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Economical and Eco-Friendly Adsorbent Derived from Coffee Waste for Efficient Adsorption of Methylene Blue: Characterization, Evaluation and Optimization Studies

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Authors' contributions

This work was carried out in collaboration between all authors. Authors MS and AA designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors SAM and ED managed the analyses of the study. Author KAA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

In this study, treated coffee ground wastes (CGW) was evaluated for adsorption of methylene blue (MB) from contaminated solution using contact time, initial dye concentrations, adsorbent dose, and solution temperature as operational factors. The adsorbent was treated using chemical activation with potassium carbonate (K_2CO_3), followed by thermomechanical treatment via an extrusion process. The characterization study of the adsorbent was conducted using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) and X-ray fluorescence spectroscopy techniques. The adsorption equilibrium was reached after 30 min for MB and it was observed also that adsorption capacity decreased but percentage removal increased with increases in adsorbent mass. The maximum adsorption capacity of K_2CO_3-coffee powder was found to be 169.49 mg/g.

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1. INTRODUCTION

Water resources are known as the sources that produce water for our various kinds of uses and also those sources that yield great benefits for humans life. Providing a clean and reliable water supply is critical for various types of beneficial products such as, food production, energy for domestic purpose, transportation, recreation, and maintenance of natural ecosystems [1-3]. Today, wastewater treatment is one of the main emerging areas of research due to rapid industrialization, domestic use, modern technologies for agriculture, and other geological, environmental and global changes. A scientific report indicates that very little fresh water that is available for use, about 1.0% of the total water on earth [1]. However, water consumption continues to increase worldwide, followed by an increase in the generation of a large amount of liquid wastes every day, which contain hazardous materials that have harmful effects on both human and aquatic life [1-8]. Scientific studies pointed out that about 300-400 million tons of hazardous materials such as heavy metals, toxic sludge, solvents, chemicals, oil, synthetic dyes, acids and alkalis, salts, surfactants, industrial wastes and other hazardous substances are still end up into the environment every year [5]. As example, about 1200 million liters of colored wastewater resulting from textile industry are discharging every day in India [9], while 2531.67 million tons of wastewater were discharged by the mining operations in China in 2014 [10].

It was reported that about 844 million people do not have a basic drinking water source and about 230 million people take over 30 min daily for collecting water from clean water streams [6]. It is also estimated that about 2.6 billion people in the world without proper sanitation facilities, representing up to 42% of the world's population, and around 1.1 billion people do not have access to any type of improved drinking water facility [1].

Synthetic dyes (SD) are widely used in many areas of high technology such as dyestuff, paper, printing, carpet, plastic, food and cosmetic, paint and textile industry to provide color for their products, and as additives in petroleum products [8]. It is reported that in the dyeing section of the textile industry, about 1000 liters of water are used for every 1000 kg of finished clothes [11]. Globally, more than 100,000 commercially available dyes have been reported nowadays. These dyes are organic contaminates and are considered the most dangerous pollutants due to their toxicity to many life forms [1-5,8,11].

A number of available physicochemical processes have been established to remove hazardous chemicals from contaminated environment, which include ion exchange, chemical precipitation, electrochemical treatment, chemical oxidation and coagulation/flocculation, to remove such contaminants [4]. However, most of these processes are not economically and environmentally approaches due to high-operating cost, and have low efficiency to treat a wide range of pollutants, toxic by product formation, high chemical reequipment; they also generate a ton of secondary waste (sludge disposal) after removal process or even during the synthesis of adsorbents [7-12]. However, adsorption process is being seen as more promising for the long-term, as it is considered as environmental friendliness and economical process for the adsorptive uptake of hazardous and toxic substances from contaminated water with low energy consumption [7, 9,13].

Commercially activated carbon (CAC) is almost the highest adsorbent material with a wide range of applications in water and wastewater treatment due to its excellent properties and high ability to adsorb both organic and inorganic pollutants. But CAC is still very expensive today [14]. For this reason, as well as in case of utilization of new potential adsorbent, it is very beneficial to use by-products resulting from the processing of various renewable potential raw materials. Therefore, researchers and scientists all over the world are interesting for the production of different alternative adsorbents to replace the expensive activated carbon [15]. Agricultural products and by-products/wastes, food wastes, as well as forestry residues are very cheap materials compared to commercial CAC. As a result of the expanding agricultural activities and food production, nearly 1.3 billion tons of food residues is generated annually around the world [15]. This waste constitutes a serious environmental issues since it is disposal by conventional ways like burning or dumping and this release a lot of hazardous material and contaminates into the environment [15]. Therefore, recycling appears the best solution to add economical value to such residues and consequently minimize its burden. As a

biomaterials, the main components of agricultural wastes are cellulose, hemicelluloses, and lignin, which contain large amounts of functional groups like hydroxyl (OH) and carboxyl groups (COOH). These functional groups can act as binding sites. Therefore, these natural materials could be utilized as bioadsorbents in their raw and modified states or even in the production of so-called activated carbon [14-17].

In recent years, several attempts are made to convert agricultural by-products into a low-cost material-based bio-adsorbents [18-22]. Agro-industrial and plant waste are inexpensive as they have no economic value. Although, unmodified plant waste, agricultural and agro-industrial residues have received a wide attention of adsorption studies due to the its abundant in nature, required a small processing and easy regeneration. But, most of the adsorbents used in the raw state still require modification to enhance their adsorption efficiency. Natural adsorbent materials can be treated by physical and chemical approaches. The process of modifying natural adsorbents derived from agricultural and plant wastes, can offer many advantages, such as enhancing porosity and stability, improving mechanical and hydrophobic properties, and modifying the removal efficiency of adsorbents [23]. In addition, such modification can solve many limitations of adsorbents such as low adsorption efficiency, high chemical oxygen demand (COD) and biological chemical demand (BOD), as well as total organic carbon (TOC) due to release of soluble organic substances contained in the plant materials, release a lot of color into water stream. The increase of the COD, BOD, and TOC can cause depletion of oxygen content in water and then can threaten the aquatic life [24,25]. Treatment process of agricultural by-product/waste is carried out by impregnation with some chemicals, which is normally an acid such as phosphoric acid (H_3PO_4), a strong base such as sodium hydroxide (NaOH), or a salt such as zinc chloride ($ZnCl_2$). Due to their corrosive natures and the harmful effects associated with their disposal, alkali hydroxide and zinc chloride are not preferred [26]. Potassium carbonate (K_2CO_3) is used as a food additive; thus it can be used safely as a chemical agent in modifying adsorbents [27].

The large quantities of waste resulting from processing coffee fruit make it one of the most polluting activities in agriculture. Scientific work has reported that coffee production reached about 680 million tons in 2008 [28]. In the last few years, the consumption of coffee has rapidly increased, especially among young people. According to a survey done in the year of 2016 by Sulyman [4,14], which included 25 cafes in the city of Tripoli, Libya, the average generation of coffee ground wastes by only the 25 cafes is estimated to be in the range of (36-45) tons, and a large amount of this waste is still kept in big plastic bags for disposal by conventional methods, burned or dumped. It is also estimated that in one of these cafes, more than 100 cups of coffee are drunk within an hour, while in the city of Gdansk, Poland, at one café that was surveyed, more than 1600 cups of coffee are consumed daily. And the average of coffee wastes at the 25 cafés is estimated to be in the range of 72-90 tons. Another study done in Australia reported that, there are about 921 cafes and coffee shops in the city of Sydney sold 100 million cups of coffee every year, which are generating approximately 3000 tons of waste coffee grounds. Only a small amount (7%) of such waste has been recycled in worm farms and gardens. But 93% of coffee wastes are still end up in landfill [29]. However, coffee grounds are carbonaceous and have the potential to be converted into an adsorbent. It has been reported that the amount of carbon dioxide produced by the combustion of one tons of coffee grounds is estimated to be 538 g [30].

