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Remediation of Bagmati River water using activated carbon from *Macrotyloma uniflorum* (gram horse) seed

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ABSTRACT

Remediation is a technique that facilitates the removable of pollutants from contaminated water. Activated carbons were prepared from indigenous *Macrotyloma uniflorum* (gram horse) seed using orthophosphoric acid as an activating agent. The chemically activated gram horse seed powder was carbonized using muffle furnace and characterized using thermo-gravimetric analysis (TGA), x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Boehm titration, methylene blue and iodine numbers. XRD and FTIR spectra indicated that the surface of amorphous activated carbon consisted of acidic and basic functional groups which efficiently adsorb pollutants from the polluted river water. The observed methylene blue and iodine numbers suggested that an impregnation ratio of 1.26:1, three hours of carbonization duration and carbonization temperature of 300 ºC were the optimum conditions for the development of micro and mesopores on the surface of the activated carbon prepared from gram horse powder. The maximum adsorption capacity of methylene blue was 312.5 mg/g and that of iodine was 1006.2 mg/g and specific surface area was 1160.44 m^2/g. The both Langmuir and Freundlich model fit well in the methylene blue adsorption. A simple column filtration was used for the purification of river water. Most of the observed water quality parameters of the sample collected from the Bagmati River exceeded the limit recommended by WHO. However, after treatment with gram horse activated carbon, concentrations of measured parameters were reduced to WHO recommended value. More than 60% of the hardness, sulphate and phosphate concentrations were removed and more than 40% of alkalinity and chlorine demand were reduced by activated carbon. Based on the results it is considered that activated carbon from gram horse seed can be an effectively used as bio-adsorbent for the remediation of highly polluted river water.

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1. Introduction

Water is the most essential compound for the survival of all living organisms. Therefore, the accessibility of safe and palatable water is of permanent importance to human health. The ideal water should be pleasant to taste, free from harmful chemicals and pathogens and non-corrosive for domestic purposes. It is considered to be polluted if it possesses high turbidity, bad taste and odor and contains microorganisms and unwanted chemicals in quantities that can put the health at risk [1]. The water sources are getting polluted day by day due to the discharge of household, domestic, sewage, agricultural, and industrial wastes without any treatment. These pollutants create a huge problem rendering water no longer fit for drinking, domestic, industrial, and agriculture, use as well as for aquatic life [2-5]. The Bagmati River is an important source of water for cultural, religious, domestic, irrigational and industrial uses in Nepal. It is a principal river in the Kathmandu valley river system. The river flows through the heart of Kathmandu valley and continues downward through the southern plain to join the Holy Ganga in India [6]. Until the last three decades, Bagmati and its tributaries were able to fulfil the drinking, irrigation, and various other need of the valley. However, unmanaged but speedy urbanization and lacks of well manage disposing system for the household and industrial waste and untreated sewage have led to water quality deterioration which harms the river ecosystem and the health of communities living along the riverside in the Kathmandu valley [3-5]. Although, there are a few small and large scale Bagmati clean up campaigns that were started in the Kathmandu valley, effective results have not been observed yet [7]. Further, the lack of efficient water treatment facilities throughout the urban and rural regions is forcing people to use polluted water for domestic, industrial and agricultural purposes. As a result, people in Nepal are facing water-borne diseases such as diarrhea, dysentery, cholera, gastroenteritis, and skin diseases. Almost 44,000 children are dying every year in Nepal from these diseases [8]. The generation of water-borne disease suggested that water should be treated before its use for drinking water production as well as for other domestic purposes. Various conventional methods were developed like filtration, chemical precipitation, ion exchange, chlorination, chemical oxidation and reduction for the treatment of water. However, these methods have certain limitations like expensive, inefficient, or generating large amounts of waste products that require further disposal [9,10]. Therefore, it is necessary to conduct research on sustainable and efficient solutions especially investigating natural sources [10]. Recently, the adsorption techniques using activated carbon becoming popular in the treatment of domestic and industrial water [11]. Activated carbon is a powerful adsorbent used regularly throughout water purification to remove contaminants and undesirable components. It is a critical and popular tool used throughout municipal and industrial water treatment facilities [11,12].

