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PISTACHIO SHELL-DERIVED ACTIVATED CARBON AS AN EFFICIENT BIO-ADSORBENT FOR RIVER WATER TREATMENT

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ABSTRACT

The remediation of river water using activated carbon is one of the economic solutions to overcome the water shortage problem. Nanoporous-activated carbons (ACs) were synthesized from pistachio shell powder using phosphoric acid as the activating agent. Various impregnation ratios of pistachio shell powder to phosphoric acid were used to activate the precursor and then carbonized at 400°C for three hours in a nitrogen atmosphere. The activated carbons (ACs) were characterized using Scanning Electron Microscopy (SEM), Raman scattering, and Fourier Transform Infrared Spectroscopy (FTIR), semi-quantitative surface information was determined using Boehm titration, and iodine and methylene blue adsorption. The iodine adsorption was maximum (758.45 mg/g) at an impregnation ratio of 1:1.5 (precursor: phosphoric acid, PSC_1.5). Boehm titration and FTIR spectra showed oxygenated functional groups such as hydroxyl, carboxyl, and carbonyl are present in the pistachio shell-derived activated carbon (PSC_1.5). Langmuir and Freundlich models are best fitted for methylene blue adsorption. The coefficient of the determinant was comparatively higher for the Langmuir model than the Freundlich model with an adsorption capacity of 243 mg/g. The efficiency of PSC_1.5 for the treatment of Bagmati river water was studied. The physical and chemical properties reveal that the river water is excessively polluted and changes to clean and clear water after the treatment with PSC_1.5. It removed more than 80% of contaminants from the river water, and significantly improved water quality to the WHO limits. Therefore, it is considered that activated carbon from pistachio shells is useful as an efficient bioadsorbent for the treatment of Bagmati River water.

Keywords: Bagmati River, chemical activation, phosphoric acid, remediation, water pollution

INTRODUCTION

Clean and safe water is enormously important for human survival (Mutlu & Kurnaz, 2017). Water should have a pleasant taste and color, be devoid of harmful substances and pathogens, and be safe for household use without causing any harm. When water exhibits high levels of cloudiness, unpleasant taste, and smell, along with the presence of microorganisms and undesirable chemicals in amounts that threaten health, it is deemed polluted (Adhikari & Bhatt, 2022). The Bagmati River water quality, particularly as it flows through the Kathmandu Valley, has significantly deteriorated over recent decades. This trend of increasing pollution is due to several factors, including inadequate wastewater treatment, urbanization, and direct discharge of untreated sewage and industrial effluents into the river (Adhikari et al., 2021). Historically, the Bagmati River used to be clean enough to be a source of drinking water, but this is no longer the case. Current water quality data show severe contamination, particularly in densely populated areas of Kathmandu. Efforts to clean the Bagmati River have been ongoing, including large-scale clean-up campaigns and infrastructural projects like the construction of reservoirs to augment water flow. However, these efforts have often fallen short due to their focus on removing

visible solid waste rather than addressing the deeper issues of water quality and untreated sewage (Mishra *et al.*, 2017) According to studies, the river's water quality frequently exceeds safe limits for water quality parameters (Sharma *et al.*, 2021). Addressing these challenges is crucial to protecting the health of both the Bagmati River ecosystem and the population relying on it in Nepal.

Several techniques were developed and employed for extracting contaminants such as coagulation, precipitation, membrane separation, ion exchange, electrochemical conversion, photocatalytic degradation, catalytic ozonation, adsorption, etc. (Tsolaki & Diamadopoulos, 2010). However, most of these techniques are costly, and/or generate large amounts of unwanted products that require further dumping (Kuok et al., 2023; Tsolaki & Diamadopoulos, 2010). It is necessary to find sustainable and efficient solutions by utilizing natural sources (Tsolaki & Diamadopoulos, 2010). Recently adsorption techniques have gained popularity in water treatment (Bhatnaga et al., 2013). Activated carbon, an efficient adsorbent is gaining popularity in the water treatment field. It is a simple and popular tool used in municipal and industrial water treatment systems (Kakom et al., 2023; Bhatnaga et al., 2013).