Therefore the main objectives of this study are summarized as follow: 1) To use coffee ground waste as a recycled material by reusing it as green adsorbent for dye removal from contaminated solution. 2) Study the characterization of adsorbent material. 3) To determine optimum conditions for removing methylene blue, from contaminated solution using modified coffee waste. 4) To examine the thermodynamic parameters. 5) To identified functional groups on the adsorbent surface, as well as the morphological behavior. 6) Economic feasibility and environmental protection are also major objectives of this study. 7) The use of thermomechanical activation under shear rate forces using extrusion process was also one of the main purposes, and this development was perhaps the novelty of this work.

2. EXPERIMENTAL WORK

2.1 Materials

The adsorbent, biomass (coffee waste) was obtained from a local coffee processing (coffee

shops) in Tripoli. Methylene blue (MB) was purchased from B.D.H. Chemicals, Ltd., England. MB has molecular formula C16H18N3ClS (Mol. wt. 319.85 g/mol). It was used without further purification. Other reagents include K_2CO_3 solution, HCl and dilute NaOH solutions. The solution pH was adjusted by base (0.1 M NaOH) and acid (0.1 M HCl). Working solution was kept constant at 100 ml for all experiments. Distilled water was used throughout the experiment. Instruments employed in this study include a FTIR spectrophotometer (Tensor 27 Bruker, USA- at the range of 450 - 4000 cm-1), digital shaker (GFL 3005 model, Germany), an Electronic weight balance (Sartorius, 1000±0.0001g), pH-meter (740 Inolab WTW with a SenTix 20 pH model double electrode), Sieves of about 50–250µm size, Themogravimetric (TA instrument (SDT Q500), and X-ray fluorescence spectroscopy (Bruker 1kw WD-XRF model S8 Tiger spectrometer). Scanning electron microscopy at acceleration voltage of 10 kV. The stock solution of dye was prepared by dissolving 1000 mg of MB dye in distilled water in a one liter volumetric flask and made to a concentration of 1000 mg/l. The working solutions of different concentrations were obtained by diluting the dye stock solution to give the appropriate concentrations (50-200 mg/l). A UV–visible spectrophotometer (Specord 205, UV-analytikjena Germany) determines the absorbance of the required MB solutions at 665 nm. The calibration curve was obtained by drawing the absorbance recorded from the spectrophotometer versus the prepared concentration of solution (Fig. 1). This curve was then used to calculate the final concentration of dye in the solution. The procedure was similar to that conducted in previous study [16]. The thermo-mechanical treatment of coffee residues was performed via the extrusion process using a single-screw extruding machine under shear forces system at processing temperature of 170^{o}C. Brunauer-Emmett-Teller (BET) nitrogen adsorption technique is conducted to evaluate the surface area of the adsorbent which involved the application of physical adsorption of nitrogen at 80^{o}C in a Micromeritics ASAP 2020 apparatus, USA.

2.2 Preparation of Adsorbent

Freshly biomass, coffee ground wastes (CGW) was collected, placed in plastic bags and immediately transported to the laboratory. The biomass was washed with warm water many times to remove the colors. This wash was repeated with distilled water followed by acetone to remove oil, impurities and other undesirable materials. It was dried in sunlight for five days followed by a microwave heating system at 600 watt. The microwave heating system was conducted three times (1 min for each), thus the total drying period was 3 minutes. The dried materials were then impregnated in K2CO3 solution in weight ratio (1:1) and left overnight. Subsequently, the treated samples were extruded via an extrusion process under a shear rate of 80 rpm and a temperature of 170^{o}C. It was grinded to desired particle less than 200 µm. Finally, the treated samples were washed several times with distilled water until a neutral pH was reached, dried and stored for further use. The plan design of this work is shown in Fig. 2.

2.3 Adsorption Process

Adsorption experiments were carried out in 250 ml flasks and the total volume of the reaction solution was kept at 100 ml. The flasks were shaken at 250 rpm for an equilibrium time of 60 min on a digital shaker. The influence of adsorbent dosage on the adsorption of MB was investigated with different adsorbent mass (0.05–0.25 g) in a 100 ml dye solution of 100 mg/l concentration, pH 7.0 and shaken till equilibrium time. Impacts of shaking time and initial concentration were investigated by shaking 0.10 g of the adsorbent at room temperature and pH of 7.0 at different time intervals and different initial concentrations. Adsorption isotherm experiments were performed by contacting 0.10 g of adsorbent with 100 ml of MB aqueous solution of (50–200) mg/l in a series of 250 ml flasks, maintained at room temperature and optimum conditions. The flasks were taken out at some intervals. After adsorption, the solid phase (adsorbent) and the supernatants were separated by filter paper and samples for analyses (5 ml) withdrawn with a clinical syringe and analyzed for residual dye concentration using a UV– Visible spectrophotometer at λ_{max} 665 nm. The capacity of adsorbent (q_e) and percentage removal (%) were estimated using Equations 1 and 2, respectively [16,17]. The influences of temperature on the removal data were investigated by performing the adsorption experiments at different temperatures (25, 40, 50 and 60^{o}C) with 0.1 g of the adsorbent and other conditions kept constant. The equilibrium data were analyzed using the Langmuir, Freundlich and Temkin isotherms and the characteristic parameters for each isotherm were estimated.