Activated carbon is carbonaceous material with different pore sizes resulting from the physical and chemical activations of raw materials at high-temperature reactions. Its specific surface area varies typically from 800 m^2/g to 1500 m^2/g [13]. A precursor is carbonized at high temperature (800-1100 ^oC) and activated using steam, carbon dioxide, air etc. in physical activation. At low temperature, diffusion dominates the activation resulting in poor development of the pore structure but at high temperature diffusion process is dominated by activation leading to well develop pores [14]. In chemical activation, precursors are impregnated with different activating agents such as phosphoric acid, zinc chloride, sodium hydroxide etc. and carbonized at low

temperature (300- 600 ^{o}C). In this process, carbonization and activation occur simultaneously, hence, the decomposition of lignocellulosic material and dehydration and volatilization of impurities occur at the same time leading to well-developed pores. A maximum pore on the activated carbon depends upon the activation temperature, activating agent, impregnation ratio and carbonization time [14-18]. The porous structure of activated carbon adsorbs materials from the water. Recently, studies were directed to develop activated carbon using locally available materials namely rice husk [15], corn-corb [16], lapsi seed [17], barro seed [18] etc. The efficiency of activated carbon depends upon the large number of functional groups namely hydroxyl, carboxyl acid group etc. in addition to pore structure. The lignocellulosic materials consist of hemicellulose, cellulose, lignin, protein and pectin which are responsible to develop the required functional groups on the surface of activated carbon during activation and carbonization [19]. Locally available Macrotyloma uniflorum (gram horse) seed contains carbohydrates, protein, dietary fiber, fat, calcium, phosphorus, iron, thiamine, riboflavin niacin etc. It is a trypsin inhibitor and source of natural phenols, such as 4-hydroxybenzoic, 3,4-dihydroxybenzoic, coumaric, caffeic, ferulic, vanillic, syringic, and sinapic acids [20]. It is one of the calcium reached pulses that has many medicinal applications. It is popular in the treatment/breakdown of kidney stones [21], for the antimicrobial activities [22], as antioxidants [23] etc. Therefore, in this study activated carbons were prepared from phenolic acid-containing gram horse seed using phosphoric acid as activating agent.

2. Material and method

The Macrotyloma uniflorum (Gram horse) seeds, brought from the local market of Darchula, were ground to a fine powder and sieved to 420 µm particle size. The fine powder was dried in an air oven after washing several times with distilled water. Thermogravimetric analysis (TGA) of the precursor was done by using a muffle furnace. 1 gram of dried powder was taken in silica crucible and subjected to pyrolysis for half an hour at each temperature in a muffle furnace and the remaining weight of the precursor was measured at different temperatures such as 100, 150, 200, 250, 300, 400, 450, 500, 550, and 600 ^{o}C [24]. The precursor was chemically activated using 65% orthophosphoric acid as an activating agent. The optimum condition for the activation was find out by subjecting precursor at different ratios (0.16:1, 0.32:1, 0.63:1, 1.26:1 and 1.58:1, phosphorus: precursor) and carbonized at different temperatures (300, 400 500 and 600 ^{o}C) for different durations (2, 3, 4 and 5 hours) in a muffle furnace. The carbonized activated carbon was cooled, washed with1 % $NaHCO_3$ and with distilled water till neutral pH was obtained then dried in an air oven at 110 ^{o}C for 24 hours. The dried activated carbon was sieved to 212 µm in size and kept in an airtight container for further analysis [25].

The activated carbons thus obtained were characterized by adsorption of methylene blue and iodine. The Boehm titration was used for the determination of surface functional groups present on the surface of the activated carbon [26]. The methylene blue and iodine adsorptions were used to determine the porosity of the activated carbon. Iodine number was calculated by ASTM D4607-94 method. The mixture of 5 mL of 5% HCl and 0.1 gram of activated carbon was boiled and cooled to room temperature. The mixture was shaken vigorously after adding 10 mL of 0.1 N iodine solution. The solution was then filtrated and titrated with 0.05 N sodium thiosulphate solution. The iodine number was calculated from the following equation [27].

$$Iodine\ number = \frac{Amount\ of\ iodine\ adsorbed}{Weight\ of\ carbon\ (g)} \quad (1)$$

Methylene blue number was calculated from the single point adsorption method. The activated carbon (0.1 gram) was mixed with 100 mL of different concentrations of methylene blue

solution such as 50, 100, 150, 200, 250, and 300 ppm and was agitated for 24 hours in a shaker at 190 rpm. The equilibrium methylene blue concentration was determined spectrophotometrically (λ_{max} = 665 nm, SSI UV 2110 spectrophotometer) [28]. The amount of methylene blue adsorbed per unit mass of the adsorbent was calculated from the following equation:

$$MB_n = \frac{(C_o - C_t)V}{M} \quad (2)$$

Where, C_o is the initial concentration of methylene blue and C_t is the concentration at time t, in mg/L. MB_n represents the amount of methylene blue adsorbed (mg/g), V and M are the volume of methylene blue and mass of activated carbon in gram, respectively. Specific surface area (m^2/g), was calculated using multi-point adsorption isotherm of methylene blue using Langmuir model. The q_e was determined from the linearized Langmuir isotherm and the specific surface area calculated from the equation below [29].

$$S_{MB} = \frac{q_e \text{ x } a_{MB} \text{ x } N_A \text{ x } 10^{-20}}{M_{MB}} \quad (3)$$