Activated carbon, is a carbon-based material notable for its diverse pore sizes, synthesized through the physical and chemical treatment of lignocellulose substances. Adsorption of pollutants from water is possible by developing a porous structure on the surface of the precursors. Several factors, including activating agent, impregnation ratio, carbonization duration and temperature, and methods affect the properties of activated carbon, particularly its pore size (Adhikari & Thapa, 2020, Amiri et al, 2018). Its surface area generally ranges from 800 to $1500 \text{ m}^2/\text{g}$. Char obtained from the carbonization of raw materials is gasified with steam, carbon dioxide, air, or their combinations at temperatures higher than 800°C in the physical activation process. Physical activation mainly involves diffusion, resulting in limited pore formation at lower temperatures. Higher temperatures lead to extensive activation and the development of well-defined pores. On the other hand, chemical activation is usually achieved at lower temperatures (300 to 800°C) and involves simultaneous carbonization and activation in a single phase. This is accomplished by thermally decomposing the raw material impregnated with chemical agents such as acids, bases, or salts. This simultaneous carbonization and activation process aids in decomposing lignocellulosic materials and eliminating impurities, resulting in well-developed pores (Joshi & Pradhananga, 2016).

Benefits of chemical activation include increased product yields and decreased energy expenses. The selection of precursor material notably impacts the properties of the resulting activated carbon. The production of activated carbon from readily available waste materials, such as rice husks, corn cobs, lapsi seeds, etc. has been the subject of research interest for the low-cost adsorbent. (Adhikari et al., 2015). Amorphous and crystalline particles combine to form the highly fibrous structure of pistachio shells. Triglycerides and cellulose composition with a high carbon content of pistachio shells possibly make them a good precursor for the activated carbons (Pratomo et al., 2015; Moussavi & Talebi, 2012). It was suggested that the pistachio shell has the potential as a flexible and effective biosorbent for a range of water treatment applications (Mkilima et al., 2024; Dias et al., 2021). Mkilima et al. (2024) investigated the possible use of pistachio shell and wheat straw-based bio-functionalized adsorbents for wastewater treatment. The results demonstrated the remarkable efficacy of the sequential series treatment in eliminating important pollutants such as turbidity, total suspended particles, fat, oil, and grease. However, there is still of study on the remediation of especially heavily polluted Bagmati River water using activated carbon. In this context, the pistachio-derived activated carbon synthesized from a chemical activation technique using phosphoric acid as an activating agent is used to remediate heavily polluted Bagmati River water. The synthesized activated carbons were characterized

using laboratory and instrumental methods. The characterized activated carbon was treated with freshly collected samples from the Bagmati River. The different water quality parameters were measured before and after treatment to determine the efficiency of pistachioderived activated carbon. The analytical output suggested that the river water was heavily polluted and after the treatment with pistachio-derived activated carbon, the water quality parameters were reduced to WHO standard.

EXPERIMENTAL

Synthesis of Activated Carbon

The pistachio shells were washed dried and ground using a mill. The powder of pistachio shells was washed and dried at 100°C for 5 hours. The precursor was treated with an activating agent, H₃PO₄ (65%), at varying impregnation ratios of 1:1 (PSC 1.0), 1:1.5 (PSS 1.5), 1:2 (PSC_2.0), and 1:4 (PSC_4.0) by weight and left for 24 hours. The impregnated precursor was pyrolyzed at 400°C for 3 hours in a split-tube furnace. An inert atmosphere was achieved by circulating N₂ gas at a 120 ml/min rate. After pyrolysis, the mixture was cooled to room temperature in ambient air, then crushed and sieved through a 400-micrometer mesh. The resulting mixtures were neutralized by washing with 0.005N NaOH then repeatedly with distilled water until the pH became 7 and dried in an oven at 110°C for 2 hours (Adhikari & Thapa, 2020). The activated carbons (PSCs) were characterized and used for water treatments.

Characterization of Activated Carbon

The iodine number was determined following the standard procedure (Adhikari & Thapa, 2020). 0.1 g of synthesized activated carbons using different amounts of activating agent were mixed with 5 ml of 5% HCl and 10 mL 0.1N iodine solution was added into the cooled mixture after boiling. The mixture was titrated with a standard (0.05N) sodium thiosulphate solution after shaking vigorously for half an hour. From the equation 1 iodine number was calculated.