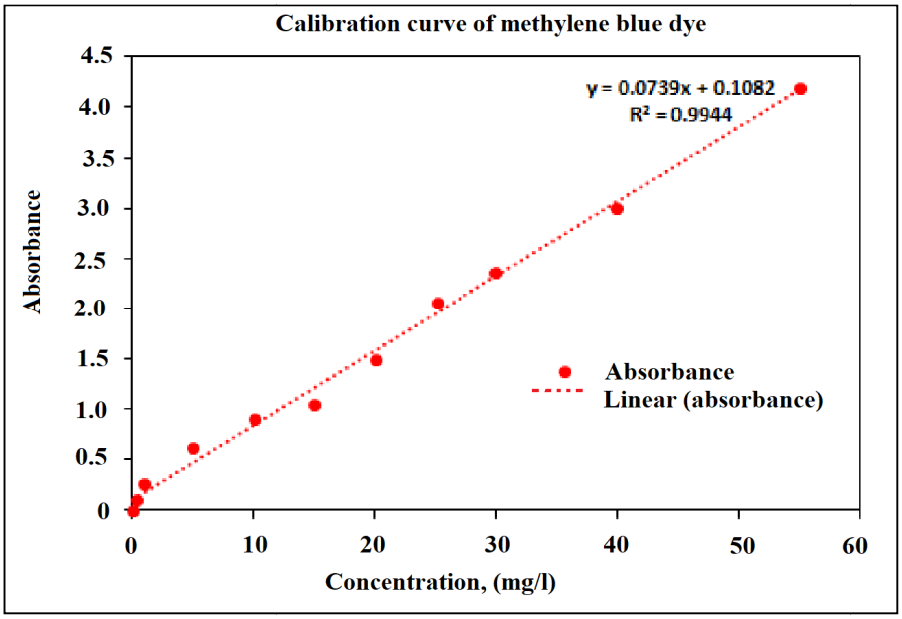


Fig. 1. Calibration curve of MB dye

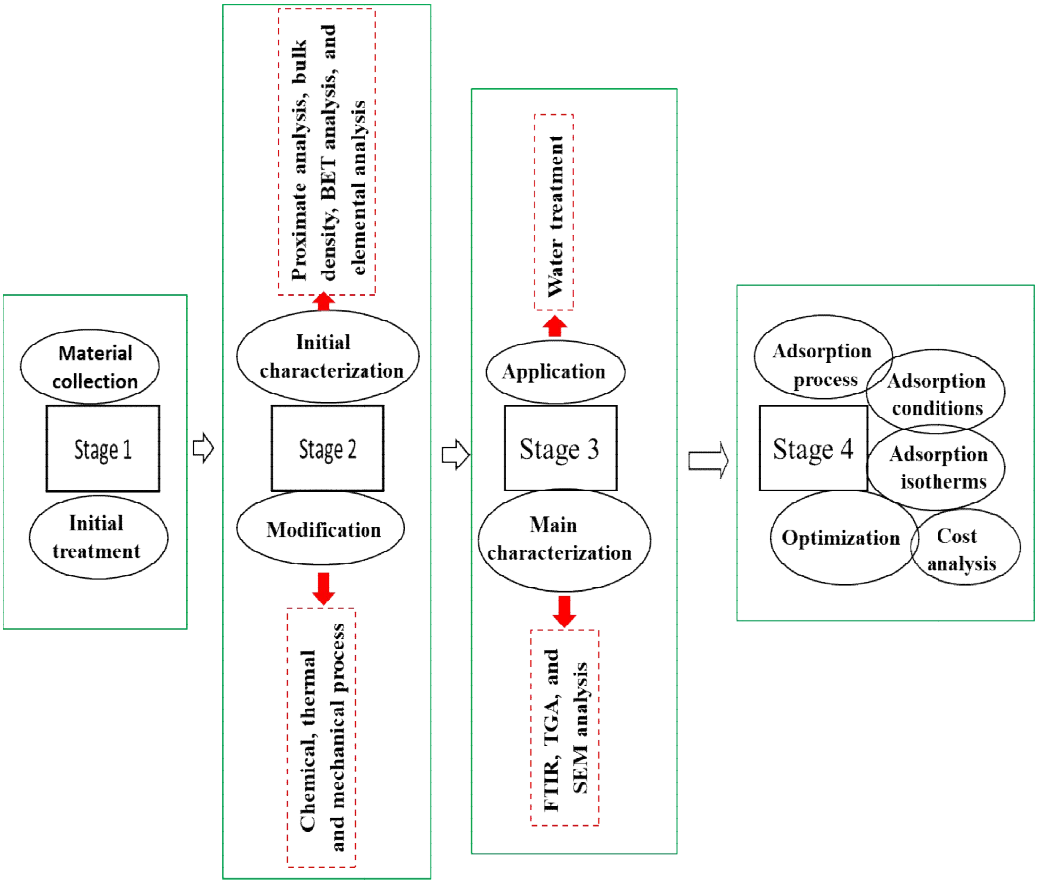


Fig. 2. Overall stages involved in this work

$$q_e = (C_o - C_e) \times (V/M) \quad (1)$$

$$\% \text{ adsorption} = (C_o - C_e / C_o) \times 100 \quad (2)$$

Where C_o and C_e are the initial and equilibrium dye concentrations, respectively (mg/l), V is the dye solution volume (L), and M is the amount of adsorbent (g), q_e is the adsorption capacity at equilibrium (mg/g).

2.4 Adsorbent Characterization

In order to understanding the adsorbent background, various characteristics of adsorbent were determined. The characterization study of adsorbent were included the following properties: bulk density, moisture content, volatile matter, fixed carbon, and the point of zero charge (pH_{pzc}). Elemental analysis of adsorbent was also investigated. Such properties were determined according to the previous studies [31-34]. Surface morphology of adsorbent, spectral analyses, thermal stability and chemical compositions were also identified. The procedure of bulk density determination was performed according to our previous study [17].

3. RESULTS AND DISCUSSION

3.1 Characterization Study of Adsorbent

3.1.1 Initial properties of coffee grounds

The characterization results of coffee ground wastes are shown in Table 1. It is clear that the content of carbon and the oxygen was the highest, which prove the organic nature of the adsorbent. A low ash content was also observed. The BET surface area was investigated, and the procedure was performed according to our previous study [35]. Surface of biomass waste including agricultural residues in either as raw materials or in form of activated carbon are pores materials in nature, containing micropores (< 2 nm which is responsible for a small molecules), mesopores (2-50 nm which is responsible for the adsorption of medium molecules), and macro-pores (>50 nm which is responsible for the uptake of large molecules) [23]. The micropores usually provide the largest proportion of the internal surface of the adsorbent and contribute to most of the total pore volume.

From the surface and structure point of view, mesopores and the macropores surface of adsorbents represent the external surface, and most of the adsorption takes place in the micropores. On the other hand, the mesopores and macropores are playing an important role in the adsorption system because they serve as passage for the substance to reach micropores. Moreover, the multilayer adsorption only takes place in mesopores and macropores [36]. In this study, according to the surface morphology of the treated coffee waste, good pore distribution was observed on the surface of the adsorbent. These pores could be responsible for multilayer adsorption of MB. A large amount of functional groups could also be presented on the adsorbents surface after pre-treatment/ modification process. All these advantages can improve the adsorption capacity of biomass based adsorbents.

In this trend, Lopicic et al. [37] used mechanical treatment of lignocellulosic waste (*Prunus persica stones*) for Cu(II) removal. The materials were processed in vibratory disk mill (PS-V) and ultra-centrifugal mill (PS-C). Surface area of processed material was reported as 0.985 and 1.837 m^2/g for PS-V and PS-C, respectively. Kyzas and his coworkers (2012) used untreated coffee residues for dye removal. Although, the surface area was low, but they obtained high adsorption capacity as 179, 295 mg/g for reactive and basic dyes, respectively. In a related study, Nasuha et al. [38] have also observed a low surface area of rejected tea (4.2 m^2/g), whereas the adsorbent capacity was obtained to be 156 mg/g at 50^oC. Inyinbor et al. [39] investigated the adsorption of Rhodamine B dye onto raw and chitosan supported mesoporous adsorbents. The BET surface areas of the prepared adsorbent were 0.0092 and 4.99 m^2/g for untreated adsorbent and modified adsorbent, respectively. While, the maximum monolayer adsorption capacities obtained from the Langmuir equation were 52.90 and 217.39 mg/g for untreated and adsorbent coated with chitosan, respectively.