Where, S_{MB} represents a specific surface area (10^{-3} m^2/g), q_e is the number of molecules of methylene blue adsorbed (mg/g), a_{MB} represents the occupied surface area of one molecule of methylene blue (197.2 Å), N_A is the Avogadro's number and M_{MB} represents the molecular weight of the methylene blue (319.85 g/mol)

The adsorption efficiency of methylene blue was analyzed using Langmuir and Freundlich adsorption models [30]. The linearized Langmuir adsorption isotherm is defined as

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, b} + \left(\frac{1}{q_{max}}\right) C_e \quad (4)$$

Where, C_e defines the equilibrium concentration of the solution (mg/L), q_e defines the amount of adsorbate adsorbed (mg/g), q_{max} represents a maximum amount adsorbed (mg/g), b is the Langmuir constant (L/mg). The plot of C_e/q_e against C_e gives the straight line. q_{max} and b were calculated from slope and intercept, respectively.

The linearized Freundlich adsorption isotherm is expressed as

$$logq_e = logK_F + \left(\frac{1}{n}\right) logC_e \quad (5)$$

Where, $q_e = x/m$, where, x is mass of substance adsorbed (mg), m is the mass of activated carbon (g), the Freundlich adsorption parameters n is the adsorption intensity, and K_F is the adsorption capacity of the adsorbent (mg/g).

Activated carbon prepared from gram horse seeds was used for the remediation of the highly polluted water from Bagmati River. The water sample was collected from the Balkhu region, one of the most polluted sites inside the Kathmandu valley [31]. The water quality parameters such as pH, conductivity, alkalinity, hardness, sulphate, ammonia and phosphate were determined before and after the treatment of water using activated carbon. In the treatment process, 2g activated carbon was taken in a column having a diameter of 2 cm and polluted water was added slowly into the column. The rate was adjusted in 100 mL per hour and thus obtained purified sample water was analyzed subsequently.

3. Results and Discussion

3.1 Thermogravimetric analysis

A thermal behavior of lignocellulosic material can be qualitatively determined from thermogravimetry analysis. Weight losses observed in the thermogravimetric analysis is found to be relevant to the composition of hemicellulose, cellulose and lignin fractions in gram horse powder [18, 24]. Figure 1 shows the thermogravimetric (TG) curve of Macrotyloma uniflorum (gram horse) seed powder with a diameter of less than 425 µm. The thermogravimetric analysis curve shows that the weight of Gram horse seed powder decreased

slightly until 200ºC, and then drastically after 250 °C. Above 300 °C the weight loss was insignificant which indicates completion of pyrolysis at 300 °C [24].

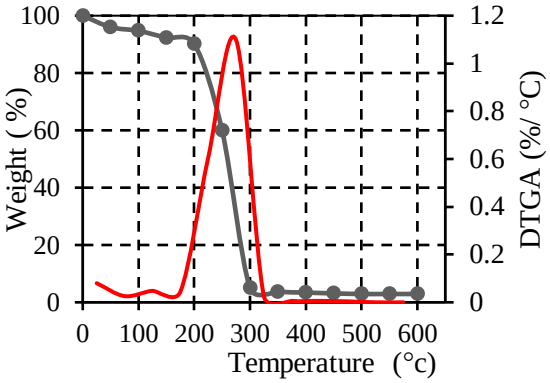

Fig 1: Thermogravimetric analysis of gram horse powder.

The derivative thermogravimetric analysis (DTGA) curve shows two peaks, a small peak in between 100 and 150 ºC and another a large peak in between 200 and 300 °C and peak was not observed beyond 400 °C. Weight loss before 200 °C was considered as evaporation of moisture and highly volatile compounds. The major weight loss between 200 and 300 °C depicts as the decomposition of hemicellulose and the degradation of lignin and cellulose [24, 32]. Above 300 °C temperature residue consists of almost carbon. Based on the TGA curve 300 °C is considered as the optimum temperature to develop porous structure in the activated carbon.

3.2 Iodine and methylene blue adsorption

The adsorption capacity of gram horse activated carbon was more efficiently determined by activating precursor with different amounts of phosphoric acid and carbonized at different temperatures with various time duration. Thus, obtained gram horse activated carbons were characterized using methylene blue and iodine adsorption. Iodine number gives information about the presence of micropores on the surface of activated carbon. Iodine numbers of different activated carbons prepared by using different amounts (ratios) of the activating agent were plotted in figure 2a. The iodine numbers of activated carbons ranged from 805 to 1006 mg/g. Figure 2a shows that initially the iodine number was about 805 mg/g and it increased almost linearly till the impregnation ratio of 0.9:1 and becomes a maximum at the ratio of 1.26:1. The iodine number is decreased further increasing the activating agent. This may be attributed to a more extensive and complete reaction of phosphoric acid and surface of carbon at 1.26:1 impregnation ratio [33].

