Application of tea leaves in the circular economy: A sustainable approach to remove synthetic dye from wastewater by alkali-activated spent tea leaves

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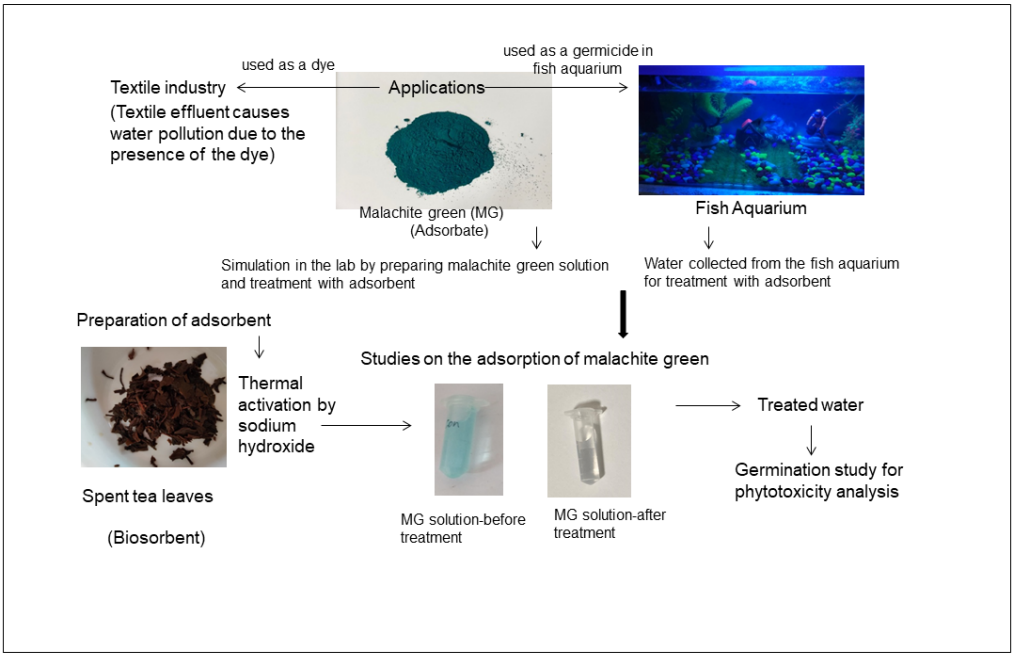

Abstract

Spent tea leaves (STL) were recycled and utilized to reduce water pollution caused by synthetic dyes. The current study used STL as a biosorbent to remove malachite green (MG) dye from aqueous solutions and fish aquarium wastewater. The dye removal efficiency was enhanced by alkali (NaOH) and thermal pretreatment and showed 98% removal efficiency. Biosorbent characteristics and dye removal mechanisms were established using BET-surface area, zeta-potential, SEM, and FTIR. An optimum adsorption capacity of 40.6 mgg^{-1} was obtained for MG. Equilibrium sorption data were analyzed by Langmuir and Freundlich isotherm. Sorption kinetics was determined by pseudo-first-order and pseudo-second-order kinetic models. Experimental data showed the best fit with Langmuir isotherm and the adsorption followed pseudo-second-order kinetics. The negative value of free energy (ΔG°) and positive value of enthalpy (ΔH°) changes obtained from the thermodynamic studies indicated the spontaneous and endothermic nature of the adsorption. In our previous study, the bioactive compound theaflavin was isolated from fresh black tea leaves to treat cancer. Also, the STL generated after the theaflavin extraction from the tea leaves or after the consumption of tea as a beverage can be used as a potential source of natural dye for the textile industries which could be a possible alternative to the

harmful synthetic dyes. Taken together, our studies close the loop of circular economy in the application of tea leaves in therapeutics, textile industries, and waste management by reusing, recycling, and repurposing the product and its wastes through multiple generations.

Keywords: Adsorption, Circular economy, Fish aquarium, wastewater treatment, Malachite green removal, Safe disposal, Sodium hydroxide pretreatment

Statements and Declaration

Competing interest

Authors share no competing interests in terms of financial or non-financial.

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1. Introduction

Over the years, literature studies indicated that agro-industrial wastes pose great potential to be valorized because they contain cellulose that can be used as the precursor of valuable materials [1]. Tea is the most popular beverage around the globe. Different types of tea, either instant tea or processed, generate solid residues of spent tea leaves (STL), which are discarded as solid waste. Tea wastes when recycled may add economic value and benefit to the environment as they are always available within the system [2]. In our studies, our goal is to establish the idea of closing loops within the industrial ecosystem by capturing the value of a product from reuse, recycling, and repurposing for multiple generations leading to sustainable development. Our previous study established the application of tea leaves in therapeutics, by showing the anticancer effect of a bioactive compound, theaflavin isolated from fresh black tea leaves which acted as a potential epigenetic modulator on colon cancer cell lines and also in a carcinogenic animal model in preventing cancer [3]. Also, the spent tea leaves left after the isolation of anticancer compounds from the fresh tea leaves or after the consumption of tea as a beverage could be used to extract natural dyes for textile applications [4,5]. In the current study, we excavate the role of waste tea leaves as a biosorbent for the removal of harmful synthetic dyes from the wastewater. Textile industries use massive amounts of water and discharge huge volumes of wastewater containing synthetic dyes produced from the dyeing and finishing process. When synthetic dyes are released into the environment, they are resistant to biodegradation and harmful to the aquatic organisms dwelling in the receiving water bodies [6]. Malachite green (MG) is one of the dyes, most commonly used for the dyeing of cotton, silk, paper, and leather and also in the manufacturing of paints and printing inks [7]. Also, MG has been effectively used for controlling the infection due to external fungi and protozoan infestation in fish. Water containing MG used in the baths of fish aquariums if not discarded carefully could penetrate the aquatic environment and disrupt the ecosystem as MG is extremely toxic to mammalian cells and causes tumors [8,9]. In our study, we utilized spent tea leaves for the removal of MG from the wastewater. Our objective is to provide an environmental solution by recycling STL. The potential of tea waste for the removal of malachite green dyes by adsorption, from aqueous solution was studied. Spent tea leaves thermally activated with NaOH, were used for malachite green removal from aqueous solution. The effects of pH,

temperature, amount of adsorbent, adsorbate amount, and contact time on malachite green removal were examined. To study the removal efficiency in a real system, MG-containing aquarium water was collected from local fish vendors and treated with alkali-activated spent tea leaves (ASTL) at optimized conditions. The water quality parameters were studied before and after the adsorption procedure and the phytotoxicity of the water after the adsorption was analyzed for safe disposal. We linked the current study with our previous findings to demonstrate the possibility of utilizing tea leaves in a virtuous circle where the product is converted to resources at the end of its service by repurposing, reusing, and recycling in light of a circular economy (Fig.1).

