Biosorption of Methylene Blue from Aqueous Solution using Unmodified Plantain Stalk (UPS) Biomass

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ABSTRACT: Plantain stalk have generally been constituted environmental waste, yearly after harvest seasons. Water coloration has been another expensive environmental pollution to remediate. In this research work, the potential removal of Methylene Blue (MB) from aqueous solution using plantain stalk as adsorbent was studied. 300 g of powdered unmodified plantain stalk (UPS) was used as sample in the adsorbent experiment. Various experimental parameters of MB were evaluated. Optimum temperature of 30 ^{0}C, pH of 5 and adsorbent dose of 1g was maintained throughout the experiment. Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and BET (Brunauer-Emmett-Teller) were also used to analyze the sample both before adsorption and after adsorption. The BET summary was; slope = 22.113, Intercept = 2.577e+00, correlation coefficient = 0.996943, C constant = 9.580, Surface Area = 141.046 m^2/g.

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1.0 INTRODUCTION

Dyes are widely used in industries such as textiles, rubber, printing, lather, cosmetics and food to add colors their products[1]. As a result, they generate a considerable amount of colored wastewater. There are more than 10,000 commercially available dyes with 7 x 10^5 tonnes of dye stuff produced annually. It is estimated that 2 % of dyes produced annually is discharged in effluents from associated industries[1,2]. Among various industries, textile industry ranks first in usage of dyes for coloration of fiber[3].

There have been environmental concerns to coloured effluents purely because of their appearance. Most coloured effluents are composed of non-biologically oxidized organic components because of the molecular size and structure of the dyestuffs[4,5]. Colour dye wastes frequently contain a spectrum of heavy toxic organic pollutants and the presence of dye may indicate the existence of toxicants. Colour in waste water has to be removed before it is discharged into the water body or onto the land. It has been demonstrated that dye colour removal by adsorption is a better effluent treatment method. New materials like; silica gel, lignite, peat, coal and agricultural by-products such as coconut husk have been investigated for their removal of colours and dyes from waste water[6].

Activated carbon has found wide acceptance as a good adsorbent by virtue of its high removal capacity, but its disadvantage is that it is expensive[3,6]. An alternative to activated carbon is biosorption. The search for new technologies involving the removal of toxic materials from waste waters has directed attention to biosorption, based on binding capacities of various agricultural by-products. Biosorption can be defined as the ability of biological materials to accumulate substrates from waste water through metabolically mediated or physico-chemical pathways of uptake. The biosorption process involves a solid phase (biosorbent i.e. the biological material) and a liquid phase (solvent, normally water) containing a dissolved specie to be sorbed (sorbate)[4]. Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms[7,8,9]. The process continues till equilibrium is established between the amount of the sorbate and its portion remaining in the solution. The mechanism of biosorption is complex, and usually involves ion exchange, chelation and adsorption[7].

Water quality is extremely important because constant access to good quality water is necessary for life as well as the economy[10]. Since rivers constitute the main inland water resources for domestic, industrial, and irrigation purposes, it is imperative to have a monitoring program, providing a representative and reliable estimation of the quality of surface waters, necessary to prevent and control water pollution[11]. Contamination of river water by industrial effluents has been given much attention due to their low biodegradability and toxic effects. Total solid (TS) are considered important in determining the usage of water[12,13,14]. They are not suitable for both irrigation and drinking purposes. The scarcity of clean water and pollution of fresh water has therefore led to a situation in which one-fifth of the urban dwellers in developing countries and three quarters of their rural dwelling population do not have access to reasonably safe water supplies[15,16]. Textile industries have been placed in the category of most polluting industries by the Ministry of Environment and Forests[17,18].

Furthermore, the improper and indiscriminate disposal of textile effluents in natural waters and land is of great concern. The textile effluent contains organic and inorganic chemical species which have adverse effect on water quality and growth of all plants and animals[19].

Textile industry can be classified into three categories viz., cotton, woolen, and synthetic fibers depending upon the used raw materials. The cotton textile industry is one of the oldest industries in China. The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, such as complex components, many aerosols, high chroma, high COD and BOD concentration as well as much more hard-degradation materials[7],[8,15]. The toxic effects of dyestuffs and other organic compounds, as well as acidic and alkaline contaminants, from industrial establishments on the general public are widely accepted. At present, the dyes are mainly aromatic and heterocyclic compounds, with color-display groups.