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

From the multipoint adsorption isotherm, the methylene blue number was determined. 25 mg of AC was added to 25 mL of methylene blue solution of different concentrations and the amount of residual methylene blue was determined after continuous shaking for three hours. The eq. 2 was used to determine the quantity of methylene blue adsorbed by the activated carbon.

$$MB_N = \frac{(C_o - C_e)V}{M} \tag{2}$$

where, the initial and equilibrium concentrations of methylene blue (mg/L) were represented by C_a and C_e , respectively.

The volume of methylene blue and the mass of activated carbon were represented by V in liter and M in gram, respectively (Adhikari & Thapa, 2020).

A point of zero charge (pH_{zpc}), also known as an isoelectric point was determined by taking 0.1M NaNO3 in a beaker and adjusting the initial pH at 2, 3, 4, 5, 6, 7, 8, 9, 10 using 0.1M HNO₃ and 0.1M NaOH and then 0.1 g activated carbon was mixed into 50 mL solution. The mixture was agitated for three hours, and the final pH was meticulously measured. pHzpc value was determined by plotting the ΔpH versus the initial pH (Sing, 1982). The acidic and basic surface functional groups of carbonaceous material were determined using Boehm titration. 0.1 g activated carbon was mixed with 25 ml of 0.05 M NaOH, NaHCO3, and Na2CO3 separately, shaken for 3 hours, and titrated with 0.05 M HCl. The amount consumed by NaHCO3 represents the presence of phenolic groups. The difference between the amounts consumed by Na₂CO₃ and NaHCO₃ is lactonic groups and the difference between the amount consumed by NaCO₃ and NaOH is the carboxylic groups on the surface (Boehm, 1994).

Advanced Instrumental Analysis

The thermogravimetric analysis (TGA) was conducted using an STA 2500 (Regulus, NETZSCH, Germany), The surface functional groups of activated carbon were qualitatively determined by Fourier-transform infrared (FTIR) spectroscopy (NICOLET iS20, Thermo-Fisher Scientific, Waltham, MA, USA). A spectroscopic technique called Raman scattering spectroscopy (NRS-3100, JASCO, Tokyo, Japan) was used to determine graphitic and defective carbons. A scanning electron microscope (SEM) (S-4800, Hitachi Co., Ltd. Tokyo, Japan) operated at 10 kV and 10 μ A was used to evaluate the surface morphology of an adsorbent.

Remediation of water

The remediation of heavily polluted Bagmati River water was studied using pistachio shell-derived activated carbon (PSC_1.5). The physicochemical parameters such as pH, hardness, alkalinity, conductivity, dissolved oxygen and ions such as chloride, sulphate, phosphate, iron, chromium ion concentrations etc. were analysed before and after treatment with activated carbon following standard procedure (Lund, 2019; APHA, 2012).

RESULTS AND DISCUSSION

The precursor, pistachio shell powder, consists of 8.972 % moisture, 60.66 % of volatile matter, 19.0 % of fixed carbon content and less than one percentage (0.665 %) of ash. The very low amounts of ash and nearly 20% of fixed carbon in the precursor suggested that the precursor is suitable for synthesizing an efficient activated carbon. The thermal stability of precursors was determined from thermogravimetry analysis. The thermogram shows that the composition of pistachio shell powder was hemicellulose, cellulose, and lignin fractions (Fig. 1). The figure shows that the weight of the precursor decreased slightly till 100°C, and then linearly after 250 °C. The weight change was insignificant above 400 °C (Carrier *et al.*, 2013).

The derivative thermogravimetric analysis (DTGA) curve was plotted in Fig 1. The figure shows three peaks, a small peak at 100, and another two large peaks between 300 and 400°C, and no peak was observed beyond 400°C. Nearly 9% weight loss at 100°C was considered as evaporation of moisture. The significant weight loss between 250 and 400°C illustrates the decomposition of hemicellulose and the degradation of cellulose and lignin (Adhikari & Lamsal, 2021; Carrier *et al.*, 2013, Saka, 2012; Shin *et al.*, 1997). Above 400°C temperature weight loss was less than 2% and considered as complete removal of volatile matter and remaining only carbon material. The TGA analysis suggested that 400 °C was the suitable temperature for the development of porous in the activated carbon.



Figure 1. Thermogravimetric curves of pistachio shell powder.

