Larhyss Journal, ISSN 1112-3680, n°55, Sept 2023, pp. 161-189
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CADMIUM METAL SCAVENGING CAPABILITY OF SPENT TEA GRAINS - AN AGRICULTURAL BIOMASS WASTE AS A LOW-COST ADSORBENT

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Research Article – Available at http://larhyss.net/ojs/index.php/larhyss/index
Received May 26, 2023, Received in revised form August 25, 2023, Accepted August 28, 2023

ABSTRACT

Over the past decade, there has been heightened attention to the advancement of eco-friendly technologies aimed at purifying heavy metal-contaminated water, recognizing the substantial risks these metals pose to human health and the environment. Amidst these emerging technologies, biosorption emerges as a highly promising method that harnesses the potential of naturally available waste materials to efficiently eliminate heavy metals. A sequence of batch experiments was performed under normal room temperature to evaluate the crucial factors that influence the adsorption of cadmium ions from synthetic solutions prepared using double distilled water onto STG, including the particle size (1180 – 75 microns) of STG, contact time provided (30-180 min), adsorbent dosage (1-10 g/L), rotary shaker speed (25-200 rpm), pH (2-7) and cadmium ion concentration (2-16 ppm). By implementing optimal conditions found through various batch study experiments, such as an initial cadmium ion concentration (C_o) of 5 ppm, a dose of 1 g/L STG, an adsorbate pH value of 6.04, a shaker speed of 200 rpm, and a 90-minute duration of exposure, the Langmuir equilibrium isotherm model revealed a maximum uptake rate (q_{max}) of 28.16 mg/g. Upon evaluating different conventional kinetics models, it was observed that the batch study data aligned with the rate kinetics well explained by the pseudosecond-order rate kinetics equation. The equilibrium state between the adsorbate and adsorbent was achieved within a period of approximately 75 to 90 minutes, following an initial rapid adsorption rate. Additionally, it was observed that both % removal and uptake capacity exhibited a direct correlation with the pH level; as the pH level transitioned from acidic (2) to nearly neutral (7), there was a substantial increase in both the percentage removal and uptake capacity. The FTIR spectroscopy analysis suggests that the adsorption mechanism of spent tea grains (STG) can be attributed to the existence of carboxyl and hydroxyl groups in the material. Based on the experimental data acquired under optimal conditions, it can be inferred that spent tea grains (STG) hold significant potential for utilization as a highly effective adsorbent.

Keywords: Heavy metal, Spent tea grains, Biosorption, Adsorption, Equilibrium kinetics.

INTRODUCTION

Rapid industrialization worldwide has led to significant concern regarding heavy metal contamination. The discharge of toxic effluents containing heavy metals poses a significant threat to the overall ecology (Jana et al., 2021; Mumthaj et al., 2023). Stringent regulations have been put in place to control the release of these metals into water bodies due to their detrimental effects on the environment. These regulations define strict limits on the maximum allowable concentrations of these metals in effluent disposal (Lee et al., 2014; Pandey et al., 2023). Cadmium, a heavy metal, is widely recognized for its high toxicity. The permissible limit set by the CPCB for the release of industrial effluents into surface water sources is 2 mg/l, while for sewers, it is 1 mg/l. In terms of drinking water, the WHO defines the permissible limit as 0.003 mg/l, and the USEPA defines it as 0.005 mg/l. The escalating release of cadmium into water streams represents a significant and concerning threat (Aroua-Berkat . and Aroua., 2022; Singh et al., 2022). Industries such as electroplating, pigments, metallurgy, and mining, which utilize cadmium, have contributed to severe environmental contamination. Cadmium contamination not only affects the environment but also poses health risks to humans, including sterility (Lim and Aris, 2014; Shekhawat et al., 2017). Extensive research has been undertaken on the potential health hazards associated with these metals, leading to the development of various treatment processes for removing Cd(II) from effluents (Sharma et al., 2014).

Conventional approaches for Cd(II) removal encompass techniques such as filtration, reverse osmosis, ion exchange, precipitation, membrane separation, and electrochemical analysis (Huang et al., 2017). However, conventional techniques have several disadvantages, such as time-consuming processes, high overall cost, challenges in disposal mechanisms, and relatively low efficiency (Pal and Maiti, 2019). Adsorption is a promising, efficient, and economically viable technique for the removal of heavy metals from various effluent sources. Over the past decade or two, extensive research has been carried out to investigate the possibilities of using agricultural biomass wastes as highly effective and economically viable adsorbents for the efficient reduction of toxic metals from various industrial contaminants (Adie Gilbert et al., 2011).