3.1.2 Thermogravimetric analysis (TGA)

Fig. 3 shows the weight change via TGA for coffee grounds. Two major weight losses took place in this graph. The first range of decomposition happened at approximately 50 to 155^oC, which represents almost 6.0% weight lost. This is most possibly due to the moisture released by the sample during heating. The largest weight loss occurred at temperature range of about 237 to 600^oC due to decomposition of lignocellulosic materials into carbons [35]. Further heating above 600^oC has no significant impact on weight change.

Therefore, in the thermomechanical treatment of coffee waste; that was conducted at 170^{o}C via an extrusion process at a speed of 80 rpm, there would be no severe chemical or structural modifications occurring during processing.

3.1.3 Spectral analyses (FTIR)

Fourier-transform Infrared Spectroscopy (FTIR) is one of the initial techniques applied for the identification of functional groups [40]. Fig. (4-a) shows the FTIR spectrum of modified coffee ground wastes. The spectra have hydroxyl peak at wave numbers 3359.12 cm−1, peak 1744 cm−1 for the C=O bonds in carboxyl groups and their esters, peaks at 1613.13cm−1 for the asymmetric stretching of the carboxylic C=O double bond, peak around 1375cm−1 attributed to the C–O bond in carboxylic groups. Some peaks in the 1110–1160 and 1040–1060 cm−1 range can be attributed to the stretching of the C–O–C and OH of polysaccharides. The wave number of the 1520cm−1 can be attributed to an amino group. Peak at 1028.44 cm−1 can be attributed to alcoholic C–O links and to C–N links [41]. The IR spectral study revealed that the adsorbent derived from biomass (coffee waste) contain mainly –OH, C=O, and –NH functional groups which were mainly responsible for the adsorption of MB) through chemical bindings [42]. After the adsorption process of dye onto the

Table 1. Properties of the ground coffee wastes

Parameters	value
i. Proximate Analysis	
Moisture content, wt%	3.11
Volatile matter, wt%	74.0
Fixed carbon, wt%	20.90
Ash content, wt%	1.99
ii. Elemental analysis	
Carbon (C) , wt%	56.5
Nitrogen (N), wt%	1.15
Hydrogen (H), wt%	7.13
Oxygen (O)	35.0
iii. Additional properties	
Point of zero charge	6.2
Bulk density, g/ml	0.54
Surface area (BET), m2/g	8.66

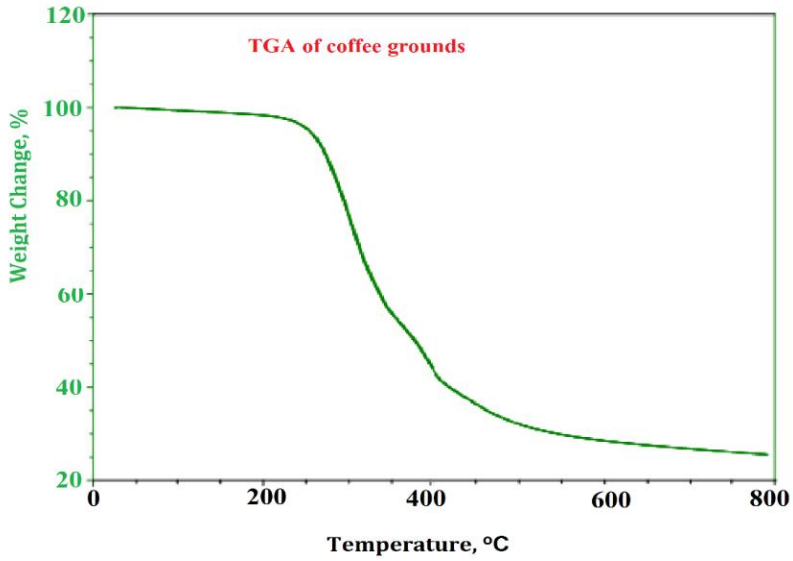


Fig. 3. TGA results of coffee ground wastes

Table 2. Main changes in the functional groups before and after adsorption

Wavenumber (cm-1)			Band
A	B	Differences	
3359.12	3329.11	30.01	O-H stretch of alcohol
1744.10	1730.33	13.77	-C=O stretch of carboxylic
1613.13	1605.14	7.99	-C=C stretch of alkanes
1375.87	1367.20	8.67	C-H bend of alkanes

A = unloaded modified coffee powder; B = coffee powder loaded with MB

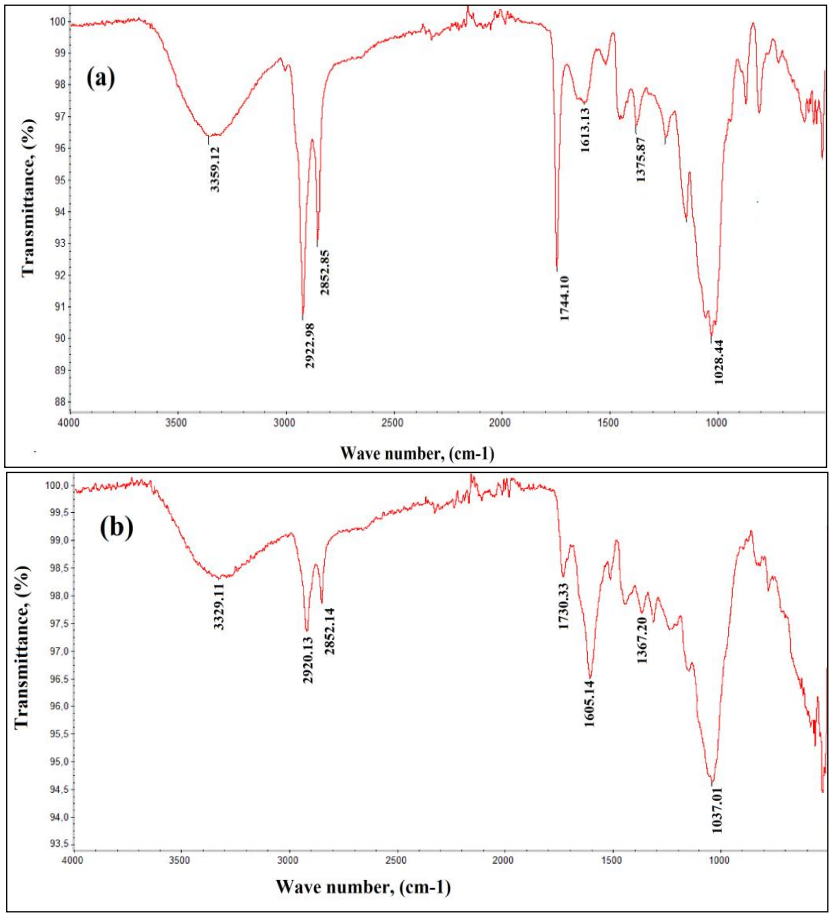


Fig. 4. FTIR (a) unloaded modified coffee powder and (b) coffee grounds powder loaded with MB

adsorbent, some minor changes were observed at the position and intensity and a little shift of these peaks (Fig. 4.b). Thus, the results of FTIR analysis indicated that the mechanism of MB dye bonding by the coffee waste powder was done. Similar observation was reported for green adsorbent derived from *gmelina aborea* leaf for sequestration of rhodamine B from aqueous solution [43]. However, the main active groups showed on the surface of adsorbent before and after adsorption process of methylene blue is presented in Table 2.