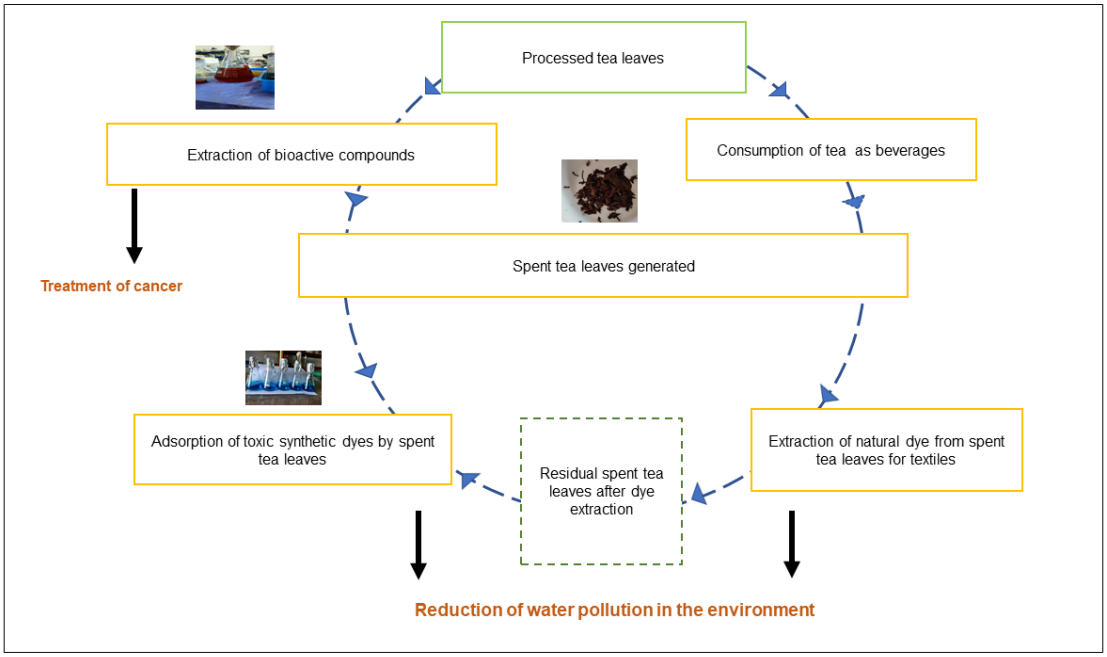

Fig.1 Schematic representation of tea leaves in the circular economy. Tea leaves have potential medicinal value and the spent tea leaves could be valuable resources for natural dye and as a biosorbent that removes toxic synthetic dye. The whole phenomenon will help to reduce the harmful effects of textile dyes on the environment along with value-added industrial applications of tea leaves at different stages.

2. Materials and Methods

2.1. Chemical pretreatment and biosorption preparation

Spent tea leaves of black tea were collected from home and canteen. They were cleaned thoroughly with tap water and then with distilled water to remove any traces of dirt sticking to the surface and washed in hot distilled water until the natural stain released from the tea leaves was removed. Then it was dried in an electric oven at 60°C ± 2°C for 48 h. The leaves were soaked in 1N NaOH and autoclaved to thermally activate the surface. Then it was washed thoroughly with distilled water to neutralize the pH and then dried at 60°C ± 2°C overnight. Then it was crushed and sieved through 300µ mesh and stored at room temperature for future use as a biosorbent. The resulting samples of ASTL were used for characterization and batch adsorption study to remove MG dye from water.

2.2. Characterization of the biosorbent

ASTL and MG-loaded ASTL samples after the adsorption were observed under SEM (Scanning Electron Microscope-Zeiss) to understand the surface morphology. The variations in the functional groups of the biosorbent samples were identified by Fourier Transform Infrared (FTIR) analysis (PerkinElmer Spectrum) using a pellet prepared with 1 mg of sample and 100 mg of KBr. To determine the Zeta potential of the samples, the samples were put in different pHs from 2 to 8 using NaOH and HCl to adjust the pH of the solution and the zeta potential was measured using a Zetasizer (Malvern Instruments Ltd). The Bet surface area of the ASTL was measured by a Micrometrics (3FLEX 3500) gas sorption analyzer.

2.3. Adsorption study

Malachite green was purchased from Sigma-Aldriche (2437-29-8) for the batch adsorption study. Different concentrations (25 to 200 ppm) of MG solutions were prepared and 0.2 g of the ASTL was added to 50ml solution in a 100ml conical flasks for each concentration. The solution was centrifuged at 4000 rpm for 5 min to separate the adsorbent from the aqueous phase as a pellet. Thereafter, the residual concentration of dye in the supernatant was detected by a UV–visible spectrophotometer (Shimadzu, Model UV 1601, Japan) at 620 nm. Adsorbed dye molecules amount per g of solid in the equilibrium, qe (mg/g) was calculated using the formula [10]:-

(1)

$$qe = \frac{(C0 - Ce)V}{m}$$

where Co and Ce (mg/L) are concentrations of MG at the initial phase and equilibrium respectively. V is the total volume of the solution and m is the dry mass of the adsorbent. The percent adsorption was calculated from the Eq (2) [11].:

(2)

$$Removal\ (\%) = \frac{(C0-Ce)}{C0} \times 100$$

Where, C0 (mg/L) is the initial concentration of MG, Ce (mg/L) is the equilibrium concentration of dye, V is the solution volume (L), and m (g), is the adsorbent mass. All the adsorption experiments were carried out at different temperatures of 20 ºC, 30 ºC, and 40ºC at 120 rpm on a thermostat shaker [12].

2.4.1. Effect of amount of adsorbent

Different amounts of adsorbent were used for the removal of MG ranging from 2–10 g/L. 100 ppm of MG dye solution in a 50ml flask was used for each amount of the adsorbent. They were agitated in a shaker incubator at 30ºC for 120 min.