Over the past decades, notable progress has been made in the field of adsorption of toxic contaminants using economically viable, indigenous adsorbents (Reddy et al., 2012). Researchers have extensively investigated various agricultural waste materials for their adsorption capabilities. These potential adsorbent biomasses are abundant locally and are readily available at low cost. Examples of such materials include rice husk (Ajmal et al., 2003), leaves (Al-Masri et al., 2010), peanut hulls (Qin Li et al., 2007), sugarcane bagasse

(Karunarathne and Amarasinghe, 2013), crop milling waste (Saeed et al., 2005), coconut shell (Bernard et al., 2013), and sawdust (Naiya et al., 2009).

Tea is one of the potential biomass materials locally available and widely consumed beverages globally and is also known for its health benefits. The structural composition of tea primarily comprises hemicelluloses, cellulose, condensed tannins, lignin, and structural proteins. Tea waste contains various oxyl groups, phenolic hydroxyl, and carboxylate, which contribute to the adsorption process for the reduction of metal contaminants from various types of industrial processes (Ahluwalia and Goyal, 2005). In the last few years, tea waste has been investigated as an adsorbent for the removal of heavy metals and found to be a potentially good adsorbent (Tee & Khan, 1988)(Datta et al., 2014)(Hussain et al., 2018).

The primary objective of this study is to comprehensively investigate the potential of an adsorbent derived from tea waste grains, a form of agricultural biomass, in efficiently removing Cd^{2+} ions from wastewater. This aspect has received limited attention in previous research, necessitating a detailed exploration. Numerous experiments were conducted to assess the influence of various key factors on the adsorption process. The parameters investigated in these experiments included the particle size of the prepared adsorbent, rotary shaker speed, adsorbent dosage, adsorbate pH, C_o, and contact time provided during adsorption of Cd ions from synthetic aqueous solutions prepared from Cd salt using double distilled water. The experimental data obtained from the batch study were subjected to analysis using various conventional isotherm models to understand the underlying mechanism of adsorption. Additionally, several kinetic models, such as Elovich, PFO, IPD, and PSO kinetics, were explored to gain a deeper understanding of the kinetics between the adsorbent and the adsorbate throughout the process.

MATERIALS AND METHODS

Chemicals and Materials

The synthetic solutions of Cd were prepared using analytical grade metal salt. A stock solution of Cd(II) with a concentration of 1000 ppm was prepared using $Cd(NO_3)_2$ salt. Various concentrations as needed were prepared after diluting the prepared concentrated solution with deionized water. Prior to the experiments, all glassware used was thoroughly cleaned and sterilized by washing with a weak acid solution (0.1 M HNO_3) and then rinsed with deionized water/double distilled water.

Preparation of adsorbent

The spent tea grains (STG) used in this study were collected from various tea shops located near IIT (BHU), India. To prepare the agricultural waste for experimentation, it was initially dried by placing it under sunlight for two days, or it could be dried using a hot-air oven at a fixed temperature of 80°C for 12 continuous hours. During the preliminary screening process, many constituents were separated from the biomass waste, such as dried ginger and small cardamom. The collected biomass waste was then subjected to repeated boiling at temperatures exceeding 100°C until the aqueous solution became colorless. Following color removal, the prepared waste was dried in a hot-air oven at a fixed temperature of 80°C for 24 hours. The resulting spent tea leaves (STG) were sieved, and particles ranging from 600 microns to 75 microns were selected for the experiments, except for the particle size test.

Adsorbent characterization

To characterize the prepared adsorbent, efforts were made to determine the functional groups present, visualize its morphology, analyze its weight loss behavior and quantify the surface charge loads involved in its structure. FTIR analysis was employed to analyze the vibrational frequencies and corresponding functional groups present in the system (STG), both prior to and following the adsorption process. Surface morphology analysis of the adsorbents was conducted employing a scanning electron microscope (SEM). In addition, thermogravimetric analysis was performed to determine their weight behavior.