3.1.4 Morphology Test (SEM)

Scanning electron microscopy (SEM) is also a widely accepted technique for characterizing the surface morphology and fundamental characteristics of the adsorbents [44], due to the great pores present on the surface of adsorbent materials. Such pores can made a good possibility for adsorbate molecules to be trapped and adsorbed into these pores [45]. SEM technique has been employed to characterize adsorbent materials and elucidate possible

adsorption mechanisms in several studies [44]. As example, research study was employed SEM technique to characterize activated carbon obtained from coconut husk for the adsorption of dyes from contaminated water. SEM was taken before and after adsorption of dye by the activated carbon. They observed that there is very distinguished dark spots which can be taken as a sign for effective adsorption of dye molecules in the pores of adsorbent. While, after adsorption process of dyes the micrographs show clearly the dye-loaded adsorbent coated by dye molecules over the whole surface [45]. In this study, the changes in the morphologies before and after adsorption process of MB dye by modified coffee ground wastes has been observed as shown in Fig. 5, which indicated the efficient of adsorption process. Similar observation have also reported by the literatures [39,43,46,47].

3.2 Influence of Operational Variables on Dye Uptake

3.2.1 Effect of contact time

To study the influence of contact time, 100 ml of aqueous solutions containing 100 mg/l of methylene blue was taken in a 250 ml conical flasks, and a specific amount of coffee ground wastes (0.1 g) was added; the flasks were shaken at 250 rpm for an adsorption time of 5-60 min at room temperature and pH 7. Fig. 6 shows the effect of contact time on the rate of dye adsorption.

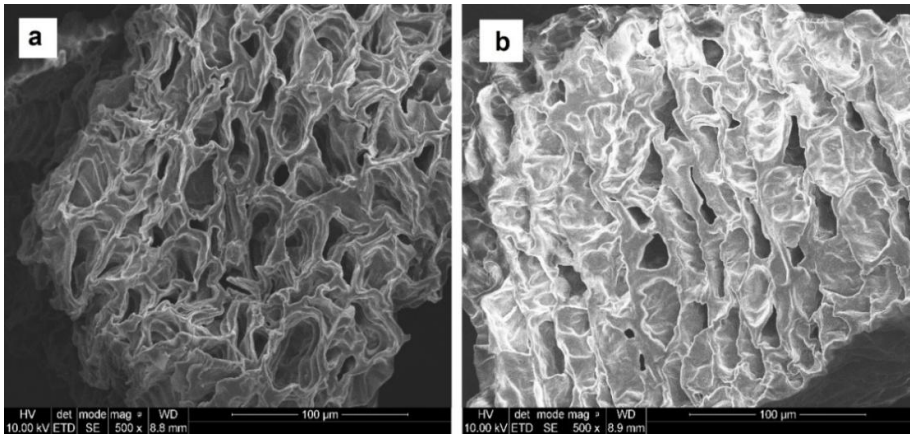


Fig. 5. SEM images of modified coffee ground wastes

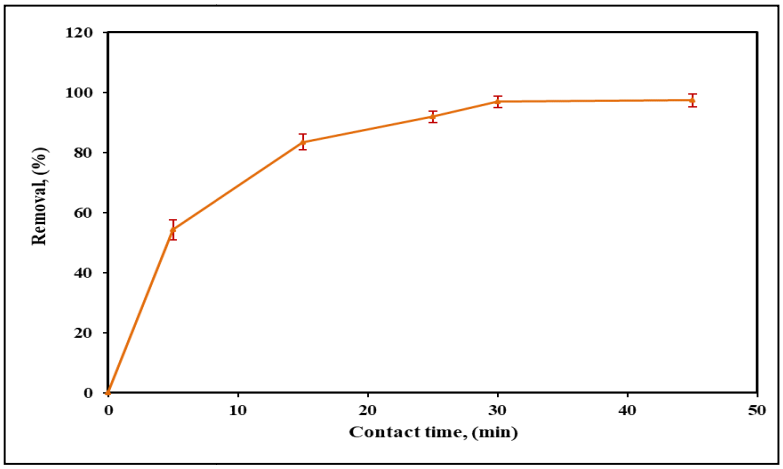


Fig. 6. The effect of contact time on removal of MB dye

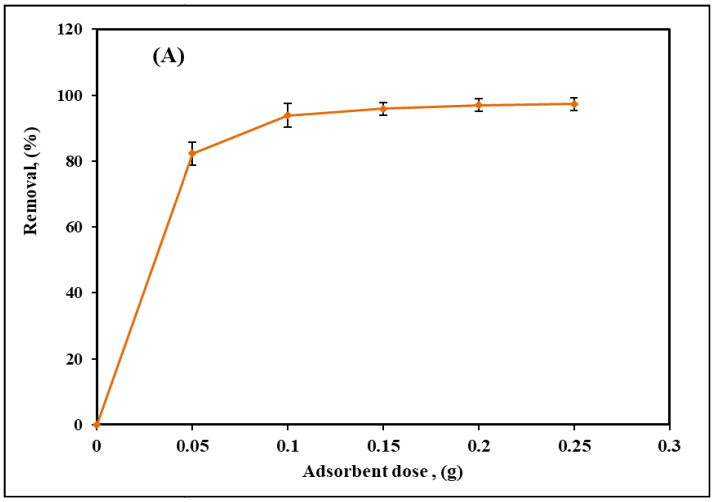
The results obtained indicated that dye removal rapid increased with increasing contact time in the initial stages of contact time (5-10 min), because of the initially large surface area and the availability of free active sites [15]. Therefore, a contact time after 30 min was selected to be the best shaking time for adsorption process. A Similar observation were found to remove contaminants from their aqueous solution using natural adsorbents derived from potential and low cost materials [8, 13, 15, 16, 17, 33].

3.2.2 Effect of adsorbent dose

The adsorbent dose is an important element of the adsorption process because it estimates the ability of adsorbents at a specific initial concentration of dye solution [16,17]. The effect of coffee ground waste (CGW) amounts on adsorbent capacity was studied by contacting 100 ml of aqueous solutions containing 100 mg/l of methylene blue dye concentration with 0.1 g of CGW, for a contact time of 30 min at a shaking rate of 250 rpm, pH 7.0 and room temperature. In order to understanding the behavior effect of an adsorbent dose on the removal rate; various amounts of CGW adsorbent (0.05-0.25 g) were used. Fig. 7 shows the influence of adsorbent amounts on the dye adsorption onto CGW. The efficiency of dye adsorption increased with increasing amounts of adsorbent material. It was increased from 82.3% to 97.3% when the adsorbent dose was increased from 0.05 to 0.25 g. It was also observed that the removal rate of the dye was almost constant beyond 0.15 g as shown in Fig. 6. The increase in removal with an increase the adsorbent dose was due to the increased surface availability of the adsorbent [8,16,17], while the adsorption capacity of the adsorbent decrease with increasing the amount of adsorbent. As example, a decrease from 165.1 mg/g to 37.0 mg/g was observed when the dose was increased from 0.05 to 0.25 g. This outcome can be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorption surface area available for the dye and an increase in the length of the diffusion path [17].