2.4.2. Kinetic study

All kinetic measurements were carried out by using 0.2 g ASTL and 50 ml of dye solution. The mixture was mechanically agitated in a shaker at different concentrations of dye solution (50ppm, 100ppm, 200ppm). After a definite interval of time, the solution was centrifuged the adsorbents were separated and thereafter the remaining dye in the solution was analyzed in a spectrophotometer.

2.4.3. Determination of the effect of pH on the adsorption

The effect of pH on the adsorption of MG onto ASTL was determined at different pH values 3, 5, 7, and also at 5.9 which was the actual pH value of MG solution in distilled water. The pH values of MG solutions were adjusted by drop-wise addition of 0.1 M HCl and 0.1 M NaOH solution and measured in a pH meter. Experimental conditions such as; initial dye concentration, temperature, contact time, and the adsorbent amount were fixed at 100 ppm, 120 min, 30^{o}C, and 4g/L, respectively.

2.5. Batch Adsorption Experiments with Fish Aquarium Water

To assess the MG removal efficiency of the biosorbent in a real system, water samples from the freshwater fish aquarium were collected from a local fish aquarium shop in Kolkata, West Bengal, India. MG is used to control the disease-causing parasites in the aquarium. Physicochemical properties such as pH, temperature, salinity, total dissolved solids, conductivity, and resistivity, Dissolved oxygen (DO) of the aquarium water were measured with Cyber scan CD 650 instrument (Eutech Instruments Pvt Ltd., Singapore). To study the efficacy of ASTL on the removal of MG from fish aquarium water, 0.2g of ASTL was added to 50 ml of the sample solution and agitated in the shaker at 30^{o}C without changing the pH. The solution was centrifuged, adsorbents were separated and the dye adsorption in the solution was measured spectrophotometrically at 620nm.

2.6. Phytotoxicity analysis of the treated water by germination study

The seeds of *Vigna mungo* were procured from an authorized company. The healthy and uniform seeds were chosen for the study. Mercuric chloride solution (0.1 % w/v) was used to sterilize the surface of the seeds and thereafter washed with sterile distilled water. Seeds were incubated at room temperature for 24 h and then exposed to treatments in sterile Petri dishes (5 cm dia). They were spread on the Whatman 42 filter paper on Petri dishes. Both untreated and ASTL-treated aqueous solutions of MG and fish aquarium water and distilled water as control were soaked in the filter papers. Seed germination on 24 h, 48 h, and 72 h were recorded and expressed as a percentage of seeds germinated. The number of seeds germinated and the root length were considered for determination of the Relative seed germination (%) and Relative root growth (%). [13, 14].

2.7. Statistical analysis

The data obtained from phytotoxicity analysis were represented as mean $\pm$ SD. One-way analysis of variance was carried out in GraphPadInStat 3 software to compare means of different treatments taking $P < 0.05$ and $P< 0.01$ as significance levels.

3. Results

3.1. Characterization

SEM images of ASTL before the adsorption and MG-loaded ASTL after the adsorption are shown in Fig.2. Before the adsorption of dye, the ASTL surface showed a rough and layered morphology with spaces in between them, which were beneficial for the adsorption of dye as shown in Fig.2a. After the adsorption of MG, the dye molecules occupy the available pores which resulted in a more dispersed and irregular mass as seen in Fig2b. The BET surface area of ASTL was 1.3122m^2/g. FTIR spectral analysis of spent tea leaves was done before and after MG adsorption. Table1 lists the peaks that are typical to spent tea leaves and also the peaks observed after MG adsorption. The respective FTIR spectra are shown in Fig.3. After adsorption with MG, the spent tea leaves exhibited FTIR spectra with a clear appearance of a band around 1510 and 1165 cm^{-1}, which specified secondary amines and C=O stretching of ether groups respectively. There was a clear disappearance of the peak at 2942 cm^{-1} and 1332 cm^{-1} corresponding to aliphatic C-H stretch and symmetric bending of CH3 respectively. Among all mentioned functional groups, bonded –OH groups, C=O stretching of ether group, aliphatic C–H group, secondary amines, and symmetric bending of CH3 have important roles in the process of adsorption of MG from aqueous solution. After the adsorption, the signature peak at 1162 cm^{-1} represented the C-N stretching vibration of MG thereby confirming the interaction of MG with spent tea leaves [15, 16].

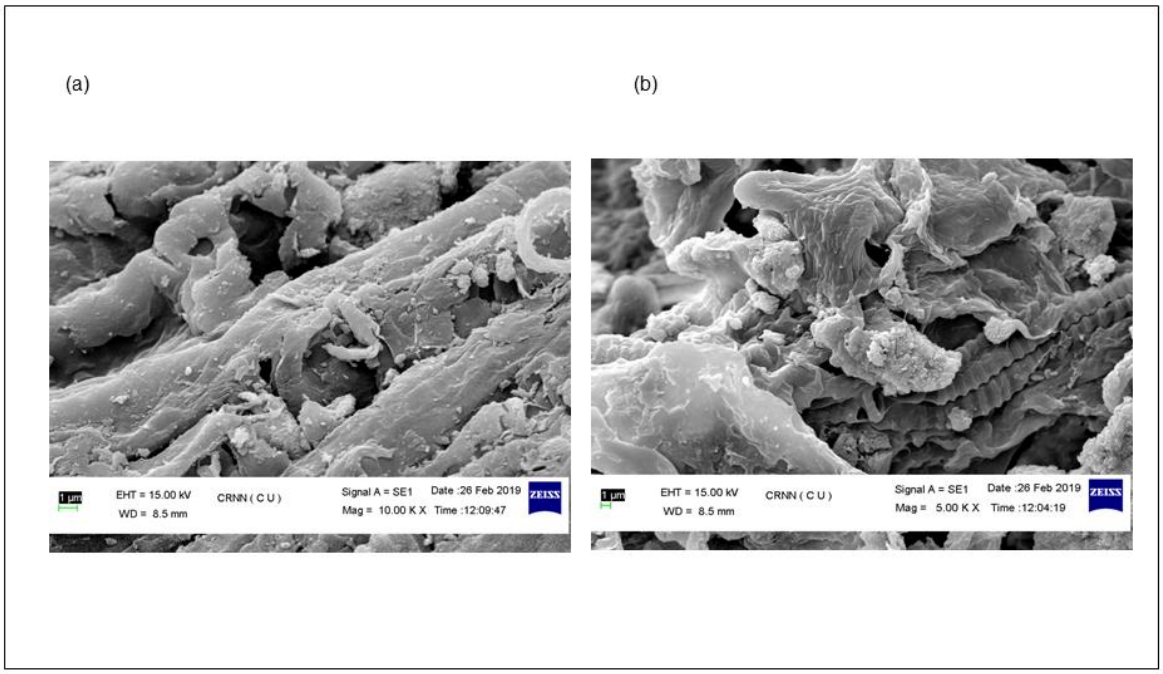

Fig.2 SEM micrographs of ASTL (a) Before the adsorption of Malachite green (MG) and (b) After the adsorption of MG