The methylene blue number was about 200 mg/g at an impregnation ratio of 0.3:1 and remained almost constant on increasing the impregnation ratio till 0.9:1 but drastically increased to 312 mg/g at the ratio of 1.26:1 and decreased with further increased in activating agent. At less amount of activating agent, reaction between phosphoric acid and carbon was not complete, however, increasing the activating agent enhanced the reaction and increased iodine and methylene blue numbers but further increasing activating agent destroyed the pore structure and decreased in iodine as well as methylene blue numbers [33, 34]. The effect of carbonization temperature was analyzed by using figure 2b, the curve reveals that iodine and methylene blue numbers were maximum, 1006.5 and 312.5 mg/g, respectively at 300 °C carbonization temperature. Both iodine and methylene blue adsorptions were decreased linearly with further increase in temperature. The TGA curve (figure 1) also support the results hence it was considered that pore structure was significantly developed by degradation of more volatile cellulose, hemicellulose materials at 300 ºC but pores were destroyed further increase in temperature due to excess burn off carbon and coalescence of micro and mesopores or expansion of pore sizes [33].

In addition to carbonization temperature, carbonization time also effects the pore density of activated carbon. Figure 2c shows that the iodine and methylene blue numbers ranged from 899 to 1006 mg/g and from 222 to 312 mg/g,

respectively for activated carbon carbonized for 2 to 6 hours. The values were maximum at 3-hour carbonization time.

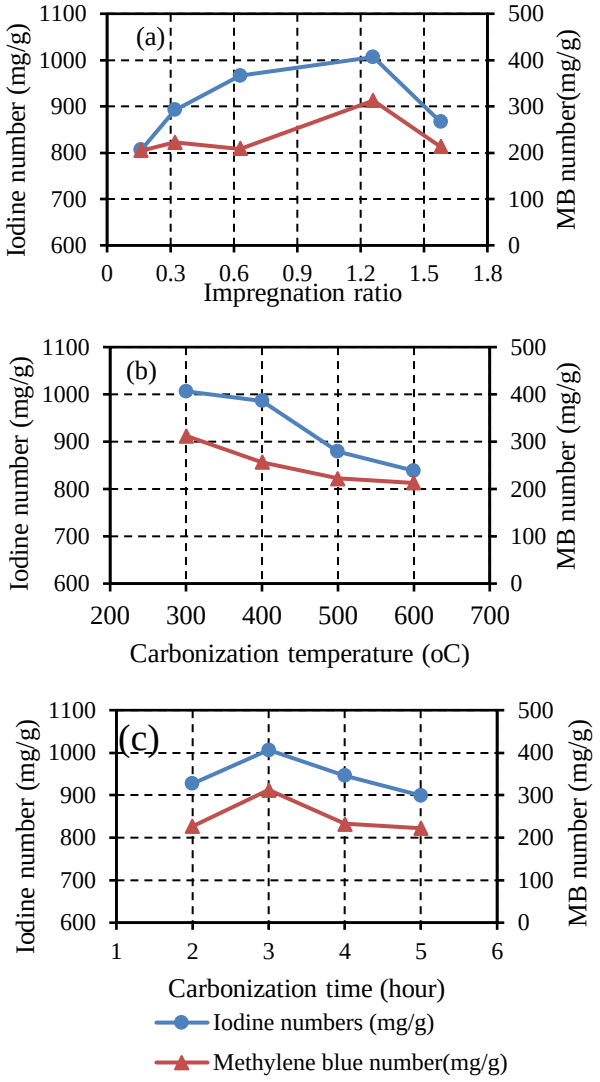

Fig 2: Iodine and methylene blue (MB) number at different (a)Impregnation ratio (b)Carbonization temperature and (c)Carbonization time.

Among the all, the activated carbon prepared by using the ratio of phosphoric acid (phosphorus) and precursor 1.26:1.0 and carbonized at 300 °C for 3 hours duration had maximum iodine (1006.5 mg/g) and methylene blue (312.50 mg/g) numbers which were almost comparable to those (1035 mg/g and 324.7 mg/g) of tea seed shells activated carbon [29].The high iodine and methylene blue numbers attributed that activated carbon consists a large density of pore hence have a great probability of a large specific surface area of gram horse activated carbon [33]. The observed iodine and methylene blue numbers of different precursors activated with phosphoric acid were tabulated in Table 1. The iodine number of gram horse seed activated carbon was higher than that observed for the other precursors. It was more than 4 times higher than that of bamboo. The methylene blue number was higher than that of other precursors except for areca nut and wood. The results suggested that phosphoric acid develops numerous micropores on the surface of activated carbon which can efficiently adsorb small ions from the aqueous solutions

Table 1: Iodine and methylene blue numbers of activated carbon prepared using different precursors