Characterization of Activated Carbon

The role of the activating agent on the efficiency of pistachio shell-derived activated carbon (PSC) was determined by varying amounts of phosphoric acids for activation. Iodine adsorption, iodine numbers, of activated carbons with various amounts of the activating agent was plotted in Fig 2. The iodine number ranged from 717 to 786 mg/g. The iodine number was about 717 mg/g at the ratio 1:1.0 and then reached a maximum at 1:1.5, further reduced with increasing the activating agent (Fig. 2). From the maximum value of iodine number, it is considered that the phosphoric acid completely and more extensively reacts with the surface of carbon at an impregnation ratio of precursor to phosphoric acid of 1:1.5 (PSC_1.5) (Saka, 2012).



Figure 2. Iodine number of pistachio shell-derived activated carbons at different impregnation ratios.

pH_{zpc} is a critical parameter in understanding the surface chemistry of activated carbon. It indicates the pH at which there is no electrical charge on the surface of the activated carbon. The surface is positively charged due to protonation of the surface functional group below the pH_{zpc}, while above the pH_{zpc}, the surface is negatively charged due to deprotonation. The value of pH_{pzc} (7.27) infers that when the solution is lower than 7.27 the surface of activated carbon is positively and negatively charged when the pH is lower and higher, respectively than 7.27 (Sing, 2082). The surface will be protonated and adsorb negatively charged anions electrostatically at low pH, and the surface will be negatively charged and adsorb positively charged cations at high pH. The surface characterizations i.e., the surface functional group, and the morphology of pores are essential to understanding the adsorption efficiency, as the adsorption occurs on the surface of a material. The functional groups such as carboxylic, lactonic, and phenolic on the surface of activated carbon were determined from Bohem titration (Boehm, 1994). As shown in Table 1, PSC 1.5 consists of 1.42, 0.601, and 0.126 m mole/g of carboxylic, lactonic, and phenolic groups, respectively.

Table 1. Functional groups and point of zero charge present on the surface of PSC_1.5.

	PSC_1.5
Carboxylic group (mmole/g)	1.42
Lactonic group (mmole/g)	0.601
Phenolic group (mmole/g)	0.128
pH _{pzc}	7.27



Figure 3. (a) FTIR spectrum (b) Raman spectrum of pistachio shell-derived activated carbon (PSC-1.5).



Figure 4. Scanning Electron microscopy (SEM) images of PSC_1.5 showing the scales of (a) 20 μ m (b) 1 μ m and (c) 40 nm

The qualitative analysis of functional groups of PSC_1.5 was carried out using Fourier Transform Infrared (FTIR) Spectroscopy (Fig. 3a). The FTIR spectrum shows a broad peak in the range 3200-3600 cm⁻¹ indicating the stretching vibrations of the hydroxyl groups. The distinct peak at 2920.66 cm⁻¹ was from the asymmetrical C-H stretching vibration and the peak at 2851.24 cm⁻¹ was due to the stretching of C-H (Gnawali *et al.*, 2023). The peak observed at 1542.77, 1420.79, and 1260.29 cm⁻¹ refers to the N-H bending of amine O-H bending vibration and C-O stretching vibration, respectively. The distinct peak at 1025.94 is the stretching vibration of C-O (Shin *et al.*, 1997). The

Boehm titration and FTIR spectrum suggested that the surface carboxylic and hydroxyl groups of PSC_1.5 will interact and remove contaminants from water. The Raman spectra of amorphous carbon usually show a broad band at about 1550 cm⁻¹, which overlaps with a wider band at about 1400 cm⁻¹. Gaussian line shapes can be used to deconvolve these spectra into the G- and Dbands, which are two peaks. In particular, the intensity ratio (Id/Ig) is a useful indicator of the ratio of sp³ to sp³ bonding in hydrogenated amorphous carbons or the size of sp² clusters (Gnawali et al., 2023). The Raman spectra of PSC_1.5 (Fig. 3b) showed the G and D bands at 1599 and 1384 cm-1, respectively. The disordered carbon structure is associated with the emergence of the D band, while defects are related to the intensity. The peak of the G band suggests the graphitic structure and the peak of the D band suggests the defect in activated carbon (Gnawali et al., 2023). Semi-quantitative data on the degree of crystallization of graphic carbon is provided by I(G)/I(D). The ratio of I(G)/I(D) (1.15) in Raman spectra of PSC_1.5 implies defects were introduced during the activation process.