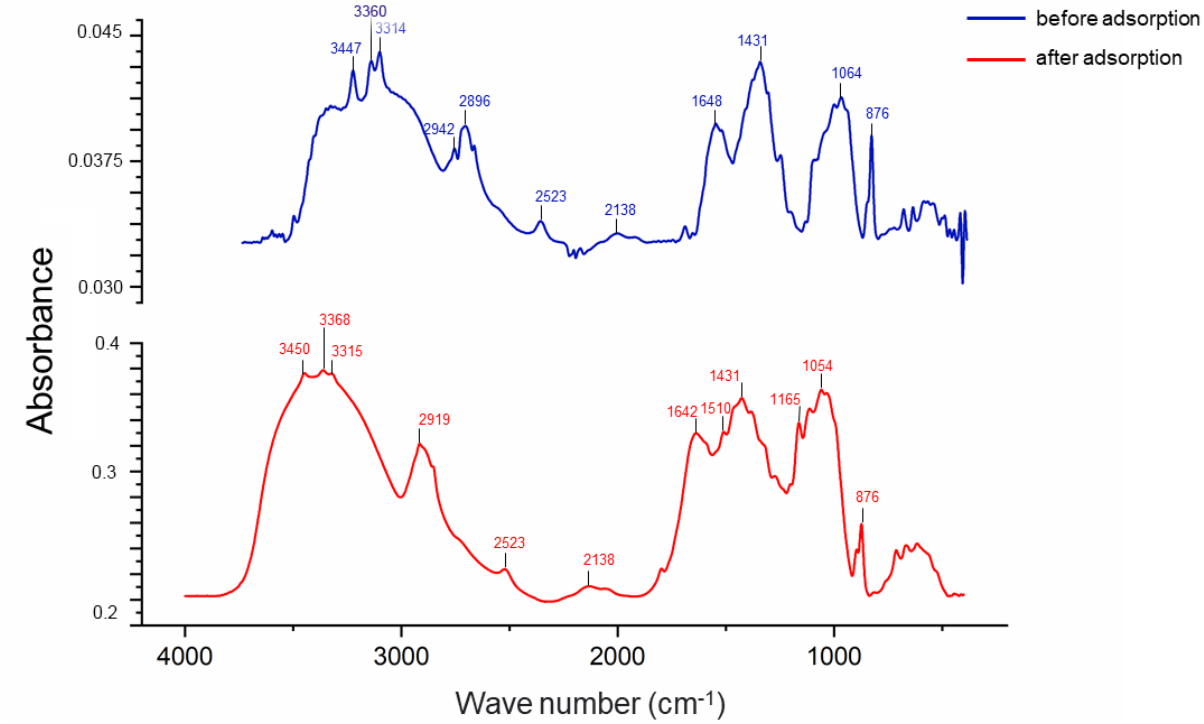

Fig.3 FTIR spectra of ASTL (a) Before adsorption and (b) After adsorption

3.2. Adsorption

3.2.1. Effect of Initial Concentration

Maximum removal efficiency of 98.5% was observed at an initial concentration of 25 ppm. as depicted in Fig.4a. The removal efficiency dropped from 98.5 to 77.5% when the initial concentration was increased from 25 to 200 ppm. The adsorption capacity increased with increasing MG concentration because more MG molecules were available for adsorption.

3.2.2. Effect of amount of adsorbent

The sorption of MG onto ASTL was investigated by changing the quantity of adsorbent from 2 g/L to 10 g/L. For this experiment, ASTL was added to 50 ml of 100 ppm of MG solution and was used for 90 min at 30°C in a thermostat shaker. Adsorption of MG was increased with increasing the amount of ASTL. This may be due to the increase in adsorbent surface area and the availability of more adsorption sites. As depicted in Fig.4b, a maximum removal efficiency of 98.05% was obtained by 4g/L of adsorbent. The removal percentage of MG remained unaltered with a further increase in adsorbent dosage as it causes less uptake due to the saturation or overlapping of active sites [17].

Table 1: FTIR peaks and assignments

FTIR Peaks	Frequencies (cm^{-1})			Assignment
	Before Adsorption	After Adsorption	Differences	
1	3447	3450	+3	Bonded -OH groups
2	3360	3368	+8	Bonded -OH groups
3	3314	3315	+1	Bonded -OH groups
4	2942	disappeared	-	Aliphatic C-H stretch
5	2896	2919	+23	Aliphatic C-H stretch
6	2523	2523	0	C=C stretch
7	2138	2138	0	C=C stretch
8	1648	1642	-6	C=O stretch
9	Not present	1510	-	Secondary amines
10	1431	1431	0	Aliphatic C-H stretch
11	1332	disappeared	-	Symmetric bending of CH3
12	Not present	1162	-	C=O stretching of the ether group
13	1064	1054	-10	C=O stretching
14	876	876	0	Aromatic C-H stretching

3.2.3. Effect of temperature

The influence of temperature on MG removal efficiency was evaluated by varying the temperature from 20°C to 40°C (Fig.4c). Maximum removal efficiency was 98.1% at 40°C.

3.2.4. Effect of time

The adsorption efficiency increased from 66.8% to 98.2 %, with an increase in time from 10 to 240 mins, and afterward, no change was observed as shown in Fig.4d. The adsorbent surface coverage becomes high and further, no adsorption takes place as time progresses. There was no significant change in equilibrium concentration after 90 mins, and the adsorption phase reached equilibrium [18].