Precursor	Iodine number	Methylene blue number
Bamboo [35]	243	156
Barro seed stone [18]	357	173
Rice husk [36]	367	196
Amaro seed stone [32]	371	256.42
Sugarcane bagasse [37]	814.67	198
Areca nut[38]	888	369
Wood(*Thevetia peruviana*) [39]	798	532
Gram horse [This study]	1006.5	312.5

3.3 Specific surface area

The adsorption efficiency of activated carbon is directly related to its surface area and pore size. The iodine and methylene blue numbers depict pore structure whereas specific surface area implies available surface area for adsorption of the adsorbate. The adsorbent has a high extent of adsorption was considered to have a large specific surface area and having a low extent of adsorption have a small specific area. The specific surface area of activated carbons was plotted in figure 3. Figures 3a, 3b and 3c depict

the effect of activating agent, carbonization temperature and carbonization time, respectively.

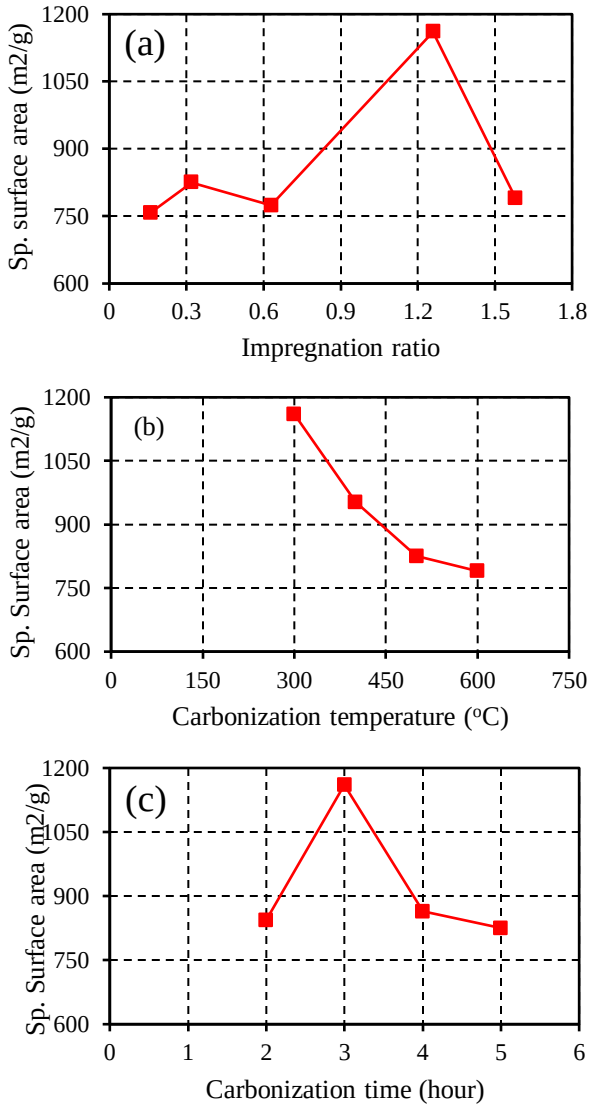

Fig. 3: Specific surface observed at different (a) impregnation ratio (b) carbonization temperature and (c) carbonization time prepared sample

The specific surface area was a maximum (1160 m^2/g) at an activation ratio of 1.26:1 which was nearly 1.5 times higher than that at other activation ratios. Similarly, specific surface area was a maximum at carbonization temperature of 300 °C, that was linearly decreased with further increase in temperature indicating high temperature caused coalescence of micro and mesopores. Figure 3c attributed that three hour of carbonization time was appropriate for the development of a maximum surface area on the surface of gram horse activated carbon [40]. A small carbonization time caused incomplete burn off which developed a low number of pores hence a low surface area. The decrease in a specific surface area after the optimum carbonization time attributed that excess burning destroyed the micro and mesopores structure. The observed specific surface area (1160 m^2/g) is higher than that reported for activated carbon from barro seed stone (537 m^2/g) [18] and amaro seed stone (581.69 m^2/g) [32] prepared using a similar technique.

3.3 Physical and chemical characterization of activated carbon

The adsorption phenomena occur on the surface of a material by which ions, metals, or substances interact with the functional group present on the surface. The seed of gram horse is rich in polyphenols flavonoids and proteins [20-22]. These functional groups can absorb ions, metals, or substances through exchange or complexation phenomena. Therefore, characterization of surface properties i.e., functional group present on the surface of a precursor is essential to understand the adsorption efficiency. Infrared spectroscopy is widely implied to explicate the functional groups present in the sample, particularly for the availability of main functional groups involved in adsorption phenomena. Figure 4a shows the FTIR spectrum of gram horse powder. The spectrum shows a broad peak in the range 3200-3600 cm^{-1} which was due to stretching vibrations of the hydroxyl group into intermolecular hydrogen bonding. The peak at 2922.70 cm^{-1} was considered as asymmetrical C-H stretching mode and the peak at 2841.32 cm^{-1} was attributed to symmetrical C-H stretching. The olefinic, C=C, stretching vibration in disubstituted (cis-) alkene caused the emergence of a peak at 1632.36 cm^{-1}. The strong peak observed at 1537.39 cm^{-1} represents the N-H bending of amine. The peaks at 1394.55

cm^{-1} and 1231.76 cm^{-1} were due to (-OH) bending vibration and C-O stretching vibration of the carboxylate group. The strong peak at 994.45 cm^{-1} was attributed to strong (C=C) bending in an alkene [41].