3.2.3 Effect of initial dye concentration

The effect of initial concentration of MB dye on the rate of removal by CGW was investigated using different initial MB concentrations ranging (50 to 200 mg/l) at room temperature, solution pH 7, adsorbent dose 0.1 g and contact time 30 min. The relationships between initial dye concentration and removal efficiency is given in Fig. 8. The rate of adsorption was evident to decrease with increasing concentration of MB. Moreover, lower concentration allows more time for MB to bind to the adsorption sites with a slower mass transfer coefficient, while, increasing the concentration of MB in solution increases the driving force, and thus these adsorption sites were occupied and the CGW surface was saturated [15-17]. It was decreased from 98.7% to 73.3%, when the initial MB concentration increased from 50 to 200 mg/l. On the other hand, an increase in the initial dye concentration increased the adsorbent loading capacity [8]. This may be attributed to the fact that the initial concentrations provides an important driving force to overcome all resistance to mass transfer of dye molecules between the aqueous and solid phases, as indicated in the literature [35].



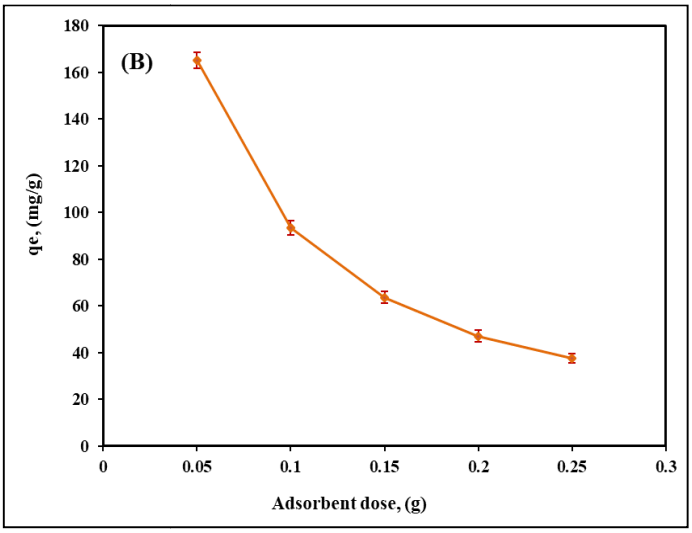


Fig. 7. The effect of adsorbent dose on the removal of dye (a), and adsorbent capacity (b)

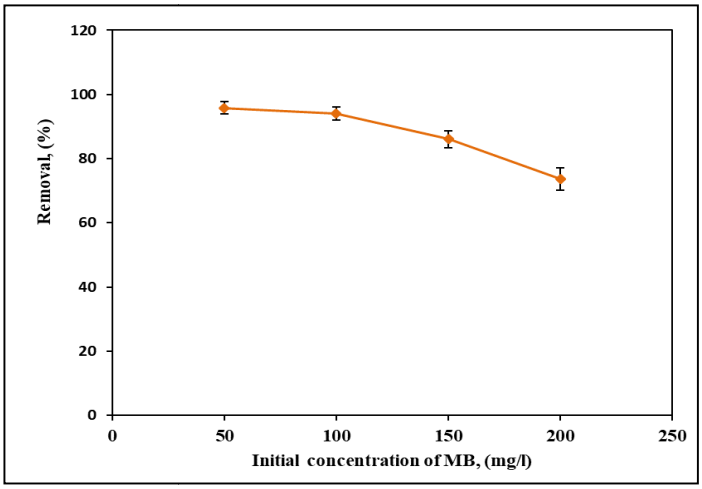


Fig. 8. The impact of initial MB concentration on the removal rate

3.3 Isotherm Studies

Adsorption isotherm provides important models in description the phenomenon of adsorption. It describes how adsorbate molecules interact with the solid phase (adsorbent) and provides explanation for the nature and mechanism of an adsorption system [16]. In the present study, Langmuir, Freundlich and Temkin isotherms were applied to investigate the adsorption phenomenon and was observed that all these models could be applied to describe adsorption behavior The Langmuir, Freundlich and Temkin isotherm Equations are presented by the equations (3) [48], (4) [49] and (5) [33, 46], respectively. The Langmuir isotherm model assumes that adsorptive of adsorbate occurs on a homogenous surface by monolayer adsorption without any interaction between the adsorbed molecules.

The Freundlich isotherm model is valid for multilayer biosorption and is derived by assuming a heterogeneous surface with interaction between adsorbed molecules with a nonuniform distribution of heat of adsorption over the surface. Whereas, the Temkin model suggests an equal distribution of binding energies over the number of the exchanging sites on the surface [46]. The Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor (R_L) that is given by Eq. (6) [17].

Fig. 9 shows the isotherm models including Langmuir, Freundlich, and Temkin isotherms for MB dye removal by CGW. While, Fig.10 presented the results obtained for the separation factor (R_L).

$$C_e/q_e = (1/b\ q_{max}) + (C_e/q_{max}) \quad (3)$$

$$\ln q_e = (1/n \ln C_e) + (\ln K_f) \quad (4)$$

$$q_e = B \ln C_e + B \ln A \quad (5)$$

$$R_L = 1 / (1 + b\ Co) \quad (6)$$

where C_e (mg/l) and q_e (mg/g) were the equilibrium concentration of the adsorbate and the amount adsorbed, respectively, q_{max} is the maximum adsorption capacity (mg/g); and b is the Langmuir constant (l/mg) related to the removal rate, K_f (l/mg) is the physical constants of the Freundlich adsorption isotherm, n is the heterogeneity factor of adsorption sites, B = RT/b, R (8.314 J/mol k) is the gas constant, T is the absolute temperature in Kelvin (K), b is the Temkin constant related to the heat of adsorption (J/mol), A is the equilibrium binding constant (L/g) and B is corresponding to the heat of sorption [46]. It is reported that if n is equal to unity, the adsorption is linear, n less than 1.0 indicates that adsorption is a chemical process; while, n higher than 1.0 is associated with a favorable adsorption [46].

The all isotherm constants were determined from the slope and intercept of the linear models. Fig.8 presents isotherm adsorption of MB dye onto coffee waste. Table 2 summarizes the maximum adsorption capacity (q_{max}) and the other isothermal parameters resulting from the fitting. As can be seen from the correlation coefficients values, the experimental data were suitable for Langmuir > Temkin > Freundlich, which were found to be (0.9999), (0.9458) and (0.8532), respectively. Similar behavior were reported for the adsorptive removal of basic cationic dyes by chemically protonated watermelon rind [50]. Jain and Gogate, (2018) also found the similar results for the adsorption of acid green 25 dye onto treated prunus dulcis [33]. The estimated maximum adsorption capacity for the adsorption of MB at room temperature and solution pH 7 was found to be 169.49 mg/g.

The value of R_L indicates the type of the isotherm to be either unfavorable (R_L >1), linear (R_L =1), and irreversible R_L = 0. The estimated values of R_L for the adsorption of MB by coffee grounds was shown in Fig. 9. The R_L values were found to be from 0.0382 to 0.00984, at initial dye concentration from 50 to 200 mg/l. Such results confirmed favorable adsorption of dye onto CGW adsorbent. Similar outcome was reported in literature [17].