3.2.5. Effect of pH

The pH of the solution influences the adsorption process significantly as seen in Fig.4e. MG is a cationic dye, which exists in an aqueous solution in the form of positively charged ions. It was observed that the removal percentage of MG was minimal at pH 3 (18% approx.). Removal percentage decreased below pH 4 because of the electrostatic repulsion between positively charged dye cations [19]. This phenomenon can be explained by the competition of excess H+ ions with dye cations for the sorption sites [20]. The removal percentage increased

up to 98.2% at pH 7 and also at pH 5.9 which is the actual pH of the malachite green solution without pH adjustment. At greater pH values, the adsorbent surface is negatively charged, thereby it increases the affinity of positively charged dye molecules to attach to the adsorbent surface [21]. MG solution tends to become colorless from pH 9. The zeta potential analysis of ASTL showed that the zero point of charge (pHzpc) value is 4.44. pH>pHpzc favors the adsorption of cationic dye as the functional groups such as OH^-, and COO^- are present. The surface charge on the adsorbent influences the degree of the adsorption of the cationic dye molecules onto the adsorbent, and again that is influenced by the pH of the solution.

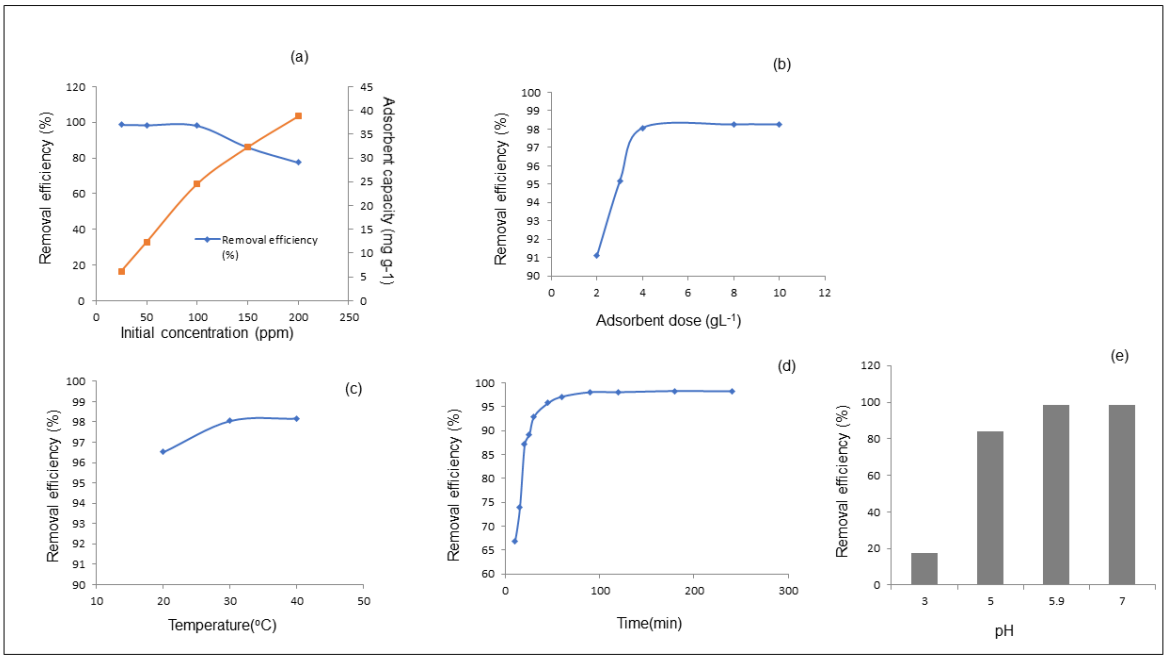

Fig.4 Adsorption process optimization for MG removal by ASTL. (a) Influence of initial concentration of MG. (b) Influence of adsorbent dose (c) Influence of temperature (°C) (d) Influence of time (e) Influence of pH

3.3. Adsorption Isotherm

The equilibrium characteristics of the adsorbents were described with the help of Langmuir and Freundlich's isotherm equations. The Langmuir isotherm theory suggests monolayer coverage of the adsorbate over a homogenous adsorbent surface. Once a site is occupied by a molecule, no further adsorption can take place at that site. The linear form of Langmuir isotherm is expressed as;

(3)

$$\frac{Ce}{qe} = \frac{1}{qml} + \frac{ce}{qm}$$

where q_e is the dye amount adsorbed at equilibrium per unit weight of adsorbent ($mg.g^{-1}$) and Ce is the equilibrium concentration of dye in solution ($mg.L^{-1}$). The constant qm is the monolayer sorption capacity ($mg.g^{-1}$) and L is associated with the adsorption energy ($L\ mg^{-1}$). Plots of Ce/qe versus Ce (Fig.5a) yield a straight line with slope 1/qm and intercept 1/qmL. The maximum adsorption capacity qm values for malachite

green sorption onto ASTL at different temperatures are listed in Table 2. The characteristics of the Langmuir isotherm can be essentially expressed in terms of dimensionless constant separation factor RL given by:

(4)

$$RL = \frac{1}{1 + bC0}$$

where b is the Langmuir constant and C_0 is the highest initial dye concentration ($mg.L^{-1}$). The parameter RL shows whether a sorption system is favorable if (0 < RL < 1) or unfavorable (RL > 1) in batch processes. The isotherm type is irreversible and linear, respectively if the RL value is zero and unity [22]. Since RL values were obtained in a range between 0 and 1, at 20 °C, 30 °C, and 40°C, it can be said that the adsorption is favorable at the operation conditions studied.

The Freundlich isotherm is an empirical equation based on a heterogeneous surface [23]. A linear form of the Freundlich expression can be presented as below:

(5)

$$logqe = logkf + nflogce$$

A plot of log qe versus log Ce enables us to determine the constant Kf and nf. Kf value represents the quantity of dye adsorbed onto the adsorbent for an equilibrium concentration. A measure of adsorption intensity or surface heterogeneity is the slope nf. It becomes more heterogeneous as its value approaches zero. Table 2 summarizes these values together with the correlation coefficients. Based upon the correlation coefficients (R^2) shown in Table 2, it can be said that Langmuir isotherm fits the data better than Freundlich, which shows that the adsorption of MG on ASTL takes place as monolayer sorption on a surface that is homogenous in sorption affinity.

3.4. Kinetic studies

The adsorption kinetics and rate-limiting step were evaluated by Pseudo-first-order and pseudo-second-order kinetic models. To investigate the suitability of the pseudo-first-order kinetic model and obtain a rate constant, the Lagergren equation was used [24].