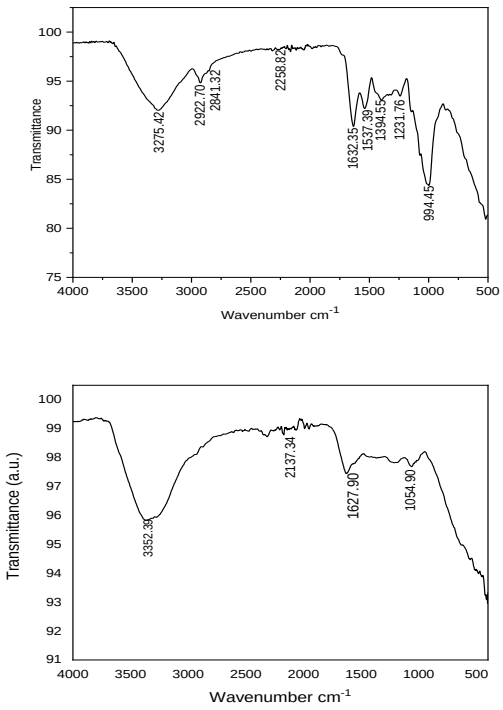

Fig 4: FTIR spectrum of (a) precursor and (b) prepared activated carbon sample

Figure 4b shows the FTIR spectrum of activated carbon. FTIR spectrum activated carbon showed a peak at 3352.39 cm^{-1} which was due to (O-H) stretching vibrations of the hydroxyl group. The stretching of hydrogen bonding of alcohol and phenols was located in the range of 3200 – 3600 cm^{-1}. The peak 2137.34 cm^{-1} was due to (C≡C) stretching vibration in alkyne. The intense peak at 1627.90 cm^{-1} is attributed to (C=C) stretching vibration in an alkene. The peak at 1054.90 is attributed to the stretching vibration of C-O group. Definite changes were observed in the FTIR spectra of activation after activation with orthophosphoric acid. Several peaks of functional groups such as carboxylic, amine disappeared which indicated that the weak bonds present in the precursor were broken during the activation process. Also, the extent of the remaining functional groups was decreased in activated carbon. This was because most of the oxygenated functional groups of precursors were lost in the form of water during activation and carbonization [41].

Table 2: Surface properties of activated carbon.

The concentration of functional groups, meq/g					
Carboxyl	Lactone	Phenol	Acidic	Basic	pH_{pzc}
0.85	0.019	0.39	1.259	1.19	5.7

Boehm's titration is another simple method used for the determination of the acidic and basic functional groups present in the activated carbon. The amount of acidic and basic functional groups of the activated carbon analyzed from Boehm's titration were shown in Table 2. The table shows that the surface of activated carbon consists of carboxylic and phenolic groups and a small amount of lactonic group. The presence of an almost equal amount of acidic and basic functional groups suggested that gram horse activated carbon may be capable to adsorb cation and anion from an aqueous solution. The pH_{pzc} implies the acidity/basicity of the surface of the adsorbent. The pH_{pzc} value of activated carbon was 5.7. This indicated that the surface of activated carbon is positively charged when the solution pH is lower and negatively charged when the solution pH is higher than pH_{pzc}. The surface of activated carbon will be protonated at low pH so negatively charge anions can electrostatically adsorb and at high pH, the surface becomes negatively charged hence can adsorb positively charged cations. The microstructure of the activated carbon was analyzed by using X-ray diffraction (XRD). Figure 5 shows two broad diffraction peaks detected at $2\boldsymbol{\theta}$ = 27º and 44º . The broad large peak detected at around 27º is due to the reflection from (002) plane and the small broad peak detected at around 44º is due to the reflection from (101) plane. The diffraction peaks at $2\boldsymbol{\theta}$ = 27º and 44º signify that

activated carbon consists of carbonaceous material [42]. The results attributed that the activated carbon prepared from gram horse seed consists of amorphous carbonaceous particles.