Pollution control is important to reduce the level of health risk it poses to the environment; thus, industries are mandated to properly dispose waste through accredited waste industrial disposal agencies which help ameliorate the adverse effect of industrial chemical disposed waste on the environment[12,13].

According to recent statistics, each year about 70 billion tonnes of wastewater from textile and dyeing industry are produced and requires proper treatment before being released into the environment. Therefore, understanding and developing effective printing-dye industrial wastewater treatment technology is environmentally important[10].

2.0 MATERIAL AND METHODS

2.1 MATERIALS

2.1.1 Apparatus/Equipment

Volumetric Flask (100 cm^3), 250 ml conical flask and 100 ml measuring cylinder, Manual grinder : corona, Pipettes, Electronic weighing balance : Ttb3 1g china, Water bath shaker : SHA – C, 0 -630LI china, Sieve with mesh size 0.2 - 0.4 mm,

Air-tight plastic containers, Electronic watch, Spatula, Drier/Oven : ST – 226, 881H6, Hungary, Six pieces of syringes, Plastic funnel, Beaker (500 and 250 cm^3), UV Spectrophotometer 668 nm : (shimadzu, model UV/700, japan), Reagent bottles, Air tight buckets, Marker, Masking tape, Sieve and Spatula.

2.1.2 Reagents

Water: Tap water and distilled water, MB (MB) dye muby chemicals, gujarat, india.
Unmodified and modified plantain stalk were used in this work.

2.2 METHODS

2.2.1 Sample Collection

The plantain stalk was collected from Akuma Oru-East Local Government Area of Imo State, where it is generated as a primary agricultural waste. It was identified by Prof. Mbagwu who is a renowned botanist, in the Department of Botany, Imo State University Owerri.

2.2.2 Preparation of the Sorbent

The collected plantain stalk was extensively washed with tap water, to remove dirt and other particulate matter that might interact with the sorbate. Then washed with distilled water, cut into small pieces and oven dried for 8 hours at the temperature of 70 ºC, the sample will be ground using manual grinder. 300 g of UPS were weighed with weighing balance and then stored in an air-tight plastic container and used for biosorption experiment.

2.2.3 Preparation of Solutions of MB

MB selected as sorbate can be use without further purification. The stock dye solution was prepared by dissolving 1g of MB in distilled water and making up the solution to 1000 cm^3 in one litre volumetric flask with distilled water. The stock solution was1000 mg/l solution (i.e. 1000mg/dm^3 solution) while the working solutions were prepared by dilution of the stock solution with distilled water when needed. The dilution was made using the relation

$$C_1V_1 = C_2V_2 \qquad 1$$

Where
C_1V_1 = Concentration and Volume of the stock solution.
C_2V_2 = Concentration and Volume of requires working solution

2.2.4 Preparation of 0.1M NaOH and 0.1M HCl

Exactly 4 g of NaOH were weighed and dissolved with same quantity of distilled water. The volume was made up to 1000 cm^3 mark in the 1 litre volumetric flask with water. 5.6 cm^3 of Conc. HCl, 1.8 g/cm^3 density and 36 % purity was diluted to 1000 cm^3 in the 1 litre volumetric flask using distilled water.

2.2.5 Percentage Removed

100 cm^3 MB concentration range 25, 50, 100, 150, 200 and 250 in mg/l was prepared and each put in a 250 cm^3 conical flask. The pH of each solution was adjusted to 5. Then, 1 g of plantain stalk powder was added into each flask. The temperature was set at 30 ºC. Absorbance of clear liquid from each was read from the spectrophotometer. Percentage removal of dye was calculated using:

$$\%\,R = \frac{C_0 - C_t}{C_0} \times \frac{100}{1} \qquad \text{…….. 2}$$

From the results of these biosorption experiments the biosorption isotherm models was plotted.