The equation is given as:

(6)

$$\ln(qe - qt) = lnqe - k1t$$

where qe (mg.g^{-1}) and qt (mg.g^{-1}) are the amount of MG sorbed at equilibrium and at any time t, respectively. k1 (min^{-1}) is the rate constant for Lagergren-first-order sorption. The straight line plots of log (qe -qt) against t were made at different initial concentrations (50,100 and 200 ppm), the values as given in Table 2. The correlation coefficients are low and calculated qe values from linear plots do not verify the experimental qe values. This shows that the adsorption of MG onto ASTL does not follow a first-order kinetics.

The pseudo-second-order model is given as follows [25]:

(7)

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qt}$$

k^2 is the pseudo-second-order rate constant (g/mg min). The calculated and experimental qe values are very close to each other as seen in Table 2. It can be said that based on correlation coefficients, the pseudo-second-order kinetic model (Fig.5b) shows a better fit than the pseudo-first-order kinetic model which means the rate of the adsorption is dependent on the adsorption capacity and not the concentration of the adsorbate.

3.5. Thermodynamics study

The values of three thermodynamic constants, $\Delta G°$ as Gibb's free energy (in J mol^{-1}), $\Delta H°$ as the enthalpy change (in J mol^{-1}), and $\Delta S°$ as the entropy change (in J mol^{-1} K^{-1}) were calculated from Eqs. (8) and (9) [26].

(8)

$$\Delta G° = -\mathrm{RTlnKd}$$

where Kd is the sorption distribution coefficient and R (8.314 J/mol_K) is the ideal gas constant. Values of Kd were calculated from the intercept of the plot ln(qe/Ce) vs. Ce. Gibbs free energy of adsorption was calculated from Eq. (9):

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (9)$$

Putting for ΔG^o, Eq. (10) can be rearranged as:

(10)

$$lnKd = \frac{\Delta \mathrm{So}}{\mathrm{R}} - \frac{\Delta \mathrm{Ho}}{\mathrm{R}} . \frac{1}{\mathrm{T}}$$

The values of ΔS^o and ΔH^o were calculated from the intercept and slope of the plot lnKd vs. 1/T. R is the gas constant (8.314 J/mol K), T is the absolute temperature in K and Kd is the equilibrium constant [26].

$\Delta G°$ for three different reaction temperatures viz. 20, 30, and 40 °C were found to be -2.08188 J mol^{-1}, -2.44286 J mol^{-1} and -2.63455 J mol^{-1}, respectively (Eq. 8). The values of $\Delta H°$ and $\Delta S°$ of the adsorption process obtained from the intercept and the slope of Eq. (10) were 6.0430309 KJ mol^{-1} and 27.82031 J mol^{-1} K^{-1}, respectively. The values of $\Delta G°$ were negative and they decreased with the increase in temperature. These values suggested a spontaneous nature of adsorption and supported the fact that better adsorption takes place at higher temperatures. That can be confirmed by the higher values of Qmax at higher temperatures. The value of ΔH^o was positive, indicating that the sorption reaction is endothermic. The positive values of $\Delta S°$ indicate physical adsorption, which is further confirmed by the relatively low values of $\Delta G°$ [27].

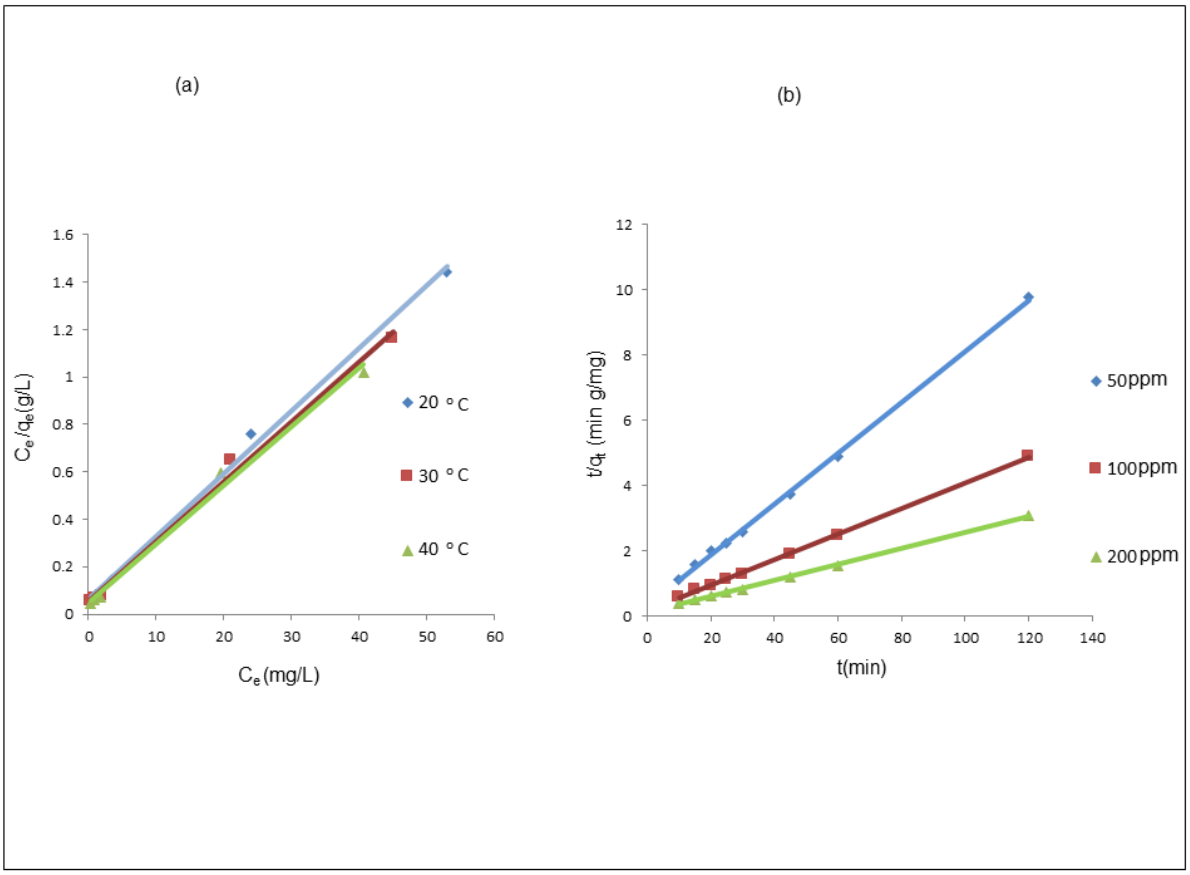

Fig.5 (a) Langmuir adsorption isotherms at 20°C, 30°C, and 40°C. (b) Pseudo-second-order kinetics with different concentrations of dye (50mg/ml, 100mg/ml, and 200mg/ml)