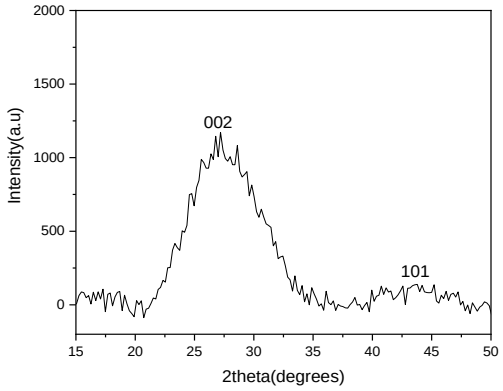

Fig. 5: XRD diagram of activated carbon

3.5 Adsorption isotherms

The adsorption efficiency of gram horse activated carbon was carried out by using the commonly used Langmuir and Freundlich adsorption model for methylene blue adsorption. Figures 6a and 6b represent the linearized curves of the Langmuir and Freundlich isotherms, respectively. Figure 6a shows a linear relation between C_e and C_e/q_e with a coefficient of determination, R^2 of 0.975 (Table 3). The maximum adsorption capacity calculated from Langmuir model was 312.5 mg/g and Langmuir constant was 0.325 (Table 3). The good correlation between the parameters depicts that there is homogeneous monolayer adsorption of methylene blue on the surface of activated carbon. The plot between log q_e and $logC_e$ represents the Freundlich adsorption model. Figure 6b shows the linear relationship between the parameters with a coefficient of determination of 0.997 (Table 3). This value is higher than that for the Langmuir model, which suggests that the gram horse activated carbon was more suitable for the Freundlich isotherm model i.e., there is the presence of ionic bonding between negative charge surface of activated carbon and positively charge methylene blue [31].

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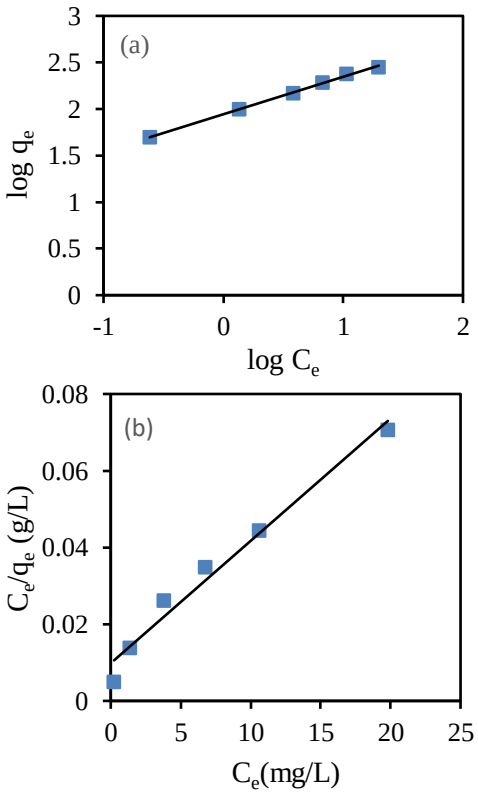

Fig. 6: (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm

Table 3: Langmuir and Freundlich adsorption parameters

Langmuir parameters	Freundlich parameters
q_{max} = 312.5 mg/g	K_F = 87.09
b = 0.325	n = 2.48
R^2 = 0.975	$1/n$ = 0.40
	R^2 = 0.997

3.5 Remediation of Bagmati River water

Bagmati River is prestigious for Hindu people because it is used for different rituals. However previous studies reported that river water is highly polluted and most of the water quality parameters exceeded the standard WHO limit. It was also reported that the river water cannot be used without treatment for a domestic, industrial and agricultural purposes [2-5, 31]]. In this study activated carbon prepared from gram horse seed was subjected for the remediation of river water. A water sample was collected from Balkhu one of the most polluted regions of the Bagmati River inside the Kathmandu Valley [31]. The physicochemical parameters of river water before and after treatment were tabulated in Table 4

Table 4: Physicochemical parameters of river water before and after treatment with activated carbon.

Measured Parameters	Before treatment	After treatment	WHO limits[43]	Removal (%)
pH	7.96	8.3	6.5-8.5	-4.27
Conductivity (µS/cm)	520	558	1500	-7.31
Total hardness (ppm)	1000	250	500	75.00
Alkalinity (ppm)	420.6	220.14	200	47.66
Sulphate (ppm)	45	13.5	300	70.00
Phosphate (ppm)	0.36	0.126	0.1	65.00
Ammonia (ppm)	0.443	0.325	0.25-32.5	26.64
Chlorine Demand (ppm)	37.70	22.14	0.2-5	41.27

Table 4 shows that the value of most of the observed water quality parameters such as hardness, alkalinity, phosphate, ammonia and chlorine demand was very high and exceeded the standard value of WHO [43]. Based on the observed water quality parameter the river water cannot be used for domestic, agricultural and industrial without treatment. The pH of the river water was slightly alkaline (7.9) and it was increased slightly after treatment with activated carbon. Although the pH of the water before and after treatment was slightly alkaline it was within the range recommended by WHO (6.5-8.5) for the drinking water. Similarly, the conductivity of the river water was slightly increased after treatment however, it was also within the WHO limit. The slight increase in pH of treated water may be due to ion exchange interactions with surface groups on activated carbon which generate hydroxide (OH^-) ions that raise the pH of water. The discharge of unbound hydroxide ions increased the conductivity of treated water [11]. Because the conductivity of water is the ability of water to pass current and increase in the concentration of ions enhance the conductivity.