2.2.6 Experimental Methods and Measurements

Biosorption experiments will be carried out in a reagent bottle containing 100 ml of dye solutions at different concentrations and initial pH values. The initial pH value of the solution will be previously adjust with 0.1 M HCl or NaOH using pH metre. The adsorbent 1g will be added to a reagent bottle containing 100 ml of 25 mg/l concentration and then will be seal to prevent any change in volume during the experiments. The solution with adsorbent will be kept for 5minutes in a water bath shaker with syringe, a small sample will be collected and will be analysed in a UV-Spectrophotometer. Wavelength 668nm. Using the same 25mg/l concentration the quantity of dye removed will be monitored at various contact time; 5, 10,15, 30, 60, 90, 120, 150, 180, 210 and 240 minutes. Similar experiment will be carried out on the reagent bottles containing 50, 100, 150, 200 and 250mg/l concentration. The results obtained from the spectrophotometer will be recorded.

Using,

$$Slope = \frac{Absorbance}{Concentration} \qquad \text{…….. 3}$$

Where

$$Concentration = \frac{Absorbance}{Slope} \qquad \text{…….4}$$

And

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad \text{…….. 5}$$

q_t , was used to calculate the biosorption capacity at a given time at mg/l.

Where;
C_0 = Initial Concentration of MB in mg/l
C_t = MB concentration in solution at time t.
m = Mass of biomass used in g/l.
V = Volume of the solution in litres (l).

2.2.7 Procedure for Adsorption at Temperatures of 25, 30, 35, 40, 45 And 50.
at constant pH of 5

200 mg/l of the MB working solution was
water bath shaker with temperature set at 25 ºC and allowed to shake for 240 minutes.
At the end of the 240 minutes in the water bath shaker, 1 ml of the solution were extracted. The
absorbance at temperature 25 ºC was obtained using the UV-Visible spectrophotometer.
This process was repeated for 30, 35, 40, 45and 50 ºC.

2.2.8 Procedure for pH (4, 5, 6, 7, 8, 9 and 10) at a constant temperature of 30°C

200 mg/l concentration of MB working solution was measured into a beaker; pH meter was used to measure the current pH of the solution. At a pH higher than 4, small drops of Hydrochloric acid (HCl) was added while stirring to acidify the solution then measured after each addition until the desired pH of 4 is achieved. If the pH is lower than 4, few drops of sodium hydroxide will be added to dilute the solution and will be measured after each addition until the desired pH of 4 is achieved. 1 gram of the adsorbent were also weighed and introduced into same sampling bottle**.** The sampling bottle containing both the adsorbent and working solution was fixed into a water bath shaker at 30 °C temperature and allowed to shake for 240 minutes. At the end of the 240 minutes in the water bath shaker, 1 ml of the solution were extracted. The adsorbance at pH 4 was obtained using the UV- Visible spectrophotometer. This process was repeated for pH 5, 6, 7, 8, 9 and10.

3.0 RESULTS AND DISCUSSION

3.1 RESULTS

Table 1: Calibration of MB at 30 °C

Conc. (Mg/L)	Absorbance (A)
0	0.000
25	0.015
50	0.028
100	0.045
150	0.071
200	0.125
250	0.133

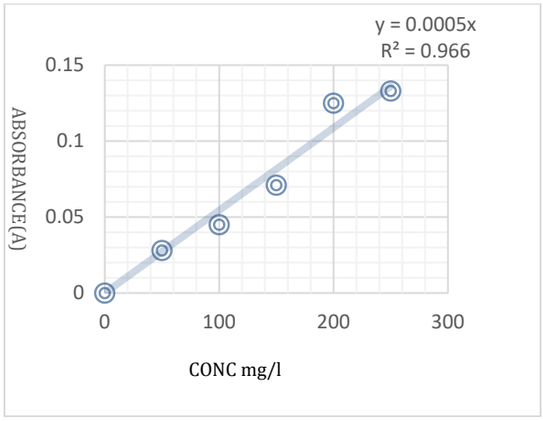


Figure 1: Calibration graph of MB

Table 2: Effect of Contact Time at 25 mg/l Initial Conc of MB at 30 °C and pH = 5 using 1g of UPS

Time (min)	100 ml of 25 mg/l Initial Conc	C_t (mg/l)	q_t (mg/g)
5	0.011	22.000	0.300
10	0.0096	19.200	0.580
15	0.0092	18.400	0.660
30	0.0085	17.000	0.800
60	0.0071	14.200	1.080
90	0.0069	13.800	1.120
120	0.0064	12.800	1.220
150	0.0061	12.200	1.280
180	0.0059	11.800	1.320
210	0.0057	11.400	1.360
240	0.0054	10.800	1.420