3.6. Adsorption mechanism

Experiments revealed that Langmuir isotherm fits the data better than Freundlich. Therefore, ASTL takes place as monolayer sorption on a surface that is homogenous in sorption affinity. The value of $\Delta H°$ was negative, indicating that the sorption reaction is endothermic. The positive values of $\Delta S°$ indicate physical adsorption, which is further confirmed by the relatively low values of $\Delta G°$.

Table 2: Isotherm study with Langmuir and Freundlich isotherm models and Pseudo first order and pseudo-second order kinetics study for adsorption of MG on ASTL

Isotherm Study				
Langmuir				
Temperature	*Q*max (mg g−1)	kL (L/mg)	R2	RL
20	37.73585	0.402124	0.9967	0.012281
30	39.52569	0.47026	0.9939	0.010521
40	40.65041	0.49497	0.992	0.010001
Freundlich				
Temperature	Nf ranging between 0 and 1,	kf	R2	
20	2.935134	11.02808	0.89	
30	2.990431	12.32253	0.8444	
40	2.955956	12.79381	0.8638	
Kinetics study				
Pseudo-first order kinetics				
C0 (mg/L)	qe(mg/g)	k1 (1/min)	R2	
50	4.948577	0.000523	0.8969	
100	7.800595	0.000388	0.9407	
200	14.54431	0.000427	0.9464	
Pseudo-second-order kinetics				
C0 (mg/L)	*Qe* calc (mg/g)	K2	R2	
50	164.7878	0.018753	0.9989	
100	654.1035	0.009449	0.9991	
200	1639.102	0.005567	0.9991	

3.7. Malachite Green Removal from Fish Aquarium

The collected MG-contaminated aquarium water was treated with ASTL at optimized conditions. More than 98% removal of MG was observed. Table 3 summarizes the change in the quality of the aquarium water before and after the adsorption. The results indicated that upon treatment with ASTL, the quality of aquarium water was restored to the normal level. Reduction in total dissolved solid shows that ASTL was not only efficient in the removal of MG in the medium but equally capable of removing MG along with other impurities from aquarium water.

3.8. Safe Disposal

The seed germination percentage of the seeds exposed to MG aqueous solution and aquarium water before and after adsorption is shown in Fig.6. An increase in germination percentage was observed in the ASTL-treated MG aqueous solution and aquarium water samples when compared to the samples from the untreated solutions. This indicated that the water after the removal of malachite green could be reused or safely discharged into the environment.

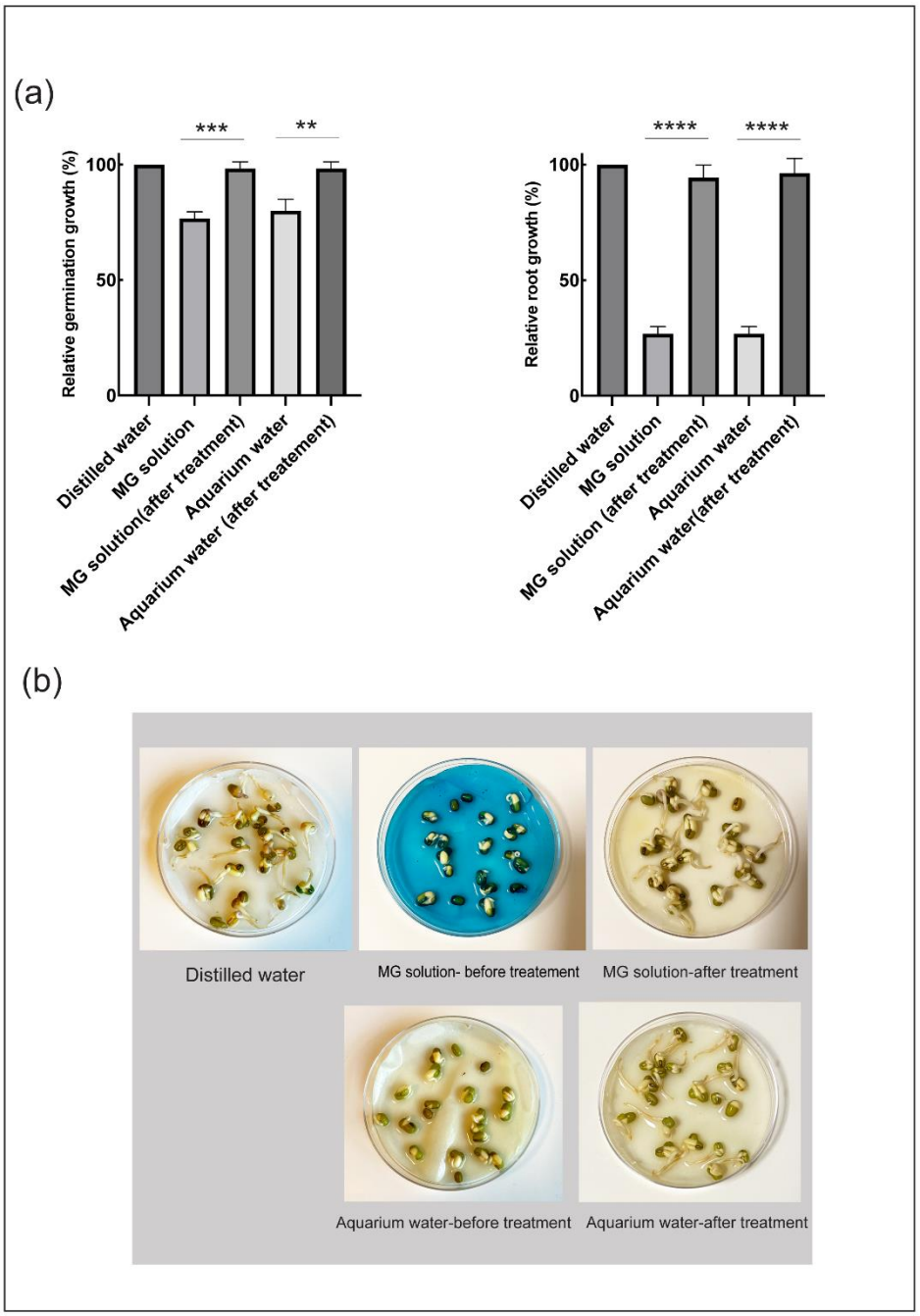

Fig.6 Phytotoxicity analysis of the effluent after the adsorption (a) Relative seed germination percentage of *Vigna mungo* (b) Relative root growth percentage of *Vigna mungo*. Each value is expressed as mean ± SD (n=3). **P<0.005 ***P<0.0008 ****P<0.0001