3.4 Thermodynamic Studies

In the current study, the effect of temperature on the adsorption process was studied at four different temperatures (25, 35, 50 and 60^{o}C). All other parameters were kept constant as pH =7, initial dye concentration (100 mg/l), contact time (30 min), and adsorbent dose (0.1 g). The thermodynamic parameters of MB adsorption were evaluated using Equations 7, 8 and 9 [8,17]. The enthalpy (ΔH^o) and entropy (ΔS^o) values were obtained from the slopes and intercepts of the linear plots of ln Kc against 1/T as shown in Fig. 11. Besides, Table 3 illustrates the thermodynamic parameters of MB adsorption by modified coffee wastes.

$$\Delta G^o = - RT \ln Kc \quad (7)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (8)$$

$$\ln Kc = (\Delta S^o /R) – (\Delta H^o /RT) \quad (9)$$

Where $Kc = q_e / C_e$ [17, 42], qe is the amount of MB adsorbed by CGW at equilibrium (mg/g), R is the gas constant (8.314 J/mol k), and C_e is the equilibrium concentration of MB in the solution (mg/l).

The adsorption of methylene blue by modified coffee grounds powder was an exothermic process which was confirmed by negative value of enthalpy. The spontaneous nature of adsorption appears due to negative value of ΔG^o (-6.796 KJ/mol). The increase in temperature results in decrease in adsorption of MB dye from aqueous phase. The maximum adsorption of dye was observed at solution temperature of 298 K. In the adsorption system, the physical reaction forces were involved by the Van der Waals forces, weak hydrogen bonding, and increase in temperature leads in breakdown of uptake forces resulting in lower MB removal efficiency at higher temperature [46]. Similar trend were reported for the adsorptive removal of indosal yellow BG onto peanut husk [46], for adsorption of Rhodamine B dye by raw and chitosan [39] and for adsorptive uptake of Pb(II) and As(III)

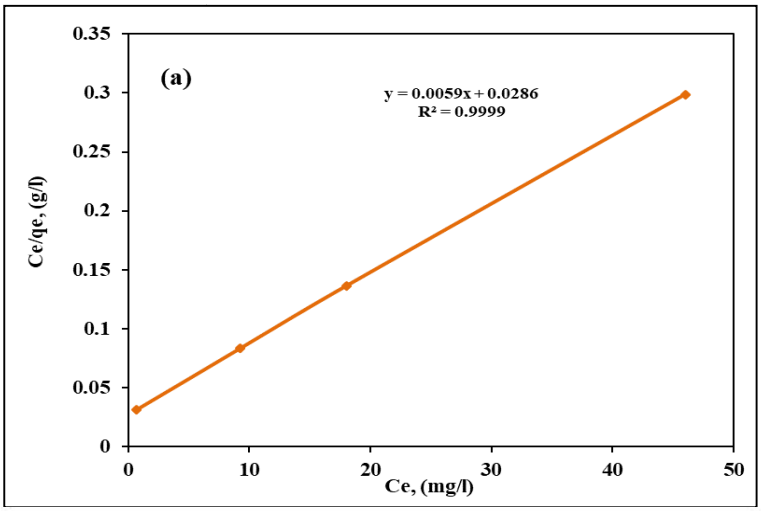
ions onto activated carbon from citrus limon tree leaves [51].

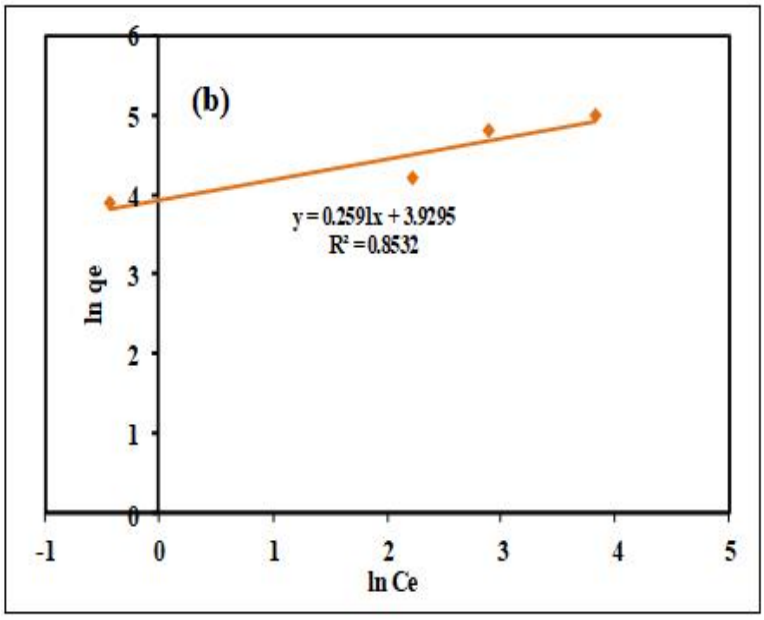
3.5 Comparison Study

It is well know that considering the cost of adsorbent materials is an important factor especially in the field of application. Moreover, from an economic and environmental point of view, green adsorbents derived from agricultural by-products/wastes are the best way to obtained low-cost, high-efficiency of adsorbents compared to those that are expensive (commercial activated carbon). Table 4 illustrated a comparison study of adsorptive removal of MB dye onto different low-cost adsorbents derived from agricultural by-product/ wastes. From the table it is clear that the obtained adsorbent (modified coffee wastes) was effective adsorbent for dye removal.

Table 3. Isotherm constants for the adsorptive removal MB by coffee ground wastes

Langmuir isotherm			Freundlich isotherm				Temkin isotherm	
q_{max}(mg/g)	b (L/mg)	R^2	n	K_f (L/mg)	R^2	B (J/mol)	A(L/mg)	R^2
169.49	0.503	0.9999	3.86	50.88	0.8532	24.45	9.55	0.9458





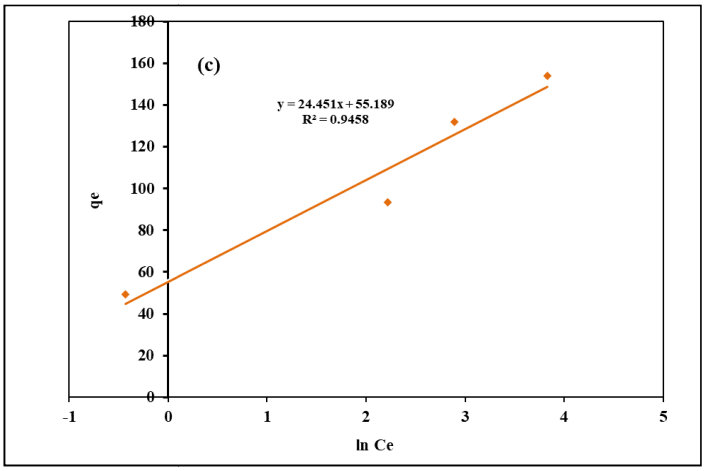


Fig. 9. (a) plot of Langmuir isotherms, (b) plot of Freundlich isotherms, and (c) plot of Temkin isotherms for MB dye removal by CGW

