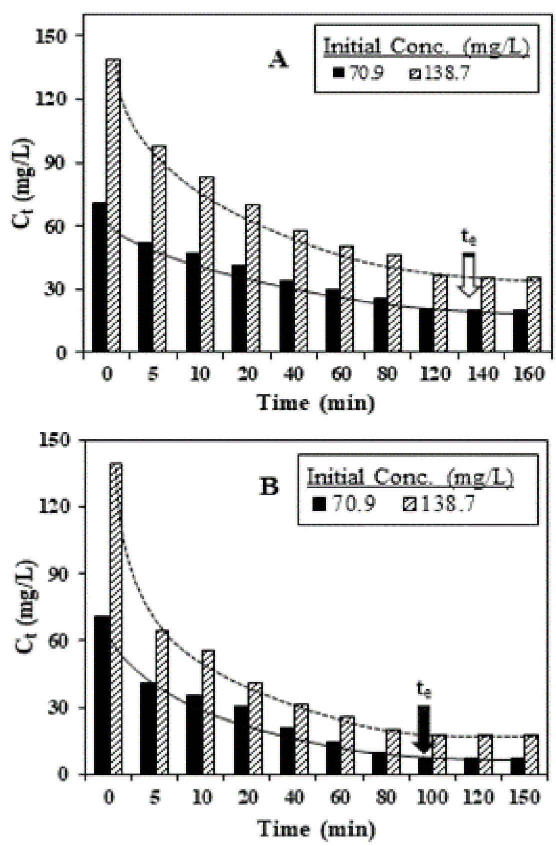

Figure 4: Contact time for adsorption of MB: (A) for BP and, (B) for MBP.

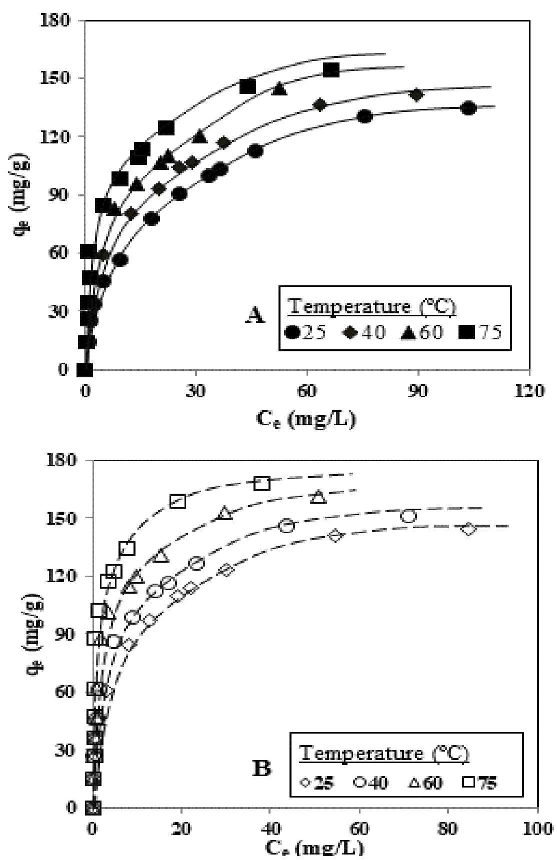

Figure 5: Equilibrium isotherms for adsorption of MB: (A) onto BP and, (B) onto MBP.

The validity of the experimental results has been predicted using a variety of isotherm models. In our work, the adsorption equilibrium data were analyzed using three of the most popular models, including the Langmuir, Freundlich, and Dubinin-Radushkevich isotherms. The Langmuir adsorption model suggests that only homogenous, specified spots within the adsorbent can undergo adsorption; once a dye molecule resides there, no further adsorption can take place, leading to monolayer adsorption. The Langmuir isotherm model's linear form is provided by:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \quad (4)$$

Where K_L is the Langmuir constant associated to the energy of adsorption ($L.mg^{-1}$), Ce is the equilibrium concentration ($mg.L^{-1}$), qe is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g).

Langmuir constants generated by plotting of $C_e.q_e^{-1}$ vs. C_e for each temperature that allows predicting Langmuir constants, Figure 6. Values of K_L, a_L and the maximum adsorption capacities, $q_{max} = K_L.a_L^{-1}$, and the correlation coefficient have been calculated and are summarized in Table 1. The adsorption capacity was increased from 147 to 196 $mg.g^{-1}$ for BP and from 150 to 175 $mg.g^{-1}$ for MBP when process temperature increased from 25 to 75ºC. The process enthalpy change, ΔH is calculated using the Langmuir constant, K_L, using the Clausius-Clapeyron equation [7], the values was found 19.2 and 17.63 $kJ.mol^{-1}$ for BP and MBP respectively that confirms the process is chemical and endothermic.