Determination of the Point of Zero Charge

The pHzc (point of zero charge) was determined using the solid addition technique. To conduct the pHzc analysis, a series of experiments was conducted by aliquoting 50 ml of a 0.1 M KNO_3 solution into separate 100 ml conical flasks. The solid addition method was employed for the pH range from 2.0-12.0. For the adjustment of pH, dilute 0.1 M HNO_3 and dilute 0.1 M NaOH were used. Subsequently, a measured quantity of the prepared adsorbent was introduced into each set of the aforementioned 100 ml conical flasks. Next, the series of conical flasks was placed on a rotary shaker and subjected to continuous agitation for 24 hours at a constant rotational speed of 150 revolutions per minute. The pH values of the sample after filtration were measured after the 24-hour period. By plotting the graph between the initial pH vs ΔpH value, the pHzc value was determined.

Batch adsorption experiments

To gather insight into the adsorption process and its kinetics, various batch adsorption experiments were performed using aqueous solutions containing Cd(II). The objective of these experiments was to identify the optimal values for various parameters that impact the efficiency of adsorption. The pH was adjusted with weak acid (dilute 0.1 M HNO_3) or weak base (dilute 0.1 M NaOH) solutions. Several factors were investigated, including the initial concentration (2 -16 mg/l), contact time (15-180 mins), pH (2-7), dosage (1-10 g/L), and stirring speed. (25-200 rpm) Additionally, considering that the adsorption effectiveness is closely linked to the available surface area, the influence of adsorbent size on % removal and adsorption capacity was also investigated. For the mentioned experiment, particle sizes ranging from 75 µm to 1.18 mm were considered.

Metal Analysis

The concentrations of Cd(II) were determined using atomic adsorption spectroscopy, which is based on Beer Lambert's Principle, using AAS-4141 supplied by ECIL India. Subsequently, the rates of Cd(II) ion adsorption and removal were determined using:

$$Q_e = \frac{(C_o - C_e) * V}{1000 * m} \tag{1}$$

$$Y(\%) = \frac{(C_o - C_e)}{C_o} * 100 \tag{2}$$

Adsorption Kinetics Study

To explore the rate kinetics mechanism of the adsorption process, four conventional kinetic models were utilized in this study, namely, the intraparticle diffusion, pseudosecond-order (PSO), pseudofirst-order (PFO), and Elovich models.

Ho and McKay (Ho & McKay, 1999) and Qingzhu Li, Liyuan Chai and Wenqing Qin (Qingzhu Li et al., 2012) expressed the kinetic equations for PFO and PSO in the following manner:

$$\log (Q_e - Q_t) = Log(Q_e) - k_1 * 2.303\, t \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{4}$$

The intraparticle diffusion model based on Weber and Morris principles will be utilized for a detailed investigation of the adsorption diffusion mechanism. This model allows for the analysis of how the adsorbate molecules diffuse within the adsorbent particles during the adsorption process. The Weber and Morris principle can be expressed as follows (Gonte & Balasubramanian, 2016):

$$q_t = k_{pi} t^{1/2} + C_i \tag{5}$$

For the investigation of chemisorption kinetics on heterogeneous surfaces, we must examine the Elovich model (Cortés-Martínez et al., 2004). It can be represented as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{6}$$

Adsorption Isotherm Study

To gain insight into the adsorbent surface behavior during its interaction with the adsorbate, various isotherm models, such as the Freundlich isotherm, Langmuir isotherm, Temkin and Pyzhev isotherm, and Dubinin–Radushkevich (D–R) isotherm, are explored.

Freundlich isotherm (Eq. 7) and the Langmuir isotherm (Eq. 8) equations are represented as:(Gonte & Balasubramanian, 2016)

$$Q_e = Kf\sqrt[n]{C_e} \tag{7}$$

$$Q_e = \frac{Q_m K_L C_e}{1+K_L C_e} \tag{8}$$

The linearized form of the Freundlich isotherm (Eq. 9) and the Langmuir isotherm (Eq. 10) equations are represented as:

$$\ln q_e = \ln K_f - \frac{1}{n} C_e \tag{9}$$

$$\frac{C_e}{Q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{10}$$

Through Temkin and Pyzhev isotherm model investigation, we can analyze the influence of indirect interactions between the adsorbent and adsorbate. As per their suggestion, these interactions result in a gradual reduction in the heat of adsorption within the adsorbate layer, displaying a linear decrease as the layer becomes progressively covered by the adsorbent. The Temkin and Pyzhev isotherm model equation can be explained by:(Farrokhzadeh et al., 2013)

$$Q_e = \frac{RT}{b_T} LN\ (A_T C_e) \tag{11}$$

The investigation will encompass the assessment of porosity, adsorption characteristics, and apparent free energy using the Dubinin–Radushkevich (D–R) isotherm model. It can be explained by:(Radhakrishnan et al., 2016)

$$q_e = Q_m \exp\left(-K\varepsilon^2\right) \tag{12}$$

RESULTS AND DISCUSSION

Adsorbent Characterization

pHzc - Point of zero charge

By examining Fig. 1 and identifying the point at which ΔpH crossed zero, the pHpzc value was determined to be 7.57.