Higher surface areas and improved adsorption capacities are usually linked to adsorbents with increased pore presence and irregular surface patterns (Gnawali *et al.*, 2023). The surface morphology of PSC_1.5 was studied by the image of scanning electron microscopy (SEM) (Fig. 4). SEM uses a focused stream of high-energy electrons arranged in a raster pattern to scan a sample and take pictures. SEM is used for the high-resolution imaging of macro and mesopores on the surface. The structural arrangement of carbons from SEM images (Fig. 4) shows the amorphous nature of activated carbons having irregular shapes and sizes. The porous surface of the particles suggested that the activation and carbonization induced pores of different sizes and shapes. The nanopores observed in the high-resolution images indicated that as suggested by iodine and methylene blue numbers, phosphoric acid successfully developed pores on the surface. The macro, meso, and micropores with charged surfaces will efficiently adsorb contaminants from the heavily polluted river water.

Langmuir and Freundlich adsorption isotherms

The methylene blue adsorption efficiency of PSC-1.5 was determined from linearized Langmuir and Freundlich adsorption isotherms (Figs. 5a, 5b). Figure 5a shows a linear relation with a coefficient of determination, R² of 0.9999 between Ce and Ce/qe (Table 2). The maximum adsorption capacity and Langmuir constant determined were 243.9 mg/g and 1.024, respectively (Table 2). The excellent correlation implies that there is homogeneous monolayer adsorption of methylene blue. Figure 5b shows the linear relationship between $\log q_e$ and $\log C_e$ with a coefficient of determination of 0.997 representing Freundlich adsorption (Table 2). The higher coefficient of the determinant of the Langmuir model suggests that the PSC 1.5 activated carbon was more suitable for chemical adsorption by forming ionic bonding between the negatively charged surface of and positively charged methylene blue (Amiri et al., 2018). The methylene blue number from the maximum capacity of the monolayer adsorption was 243.9 mg/g, which is very high compared to 19.09 mg/g of apricot stone-derived activated carbon (Kavci et al., 2021) lower than 312.5 mg/g of gram horse activated carbon (Adhikari & Bhatt, 2022) and comparable to 256.42 mg/g of amaro seed stone (Adhikari & Thapa, 2020).



Figure 5. Linearized curves of (a) Langmuir adsorption and (b) Freundlich adsorption isotherms

Table 2. The parameters of Langmuir and Freundlich adsorption

Langmuir parameters	Freundlich parameters
$q_{max} = 243.9 \text{ mg/g}$	$K_F = 87.53$
b = 1.024 L/gm	n = 2.45
$R^2 = 0.9999$	1/n = 0.41
	$R^2 = 0.9171$

Remediation of heavily polluted Bagmati River water

People use Bagmati River water in different rituals. However, previous studies showed that the value of water quality parameters is higher than the standard WHO limit suggesting that the river water cannot be used as such for domestic, agricultural, industrial, etc. uses (Mishra *et al.*, 2017; Adhikari *et al.*, 2021; Sharma *et*

al., 2021; Adhikari & Bhatt, 2022). Pistachio shellderived carbon (PSC_1.5) was subjected to determine the efficacy of PSC_1.5 remediation of heavily polluted river water. The value of physicochemical parameters before and after the treatment of water collected from one of the polluted locations of the Bagmati River inside the Katmandu Valley was tabulated in Table 3. The value of most of the observed water quality parameters such as alkalinity, hardness, ammonia, phosphates, and chlorine demand exceeded the limit of the standard value of WHO (Table 3). The water quality parameter indicated that the river water is harmful and can't be used without treatment for domestic, industrial, or agricultural uses. The pH (7.4) of the river water was increased by 2 % after treatment and lies within the WHO recommended range (6.5-8.5). The treatment reduced the conductivity of the river water by 10.33% from 823 to 738 μ S/cm. The slight increase in pH after treatment may be due to the release of hydroxide ions by the interactions with surface groups on activated carbon. The release of unbound hydroxide ions increased the conductivity, this may be the cause of less reduction of the conductivity of treated water (Bhatnaga *et al.*, 2013).