Table 3: Effect of Contact Time at 50 mg/l Initial Conc of MB at 30 °C and pH = 5 using 1g of UPS

Time (min)	100 ml of 50 mg/l Initial Conc	C_t (mg/l)	q_t (mg/g)	%R
5	0.0024	48.000	0.200	4.000
10	0.023	46.000	0.400	8.000
15	0.0224	44.800	0.520	10.400
30	0.022	44.000	0.600	12.000
60	0.020	40.000	1.000	20.000
90	0.018	36.000	1.400	28.000
120	0.017	34.000	1.600	32.000
150	0.015	30.000	2.000	40.000
180	0.013	26.000	2.400	48.000
210	0.011	22.000	2.800	56.000
240	0.010	20.000	3.000	60.000

Table 4: Effect of Contact time at 100mg/l Initial Conc of MB at 30°C and pH = 5 using 1g of UPS

Time (mins)	100 ml of 100 mg/l Initial Conc	C_t (mg/l)	q_t (mg/g)	%R
5	0.045	90.0	1.00	10.0
10	0.044	88.0	1.20	12.0
15	0.041	82.0	1.80	18.0
30	0.039	78.0	2.20	22.0
60	0.037	74.0	2.60	26.0
90	0.035	70.0	3.00	30.0
120	0.025	50.0	5.00	50.0
150	0.023	46.0	5.40	54.0
180	0.021	42.0	5.80	58.0
210	0.019	38.0	6.20	62.0
240	0.015	29.0	7.00	71.0

Table 5: Effect of Contact Time at 150 mg/l Initial Conc of MB at 30°C and pH = 5 using 1g of UPS

Time (mins)	100 ml of 150 mg/l Initial Conc	C_t (mg/l)	q_t (mg/g)	%R
5	0.071	142.0	0.800	5.33
10	0.070	140.0	1.000	6.66
15	0.068	136.0	1.400	9.33
30	0.066	132.0	1.800	12.00
60	0.064	128.0	2.200	14.67
90	0.056	112.0	3.800	25.33
120	0.054	108.0	4.200	28.00
150	0.050	100.0	5.000	33.33
180	0.044	88.00	6.200	41.33
210	0.032	64.00	8.600	57.33
240	0.014	28.00	12.20	81.33

Table 6: Effect of Contact Time at 200 mg/l Initial Conc of MB at 30°C and pH = 5 using 1g of UPS

Time (mins)	100 ml of 200 mg/l Initial Conc	C_t (mg/l)	q_t	%R
5	0.098	196.000	0.40	2.00
10	0.097	194.000	0.60	3.00
15	0.096	190.000	1.00	5.00
30	0.091	182.000	1.80	9.00
60	0.085	170.000	3.00	15.0
90	0.081	162.000	3.80	19.0
120	0.070	140.000	6.000	30.000
150	0.060	120.000	8.000	40.000
180	0.050	100.000	10.000	50.000
210	0.025	50.000	15.000	75.000
240	0.015	30.000	17.000	85.000

Table 7: Effect of Contact Time at 250 mg/l Initial Conc of MB at 30 °C and pH = 5 using 1g of UPS

Time (mins)	100 ml of 250 mg/l Initial Conc	C_t (mg/l)	q_t (mg/g)	%R
5	0.123	248	0.20	0.80
10	0.122	244	0.60	2.40
15	0.120	240	1.60	4.00
30	0.116	232	1.80	7.20
60	0.112	224	2.60	10.40
90	0.106	212	3.80	15.20
120	0.102	204	4.60	18.40
150	0.081	162	8.80	35.20
180	0.055	110	14.0	56.00
210	0.035	70.0	18.0	72.00
240	0.015	30.0	22.0	88.00