Table 3: Physico-chemical qualities of MG containing aquarium water before and after the adsorption of MG by ASTL

Parameters	Before treatment	After treatment	Standard freshwater [39]
pH	6.23	6.4	6.5-8.3
DO	4.11 mg/ml	4.5 mg/ml	>5mg/l mg/ml
TDS	1.477 ppt	709.4ppm	50-500ppm
Salinity	1.402 ppt	721.6ppm	<0.5 ppt
Conductivity	1.48 mS/cm	746.3µS/cm	0-1500µS/cm
Resistivity	357.6 Ω	704.7 Ω	1000-5000Ω

4. **Discussion**

Recent research on adsorbents for the remediation of wastewater highlights the use of materials derived from waste as the source of biosorbents for their cost-effectiveness, easy availability, and efficiency [28,29]. Studies revealed the binding of contaminants onto biomass through physicochemical interactions [30]. Several studies supported the utilization of biomass as the source of adsorbent for sustainable wastewater management as the adsorbent production from industrial wastes may be costly and generate toxic byproducts [31, 32].

Tea is the most popular beverage in the world and the consumption of tea generates huge amounts of STL which are disposed of and eventually creates a burden to the environment. 'Waste' tea leaves were converted into 'wealth' in our study for utilization as a biosorbent in the adsorption of toxic malachite green dye from the aqueous solution. The relatively high content of cellulose, hemicellulose, and lignin in the tea leaves makes them ideal to be used as a biosorbent [33]. For the removal of positively charged, MG dye, STL was pretreated with alkali (NaOH) and thermally activated which improved its removal efficiency to 98%. It was observed from our study, that pH plays a significant role in the adsorption process. MG exists in the form of positively charged ions in the aqueous solution. The surface of the adsorbents at high pH values is negatively charged and due to the presence of OH^-, and COO^- functional groups in the adsorbents, it increases the affinity of the cationic dye molecules to bind to its surface. Our study also provided a mechanistic overview of the adsorption process of ASTL. Langmuir isotherm model fits the data better than Freundlich which means it is a monolayer sorption process on a homogenous surface. It is a physical adsorption process and is endothermic as indicated by the positive value of $\Delta S°$ and a negative $\Delta H°$ value respectively. It showed the nature of the adsorption was spontaneous with better adsorption taking place at higher temperatures supported by the values of $\Delta G°$ which

decreased with the increase in temperature. To examine the adsorption efficiency of ASTL in a real system, fish aquarium water was treated with MG. The condition of the aquarium water returned to the normal level when compared to the distilled water. ASTL not only removed the MG from the aquarium water, but it was also capable of removing other impurities in the water as indicated by the reduced level of TDS in the water. This opens up a new direction to study the efficacy of ASTL to remove mixed contaminants in wastewater which could show some directions to resolve the difficulties for wastewater treatment as in the real environment the effluent contains a mixture of contaminants.

The toxic effluent, if treated efficiently could be reused for industrial or domestic purposes or safely disposed to the environment [34]. In our studies, the toxicity of the solutions after the absorption was assessed to find out the reusability of the water after the removal of MG from the aqueous solution and the aquarium water. The solutions were used to grow *Vigna mungo* seeds and the germination percentage of the seeds indicated that it could be safely discharged into the environment or reused for another purpose. The disposal of the dye-loaded spent tea leaves has to be addressed in our future studies. STL extract was reported to promote early growth of seedlings *in vitro* [35]. Therefore, the MG-loaded adsorbent after the adsorption could be a potential source for composting. Another study showed that the lead-loaded spent biosorbent was utilized in the preparation of bricks for building houses [36]. Incorporation into the glass matrix is also another possible approach [15, 10]. Different innovative methods and sustainable approaches to utilizing the MG-loaded STL are the topics to be explored in our future studies keeping in mind the circular economy.

We further, drew a connection between our current experimental results and our previous findings to establish the use of tea leaves through multiple generations closing the loop of the circular economy (Fig.1). In our previous study, we proved that besides being a popular beverage, tea leaves have the potential to be used as cost-effective therapeutics for cancer treatment. Also, previous studies showed the extract from the spent tea leaves could be used as a natural dye on fabric after improving the quality of the dye [4,5]. The fast-growing fashion industries are infamous for environmental problems, resource exploitation, and pollution which need to be addressed through minimization of the intake of natural resources as well as the waste output by introducing the practice of a circular economy such as increasing the material lifetime using chemical recycling and replacement of input materials such as the substitution of chemical dyes with natural dyes which in turn could reduce the load of pollutants in the effluent [37, 38]. The utilization of STL as a natural dye as well as a biosorbent for the removal of synthetic dye could overall reduce the burden of water pollution in the environment cost-effectively and sustainably. Overall, the study supports the idea of valorization of agro-industrial waste products in a circular economy toward sustainability.

5. Conclusion

It can be concluded from the experiments that the ASTL could be used as a potential source of an efficient low-cost adsorbent for the removal of malachite green from wastewater. Langmuir isotherm fits better than Freundlich. The kinetics of adsorption followed pseudo-second-order kinetics. The removal efficiency increases with the increase in temperature and hence adsorption process is endothermic. Experimental results showed that ASTL successfully removed MG from fish aquarium water. Phytotoxic analysis of the water after the adsorption indicated that the water could be safely disposed of in the environment or reused by the industry. Also, drawing

a connection with our previous findings indicates the potential of tea leaves to be used through multiple generations and STL could be converted from 'waste to wealth' in the light of a circular economy leading to sustainability by capturing its value by recycling and reusing.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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