Parameters	Before treatment	After treatment	WHO standard (WHO, 2011)	Removal (%)
Color	black	Colorless	Colorless	· /
рН	7.4	7.55	6.5-8.5	2.03
Conductivity (μ S/cm)	823	738	1500	10.33
Turbidity (FNU)	333	32.0	<4	90.39
ORP (mV)	-214	99.2	-	-146.36
TDS (ppm)	411	369		10.22
Acidity (ppm)	107.5	72	500	91.63
Alkalinity (ppm)	350	45.5	200	87.00
Hardness (ppm)	860	72	500	91.63
Sulphate (ppm)	35.04	1.88	300	94.63
Phosphate (ppm)	13.465	2.582	0.1	80.82
Nitrate ions (ppm)	151	44	50	70.86
Chloride ions (ppm)	54	8.02	<5	85.15
Iron (ppm)	1.764	0.0031	0.3	99.82
Chromium (ppm)	1.716	0.232	0.05	86.50

Table 3. Water quality parameters of river water before and after treatment with activated carbon.

The concentration of bicarbonates, chloride, and sulfate ions in the form of calcium and magnesium ions is measured in terms of total hardness, whereas the concentration of carbonate, bicarbonate, and hydroxide ions is represented by alkalinity. The values of total hardness and alkalinity were 860.0 and 350 ppm, respectively. Both values were nearly 2 times higher than the WHO-recommended value (Table 4). The total hardness and alkalinity reduced by 91.63 and 87 %, respectively after treatment and are within the limit of the WHO value. The reduction in the concentration suggested that activated carbon can remove alkalinity and hardness efficiently from the polluted river water (Amosa, 2016; Kannan & Mani, 2014). Sulfate, chloride, phosphate, and nitrate ion concentrations are the pollution-indicating parameters. The observed concentration of sulfate and chloride was within the WHO limit however, the nitrate and phosphate concentration exceeded the WHO limits. The PSC_1.5 decreased by more than 80 % of phosphate, chloride, sulfate, and about 70.86 % nitrate ion concentration (Table 4). Similarly, PSC_1.5 reduced heavy metals such as iron and chromium from 1.764 and 1.716 ppm to 0.0031 and 0.232 ppm, respectively. As indicated by Boehm titration acidic and basic charges of activated carbon efficiently adsorbed oppositely charged ions from heavily polluted river water (Shi & Yao, 2011; Kannan & Mani 2014; Amosa, 2016; Adhikari & Bhatt, 2022). The reduction of more than 80% of all observed positively and negatively charged particles suggested that

pistachio shell-derived activated carbon be an efficient adsorbent for the remediation of river water.

CONCLUSIONS

Activated carbons from pistachio shell powder were synthesized by chemical activation using orthophosphoric acid as an activating agent. The surface characteristics were determined from Scanning Electron Microscopy (SEM), Fourier-transform Infrared Spectroscopy (FTIR), Raman spectroscopy, Boehm's titration, iodine and methylene blue numbers, and point of zero charge (pH_{pzc}). The FTIR spectrum and Boehm titration suggest that activated carbon consists of acidic and basic functional groups at the surface. The SEM images attributed that the activated carbon is amorphous with variations in sizes and shapes and consists of macro, meso, and micropores that enhance the surface area for adsorption. The activated carbons synthesized at different impregnation ratios suggested that a maximum (786.9 mg/g) iodine was adsorbed by activated carbon at an impregnation ratio of 1:1.5 (PSC_1.5), carbonized for 3 hours duration at 400 °C temperature in N2 atmosphere in a split tube furnace. Both Langmuir and Freundlich models suggested that the Pistachio shellderived activated carbon (PSC_1.5) efficiently adsorbs methylene blue. The physicochemical quality parameterization attributed that the river water is excessively contaminated by positive and negative ions which increased the conductivity, turbidity, hardness, and alkalinity and reduced oxidation-reduction potential (ORP). The hardness and alkalinity were nearly 2 folds higher than the WHO-recommended value. Treatment with PSC 1.5 removed more than 80% of most of the contaminants. Most of the measured parameters fall on the WHO limit after the treatment. It is considered that activated carbon from the pistachio shell can efficiently reduce pollutants up to the WHO-recommended value from the heavily polluted Bagmati River.

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AUTHOR CONTRIBUTIONS

Mandira Pradhananga Adhikari supervision, conceptualization and revision, Nanda Bikram Adhikari conceptualization, writing, editing, Bishal Nepal material preparation, Dhurba Suwal experimental analysis. Sarita Manandhar and Sabina Shahi instrumental analysis and Amar Prasad Yadav writing and editing.

CONFLICTS OF INTEREST

The authors declare no conflict of interest

DATA AVAILABILITY

The data used in this study is available from the corresponding author, upon reasonable request.

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