Total hardness measures the concentration of calcium and magnesium present in the water in the form of bicarbonates, chloride, and sulfate and alkalinity is measures the concentration of carbonate, bicarbonate, and hydroxide ions. The total hardness and alkalinity of the river water were 1000 and 420 ppm, respectively. Both the parameters were 2 times higher than that of the value recommended by WHO (Table 4). After treatment, the total hardness reduced by four times to 250 ppm which is within the limit of the WHO value. Similarly, alkalinity reduced by two times to 220 ppm, which is slightly higher than WHO recommended value. This enormous reduction in the concentration will reduce the pollutant loading of the rivers. The result suggested that alkalinity and hardness can be removed efficiently from the polluted river water using activated carbon [44, 45]. Sulphate, phosphate and ammonia concentrations are the water quality parameter that indicates water pollution. The sulfate concentration in the river water was within the WHO limit however, the concentration of ammonia and phosphate exceeded the WHO limits. The gram horse activated carbon reduced more than 65% of phosphate and sulphate and about 26% of ammonia concentration (Table 4). As indicated by Boehm titration the surface of activated

carbon consists of acidic and basic functional groups which are responsible to adsorb negatively charged sulphate and phosphate ions and positively charged ammonium ions [46]. The activated carbon adsorbed sulfate ion efficiently and reduced its concentration of it to 13.5 mg/L. Other common water pollutants are pathogenic microorganisms and organic compounds. Chlorine demand indicates the amount of the pathogenic microorganisms and organic pollutants present in water. Table 4 shows that the chlorine demand of river water was 37.70 ppm indicating that the river water was highly contaminated with pathogenic microorganisms and organic pollutants. It was observed that after treatment the chlorine demand of the water sample decreased to 22.14 ppm. The decrease in total chlorine demand for treated water indicated that activated carbon also removed organic compounds [47] and may be pathogenic microorganisms from the water. These results suggested that gram horse activated carbon can be used efficiently for the purification of river water and possibly treated river water can be used for agricultural, industrial, irrigation and livestock drinking purpose provided that all other pollutants of concern are also within the recommended standard value.

4. Conclusions

Activated carbons were prepared from M. uniflorum (gram horse) seeds by chemical activation with orthophosphoric acid in a muffle furnace. The activated carbons were prepared using different impregnation ratios, different carbonization temperatures and times for the optimum condition determination. The surface morphology and functional group present on the surface of activated carbon were determined by using x-ray diffraction (XRD), Boehm's titration and Fourier-transform infrared spectroscopy (FTIR). Iodine and methylene blue numbers and specific surface area were used for the characterization of pore size and density. The methylene blue adsorption capacity of activated carbon was determined by Langmuir and Freundlich adsorption models. The Boehm titration and FTIR spectrum of activated carbon show that the surface of activated carbon contents almost equal amounts of acidic and basic functional groups with the point of zero charges is at pH 5.6. The broad two peaks in the XRD spectrum suggested that the activated carbon is amorphous. The activated carbon prepared by using different impregnation ratios, carbonization times and temperatures adsorbed 204 to 312 mg/g of methylene blue and 805 to 1006 mg/g of iodine. The maximum specific surface area (1160 m^2/g) was observed for the activated carbon prepared using phosphoric acid (phosphorus) to precursor impregnation ratio of 1.26:1 and carbonization at 300 ^oC. Both the Langmuir and Freundlich models suggested that the gram horse activated carbon could adsorb methylene blue efficiently. As expected, the physicochemical parameters of Bagmati River water revealed that the river water was highly polluted. It was observed that the total alkalinity and hardness content of the Bagmati River water were 2 times higher than the limit recommended by WHO, whereas phosphate content was 3 times higher than that of WHO standards. The results indicate that river water is unsafe for human consumption, domestic and industrial uses. However, bio-remediation of Bagmati River water using gram horse activated carbon attributed that it can remove 75% of hardness, 70% sulfate, 65.7% phosphate and 47.66% alkalinity from highly polluted river water. The value of all the parameters was reduced within the WHO limit after the treatment. All the results qualified that activated carbon prepared from gram horse seed acts as an excellent adsorbent. It purified river water very efficiently by reducing all the measured physicochemical parameters within the WHO limit.

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