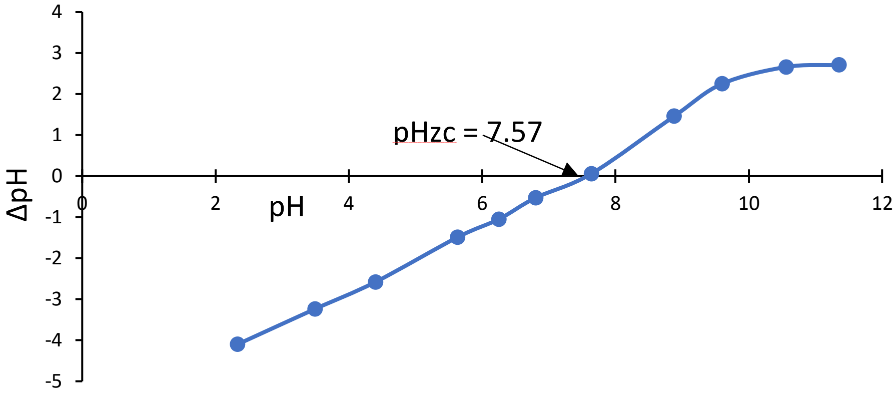


Figure 1: Point of Zero Charge (pHzc) of Raw Spent Tea Grains (STG)

TGA analysis of raw spent tea grains (STG)

The behavior of the prepared adsorbent under various thermal conditions was examined using TGA (Thermogravimetric Analysis) analysis, performed with the TGA-50 instrument supplied by M/s Shimadzu (Asia Pacific) Pvt. Ltd. This analysis provides valuable information about the moisture content, biomass composition, and volatile matter present in the adsorbent. TGA was performed to investigate the thermal stability and decomposition profile of the STG adsorbent. Fig. 2 illustrates the thermogravimetric (TG) curve associated with STG.

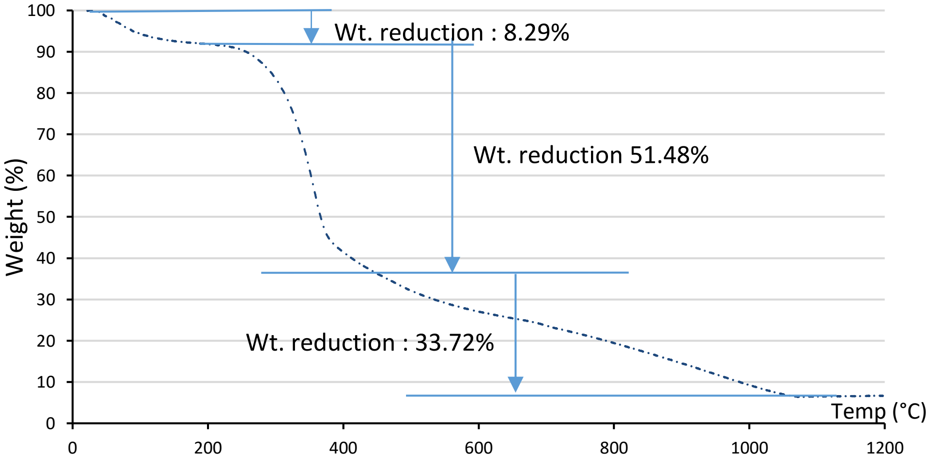


Figure 2: Thermogravimetric Analysis of Raw STG-Source: (Chauhan et al., 2023)