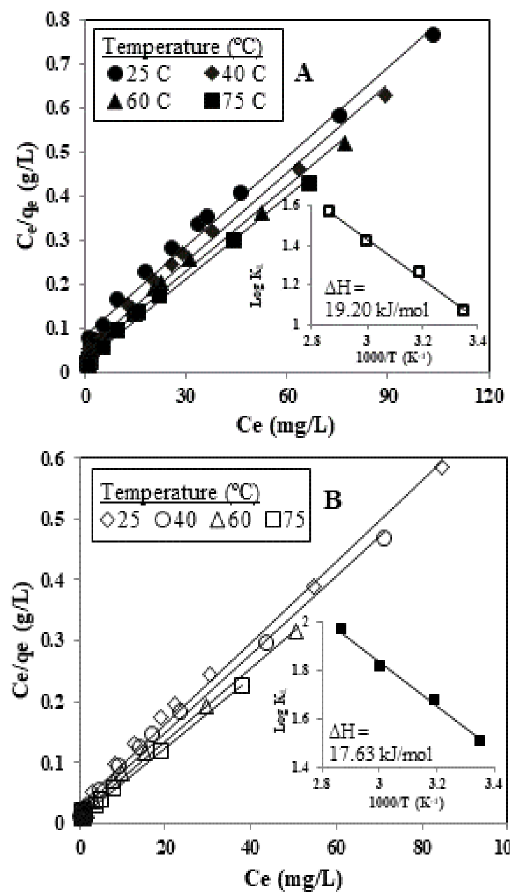

Figure 6: Langmuir plots for MB: (A) onto BP and, (B) onto MBP

The Freundlich isotherm is based on an idea that sorption takes place on heterogeneous surfaces or surfaces with a variety of affinities, these surfaces are characterized by the heterogeneity factor n^{-1}, where n is a measurement of the adsorption's departure from linearity. It based on assumption that stronger binding sites are built first, and the binding strength is weaker as site occupancy increases. The Freundlich model's linear form is as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Table 1: Parameters of Langmuir isotherm for BP and MBP at different temperatures.

Absorbent		Langmuir model K_L ($L.g^{-1}$)	a_L ($L.mg^{-1}$)	q_m ($mg.g^{-1}$)	R^2 (-)
BP	**T (ºC)**				
	25	11.64	0.079	147.1	0.99
	40	18.21	0.120	151.5	0.99
	60	25.97	0.166	156.3	0.99
	75	36.63	0.227	161.3	0.99
MBP	**T (ºC)**				
	25	32.26	0.216	149.2	0.99
	40	47.17	0.302	156.3	0.99
	60	65.36	0.392	166.7	0.99
	75	92.59	0.528	175.4	0.99

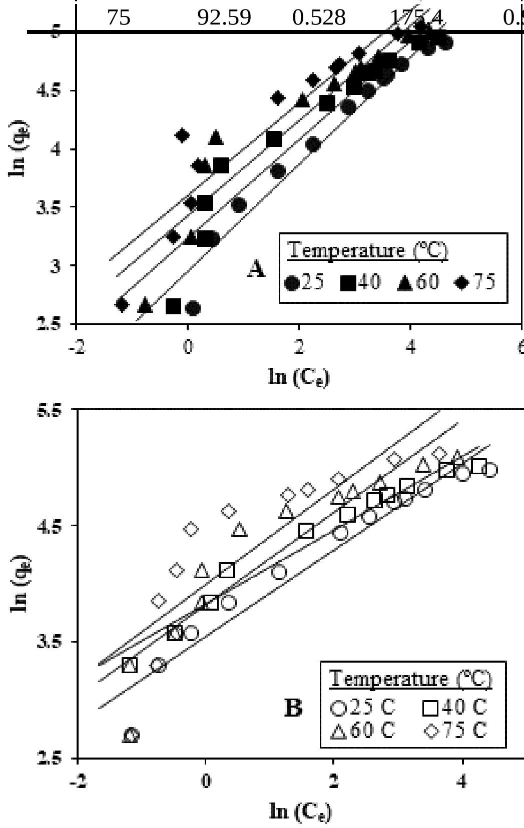

Figure 7: Freunlich plots for MB: (A) onto BP and, (B) onto MBP.

The model parameters is obtained from plotting of logarithmic values of q_e against C_e as shown in Figure 7 and are reported in Table 2. The estimated values of n are greater than one (n≥2.17), indicating that dye adsorption onto both adsorbents is favorably.