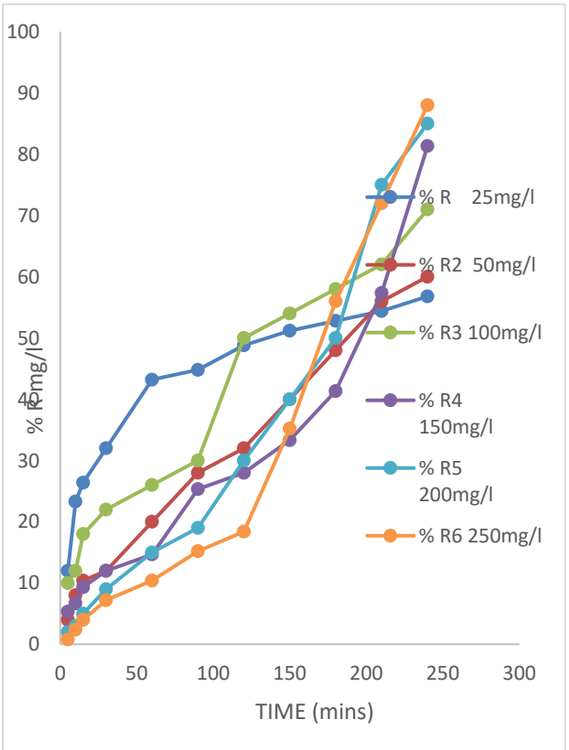


Fig 2: Effect of Contact Time at various Conc of MB at 30 °C and pH = 5 using 1g of UPS

Table 8: Effect of T oC at 200 mg/l Initial Conc of MB at pH = 5 using 1g of UPS

T (^{0}C)	25	30	35	40	45	50
Abs (A)	0.014	0.008	0.015	0.016	0.020	0.021
C_e(mg/l)	28.0	16.0	30.0	32.0	42.0	40.0
C_0-C_e (mg/l)	172.0	184.0	170.0	168.0	160.0	158.0
q_e(mg/l)	17.20	18.40	17.00	16.80	16.00	15.80
R%	86.0	92.0	85.0	84.0	80.0	79.0

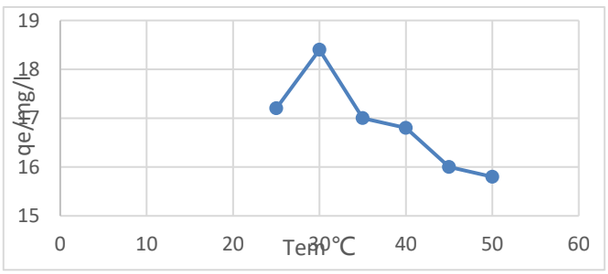


Fig 3: Effect of T ^{o}C at 200 mg/l Initial Conc of MB at pH 5 using 1g of UPS

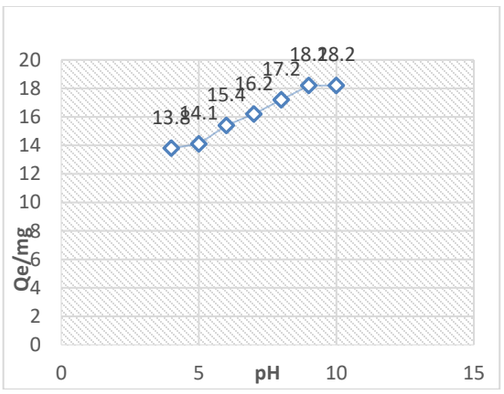


Fig. 4: Effect of pH at 200mg/l Initial Concentration of MB at 30^{o}C using 1g of UPS