The prepared adsorbent exhibited a thermal degradation profile characterized by three main stages. The initial weight loss, ranging from 20°C to 200°C, can be attributed to the evaporation of physically weak, chemically strong bonded moisture and lightweight volatiles in the adsorbent. The first-stage weight loss percentage was calculated to be approximately 8.29%. The second-stage adsorbent degradation occurred between approximately 250°C and 415°C. A rapid devolatilization of the components was observed starting from approximately 200°C and continued until temperatures of 410°C-415°C, indicating the degradation of the fibrous content of the adsorbent, including holocellulose, cellulose, hemicellulose, and a slight degradation of the lignin content present in the adsorbent. A weight loss of approximately 51.48% was noted during the second stage until the maximum degradation temperature of approximately 415°C. As the temperature increased further, the second stage exhibited a significant weight drop, indicating the reduction of the various fibrous contents through decarboxylation, dehydration, and decarbonization. The third stage of adsorbent thermal decomposition occurred during the range 415°C-1100°C, primarily due to the lignin content reduction. The maximum temperature reached during this stage was approximately 1100°C. At 1100°C, considering all three stages, the total weight loss of the adsorbent reached 93.49%. The high decomposition temperature of STG confirms its suitability for high-temperature applications. Therefore, when the oven drying temperature was set at 90°C, no chemical or structural modifications occurred due to heating. As a result, the degradation of cellulose and lignin, which are potentially responsible for the adsorption of heavy metal ions, would be eliminated or inhibited.

FTIR Spectroscopy of adsorbent and Cd^{2+} applied adsorbent

FTIR spectroscopy was employed to detect and characterize the wide array of functional groups present in STG and to acquire a deeper understanding of their potential for heavy metal scavenging and adsorption mechanisms. FTIR analysis was conducted using a Nicolet iS5 model from Thermo Electron Scientific Instruments LLC (Wan et al., 2014). This spectroscopy technique was employed to investigate the carbon composition within the spectral range of 500-4000 cm^{-1}. The complexity of the acquired spectra was attributed to the presence of a wide range of functional groups on the surface of the adsorbent.

The presence of cellulose and lignin was confirmed by a broad absorption band observed at a wavenumber of 3351.2 cm^{-1}, which indicated -OH stretching. Observation of peaks within the range of approximately 3016.6 cm^{-1} to 2859.5 cm^{-1} indicates the presence of aliphatic C-H groups, along with stretching in CH, CH_2, and CH_3 groups. The presence of peaks at 1641.96 cm^{-1} can be associated with the occurrence of asymmetric stretching vibrations of the C=O group, particularly the amide group. In addition, the detection of an extra peak at approximately 1475.51 cm^{-1} indicated the presence of aromatic compounds, particularly the N-H bending bonds of amide (II). Noteworthy bands were observed at approximately 1036.18 cm^{-1} and 1228.55 cm^{-1}, representing the C=O and NH_2 groups, along with the C-O stretching in alcohols.

Further analysis of the spectra revealed additional peaks in both samples. Fig. 3 illustrates the observed shifts in peaks and bands. The alterations in functional groups such as hydroxyl (-OH), carbonyl (C=O), amino ($-NH_2$), and methyl (-CH) groups in tea leaves, both pre- and postadsorption of heavy metals, suggest potential interactions between these functional groups and Cd(II) ions. The mechanisms facilitating these interactions are likely mediated through surface complexation, surface coordination, hydrogen bonding, and Coulombic interactions.