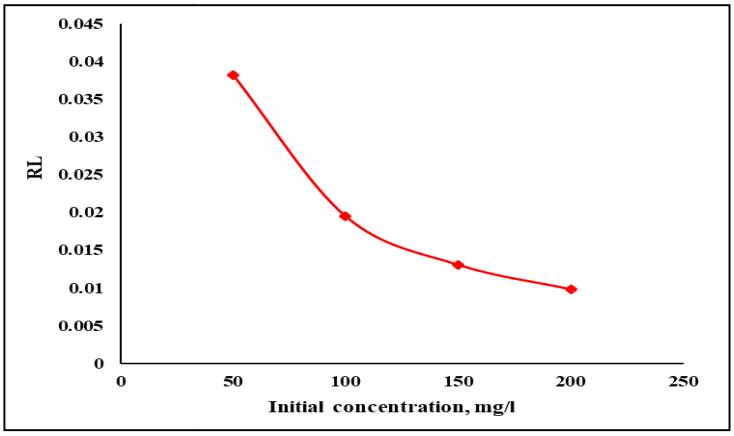


Fig. 10. Separation factor as function of initial dye concentration

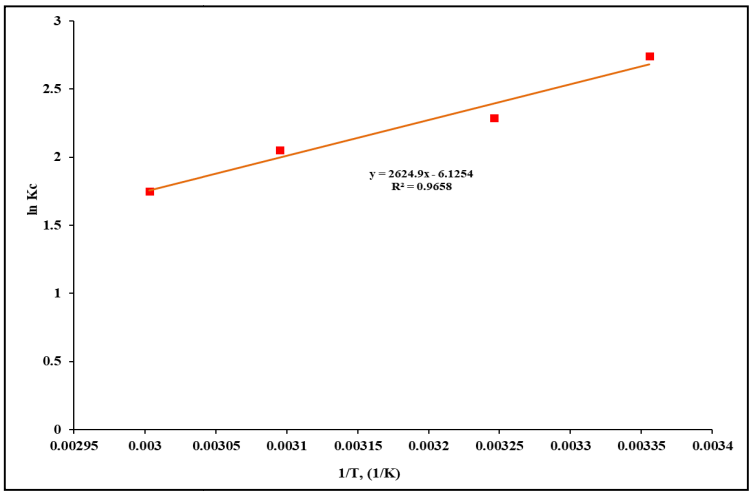


Fig. 11. Van't Hoff plot for the removal of MB by coffee ground powder

Table 4. Thermodynamics parameters for adsorption of MB by CGW

ΔH° (KJ/mol)	ΔS° (J/mol)	ΔG° (KJ/mol)			
		298	308	323	333
-21.82	-50.92	-6.795	-5.65	-5.51	-4.98

Table 5. Comparison of adsorption capacities for adsorption of MB dye various low-cost adsorbents

Adsorbent	Optimum conditions					
	Initial conc (mg/l)	A	B	C	qmax	Ref.
Indian rosewood sawdust	50-250	0.4 g/100ml	30	7.0	46.1	[52]
Acid-treated leaves	10-300	3 g/l	240	8.0	194.34	[53]
Hazelnut	50-1000	10g/l	60	2.5-4.2	76.9	[54]
Walnut sawdust	50-1000	10g/l	60	2.5-4.2	59.17	[54]
Cherry sawdust	50-1000	10g/l	120	2.5-4.2	39.84	[54]
Oak sawdust	50-1000	10g/l	60	2.5-4.2	29.94	[54]
Pitch-pine sawdust	50-1000	10g/l	60	2.5-4.2	27.78	[54]
Orange peel powder	10-70	0.3 g/50ml	30	6-7	25.87	[55]
Carica papaya wood	10-50	0.1 g	100	10.0	32.25	[56]
Haloxylon recurvum stems	10-100	2 g/l	40	8.0	22.94	[57]
Sea plant leaves	10-70	0.1g/50ml	60	7.0	27.78	[17]
Oak leaves powder	10-70	0.1g/50ml	60	7.0	33.5	[58]
Ficus carica bast-AC	10-70	0.5 g/100ml	90	8.0	47.62	[59]
Wheat bran	50-200	5 g/l	60	7.0	25.18	[60]
P. ceanica fibers	10-50	10 g/l	10	6.0	5.56	[61]
Bush cane bark powder	25-125	0.5g	80	8.0	23.49	[62]
Modified bagasse	100-300	0.4 g	25	9.0	69.93	[63]
Kenaf core fiber-AC	50-300	0.1 g	120	7.0	131.6	[64]
Date stones	70-700	10 g/l	50	6.3	43.47	[65]
Palm-trees waste	70-700	10 g/l	150	6.3	39.47	[65]
Raw swede rape straw	300-700	1.0 g/l	180	8.0	143	[66]
Modified *ficus carica*	50-500	0.5 g	210	8.0	75.87	[67]
Raw-pine apple peel	50-300	0.3g/200ml	280	10.0	79.09	[68]
Modified- Banana pith	50-500	1.17 g/l	120	7.0	85.47	[69]
Spent tea leaves	30-390	3.5 g/l	120	4-9	300.025	[70]
Soybean hulls	5-400	0.025 g/l	180	6.3	169.9	[71]
Mango leaf powder	100-350	0.25 g	120	10	156	[72]
Banana leaves	50-300	0.3g/200ml	280	7.0	109.89	[73]
Banana peel	100-500	0.1g/30ml	60	10.0	256.66	[74]
Cotton stalk	50-1150	4.0 g/l	100	11.0	147.06	[75]
Treated-coffee grounds	50-200	0.1 g/100ml	30.0	7.0	169.49	This study

A = Adsorbent dose, B = Contact time (min), and C = Solution pH

4. COST ESTIMATION

Nowadays, locally available, and low cost adsorbents derives from renewable sources is an important topic, and has been gained great interest from technologists and industrial applications. Since, the global activated carbon market accounted for $ 4.12 billion in the year of 2017 and is expected to reach $ 14.21 billion by the year of 2026 [76]. In this study, an alternative adsorbent was obtained from the recycling of coffee solid waste. Total cost of the prepared adsorbent (0.99 US$/Kg) including raw material and transportation, distilled water, electricity, and cost of chemicals such as K_2CO_3 was determined and listed in Table 5. Results noted that the cost of locally adsorbent obtained from the modified solid coffee wastes was much cheaper than commercial activated carbon ($259.5) [77]. Moreover, from an economic point

of view, coffee waste was an effective adsorbent that could be used successfully to remove toxic substances from polluted water. Similar observations were reported for adsorbents based modified agricultural wastes ($10.714/kg) [78], activated carbon derived from *gmelina aborea* leaves ($42.96/kg) [77], activated carbon derived from *glyricidia sepium* wood chip ($0.57/kg) [76] and modified *ficus carica* fiber ($0.2/kg) [79].

5. CONCLUSION

During this study, coffee waste biomass was used as a renewable source for preparing adsorbent. Modified coffee residue using chemical, heat and mechanical treatment showed an effective adsorbent for removing methylene blue from contaminated solution at a neutral pH. Maximum dye removal was obtained at 99% and increased with increase the amount of coffee waste adsorbent, as well as shaking time, whereas increase in initial MB concentration resulted in decreased removal efficiency. Equilibrium was reached within 30 min of contact time. Equilibrium data were well fit with the Langmuir isotherm model. The maximum capacity of coffee waste material was obtained to be 169.49 mg/g. The thermodynamic investigation demonstrates the exothermic process. The results indicated that coffee residues could be successfully used to remove toxic substances from contaminated water.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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