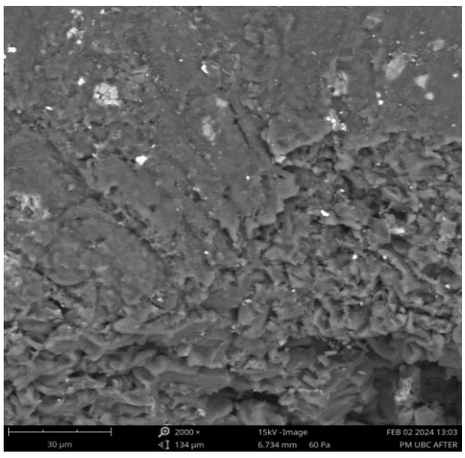


Fig. 5: SEM View of UPS Before Adsorption Using 250 mg/L Conc of MB At 30^{o}C

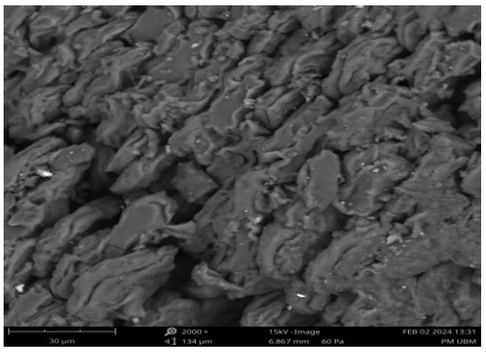
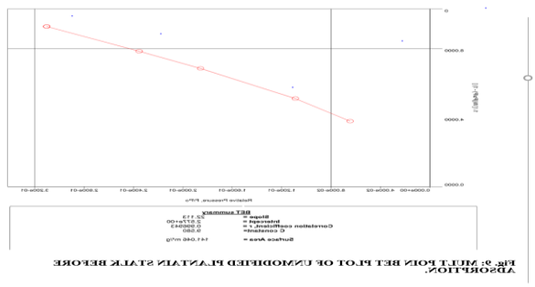


Fig. 6: Sem View of UPS After Adsorption Using 250 mg/L Conc of MB At 30 ^{o}C Using 1g of UPS



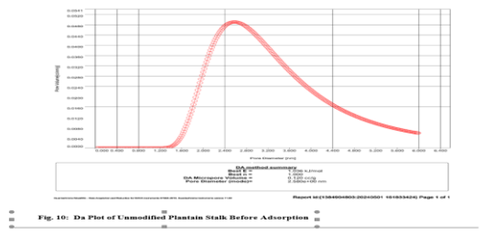


Fig. 10: Da Plot of Unmodified Plantain Stalk Before Adsorption

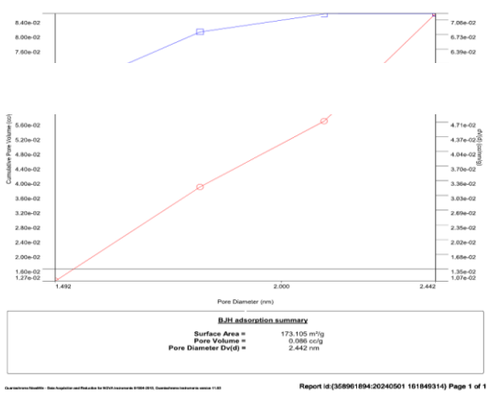


Fig. 11: BJB Method Adsorption of Unmodified Plantain Stalk Before Adsorption Process

3.2 DISCUSSION

The Percentage sorption increases as the concentration increases. The adsorption of MB on UPS at pH of 5, 200 mg/l initial concentration of MB for 240mins, the dye uptake was found to be at optimum when the temperature was 30˚C. Therefore, the best temperature for methylene dye adsorption or removal was achieved when the temperature was 30°C. The adsorption of MB increases as the pH increases at 30˚C 200mg/L initial concentration of MB for 240 mins.

The FTIR spectra of untreated plantain stalk were taken before and after the adsorption of MB to ascertain the possible involvement of the functional groups on the surface of adsorption of MB.

From the FTIR result both before and after adsorption it reveals that the major functional groups responsible for adsorption was OH 3500-3000cm^{-1} stretching or vibration occurred at this point, other functional groups includes band at 3287.5cm^{-1} , 2318.5cm^{-1} 90.411cm^{-1} 2146.9cm^{-1} 1733.2cm^{-1} and 1585.3cm^{-1} were shifted to 3324.8cm^{-1} 2322.1cm^{-1}, 99.094 cm^{-1}, 2195.4 cm^{-1} 1739.6cm^{-1} and 1595.9cm^{-1} after MB adsorption.

This is an indication that OH, C=O, C−C, C=C, COOH and C=C group could be involved in the adsorption of MB (this shifting was more noticeable when modified plantain stalk were used)[20].

CONCLUSION

From the results obtained, the viability of using processed plantain stalk as an improved, inexpensive and recyclable sorbent material for MB removal from aqueous solutions showed a great potentials[21]. Further studies are recommended on industrial, scale-up and commercialization strategies for this particular sorbent.

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