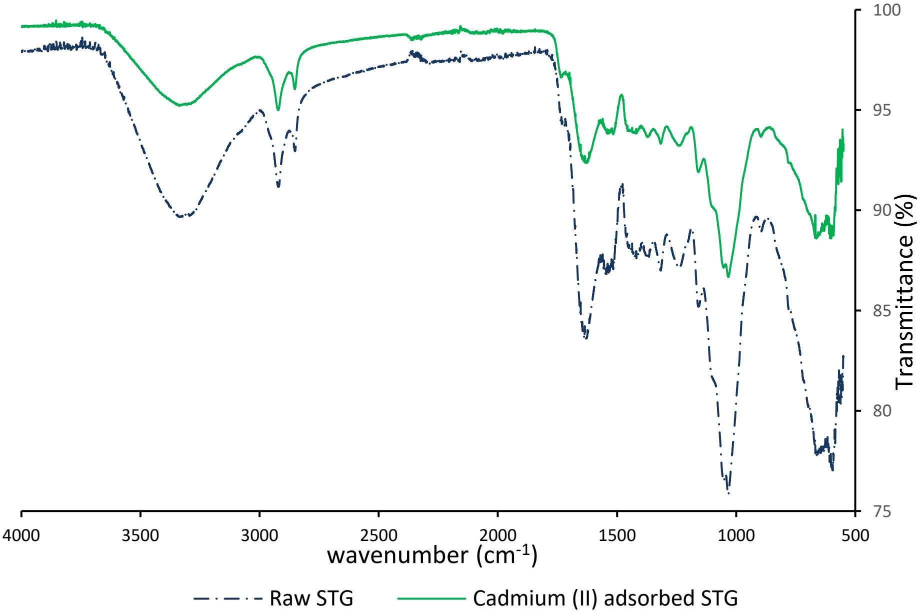
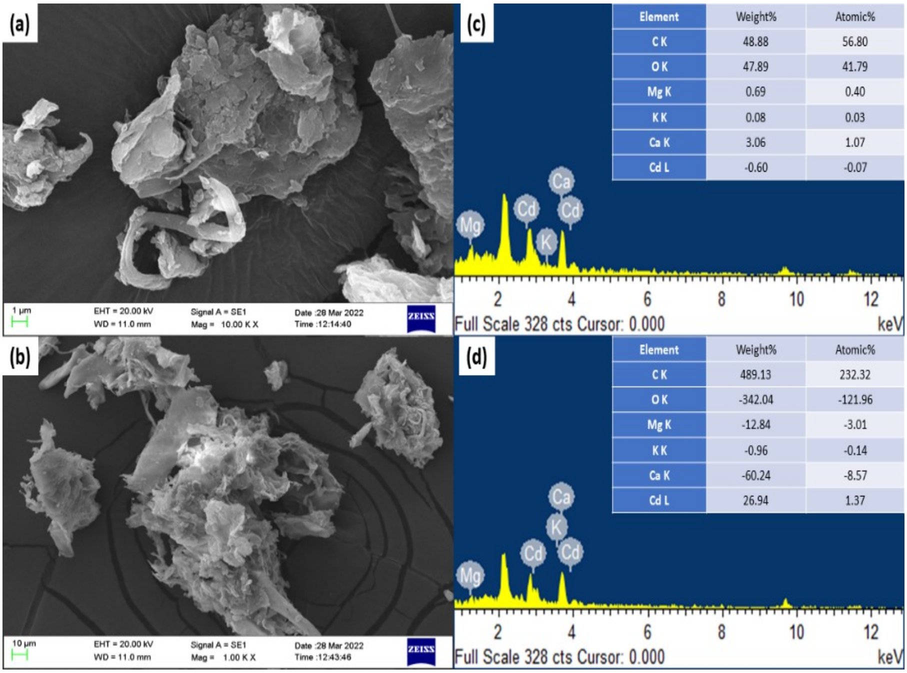


Figure 3: FTIR - Raw adsorbent and Cd^{2+} adsorbed adsorbent

SEM–EDS characterization of unprocessed STG and STG samples adsorbed with cadmium ions

SEM–EDS analysis was utilized to evaluate the morphological characteristics of STG. To achieve this, a scanning electron microscope (SEM) equipped with an integrated energy-dispersive X-ray spectroscopy (EDS) system was utilized. The surface topography of the biosorbent was examined using SEM imaging. Scanning electron microscopy (SEM) micrographs of the untreated spent tea grains (STG) were obtained both prior to and following the biosorption of Cd(II) ions, as depicted in Fig. 4a and 4b, respectively. The SEM micrographs illustrate that the surface topography of the untreated tea leaves exhibits irregularities, roughness, and heterogeneity. Numerous cracks with voids can be observed, along with a few grains of various sizes distributed within large holes. However, following the adsorption of Cd(II) ions (Fig. 4b), the STG surface exhibits predominant coverage of Cd(II) ions, suggesting that the adsorption mechanism of Cd(II) ions takes place within the interstices of the spent tea grains.

To identify the primary constituents of the untreated biosorbent as well as the biosorbent prior to and after the adsorption of Cd(II) ions, energy-dispersive X-ray spectroscopy (EDX) analysis was performed, as depicted in Fig. 4c and 4d, respectively. The EDX analysis revealed that the untreated tea leaves primarily consisted of carbon (C) and oxygen (O), without any indication of the presence of toxic Cd(II) ions. The energy-dispersive X-ray spectroscopy (EDX) examination of the STG subsequent to the adsorption of Cd(II) metal ions distinctly indicates the existence of Cd(II), affirming its attachment to the biosorbent.