Table 2: Parameters of Freunlich isotherm for MB adsorption onto BP and MBP at different temperatures

Absorbent		Freundlich model		
		K_F ($L.g^{-1}$)	n (-)	R^2 (-)
BP	**T (ºC)**			
	25	19.13	2.17	0.96
	40	25.48	2.37	0.91
	60	30.89	2.46	0.89
	75	36.34	2.51	0.88
MBP	**T (ºC)**			
	25	34.72	2.69	0.94
	40	45.97	3.14	0.96
	60	45.93	2.53	0.85
	75	54.79	2.44	0.72

The Dubinin-Radushkevich isotherm model, the third model in this investigation defined as:

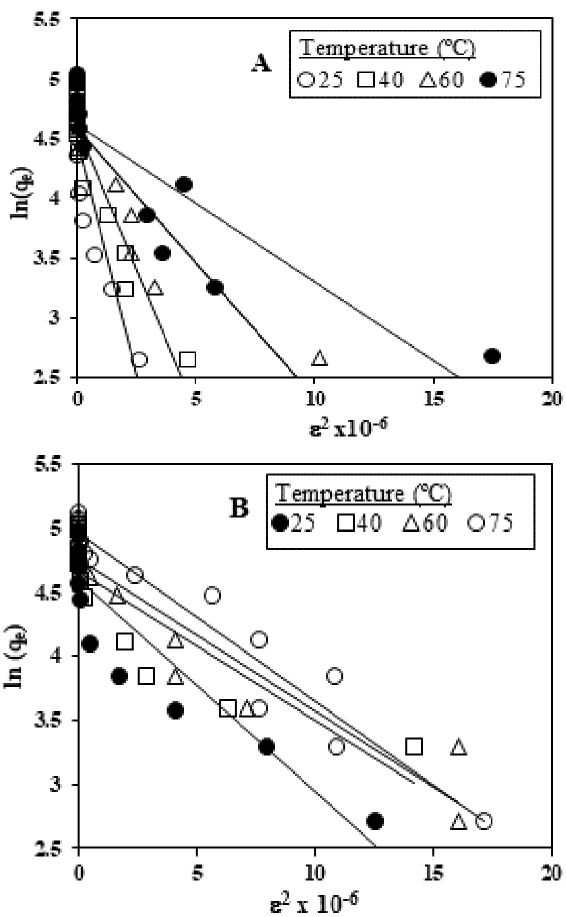

Figure 8. Dubinin–Radushkevich plots for MB: (A) onto BP and, (B) onto MBP.

$$q_e = q_m \, Exp(-B_{DR}\varepsilon^2) \qquad (6)$$

Where $\varepsilon = RT\,\ln(1+C_e^{-1})$

The constant B_{DR} gives the mean free energy E of sorption per molecule of dye when it is transferred to the surface of the adsorbent from infinity in the solution.

$$\ln q_e = \ln q_m - B_{DR}.\varepsilon^2 \qquad (7)$$

The model constants B_{DR} and q_m can be found from the slope and intercept of plotting ln qe against ε^2, as shown in Figure 8, the predicted values are reported in Table 3. The plots suggest the non-applicability of this model for the present system as well as B_{DR} values confirms a chemical nature of the process.

Table 3: Parameters of Dubinin–Radushkevich isotherm for MB adsorption onto BP and MBP at different temperatures.

Absorbent		Dubinin-Radushkevich model		
		$(2B_{RD})^{-0.5}$ ($J.mol^{-1}$)	q_m ($mg.g^{-1}$)	R^2 (-)
BP	**T (ºC)**			
	25	7910	89.1	0.77
	40	1000	98.6	0.79
	60	1580	97.9	0.87
	75	2240	100.3	0.81
MBP	**T (ºC)**			
	25	1580	99.2	0.85
	40	2240	105.3	0.76
	60	2240	116.5	0.98
	75	2240	143.7	0.93

The highest value of correlation coefficient (R^2) (closer to unity), which represents the fitness of the isotherm to experimental data, was used to select the optimal model. The Langmuir model demonstrated a better fit to the experimental data than the other models, as is evident from the predicted parameters presented in above tables, R^2 = 0.99, that means dye was applied to the pith surface as a monolayer.

4. CONCLUSIONS

Magnetic bagasse pith was synthesized, characterized and its ability as an adsorbent was investigated. Magnetization does not contribute to any drawback on the porosity, surface area of BP and performance of the adsorption process. Remediation of a basic blue dye from aqueous solutions onto conventional bagasse pith and that modified with magnetite particles was investigated at different operating temperatures. The adsorption capacity was slightly improved due to the magnetization of pith as well as the process time decreased, which is a good advantage from an economic point of view. Three distinct isotherm models were used to fit the equilibrium data. The nature of dye adsorption on bagasse pith is consistent with Langmuir assumptions as evidenced by the greater correlation coefficient (0.99) for this model. The maximum capacities were 149.2, 156.3, 166.7 and 175.4 $mg.g^{-1}$ for magnetic pith at 25, 40, 60 and 75ºC processes temperature respectively. Hence, the magnetic bagasse pith (MBP) is a feasible option in replacing conventional one for wastewater treatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this study.

Declaration of Funding

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