Element	Weight%	Atomic%
C K	48.88	56.80
O K	47.89	41.79
Mg K	0.69	0.40
K K	0.08	0.03
Ca K	3.06	1.07
Cd L	-0.60	-0.07

Element	Weight%	Atomic%
C K	489.13	232.32
O K	-342.04	-121.96
Mg K	-12.84	-3.01
K K	-0.96	-0.14
Ca K	-60.24	-8.57
Cd L	26.94	1.37

Figure 4: SEM images: (a) Raw adsorbent, (b) Cd^{2+}-adsorbed adsorbent, EDX Analysis: (c) Raw STG, (d) Cd^{2+}-adsorbed adsorbent.

Influence of various parameters

Influence of pH

The pH value of the aqueous solution is a critical factor that significantly influences the efficacy of heavy metal removal through the utilization of adsorbents. The assessment of wastewater pH should be conducted as a preliminary step before examining other parameters, as it can impact both the surface interactions of the adsorbent and the degree of heavy metal ionization within the system. In this study, the pH values were adjusted within the range of 2.0-7.0. It is worth noting that heavy metals generally exhibit low solubility under neutral or alkaline pH conditions, and evaluating the extent of metal contamination at pH values ≥ 7 can be deceptive or misleading. Moreover, the precipitation of heavy metal ions as hydroxides is likely to transpire at pH values exceeding 7, which can potentially influence the outcomes of adsorption. To ascertain the optimal pH, the study considered three distinct adsorbent doses, three varying initial metal ion concentrations, and three different contact times. The remaining variables were maintained at consistent levels throughout the experiments, encompassing ambient temperature and a shaker agitation speed of 150 revolutions per minute (rpm).

Fig. 5 (a - c) demonstrates that the efficiency of Cd removal was comparatively diminished at pH 2 or 3, attributed to the prevalence of nonionized functional group species under acidic conditions. Nonetheless, a significant augmentation in the percentage of Cd ion removal was observed with the increase in pH from 2 to 6 at the prevailing ambient temperature. The Cd ion removal efficiency varied between 51.55% and 83.20% within the experimental parameters of an initial concentration (C_o) of 5 ppm, an equilibrium contact time of 90 minutes, and a dosage of 1 g/L. Similar trends were observed for other variations as well.

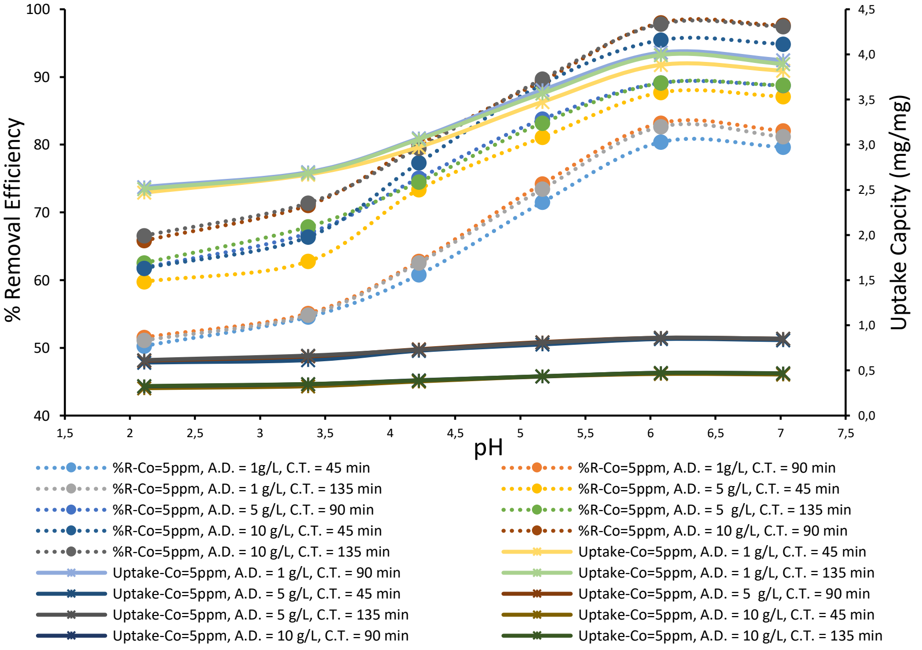


Figure 5 (a): pH influence on adsorption of Cd^{2+} onto STG at room temp. (Optimum pH and contact time, stirring speed = 150 rpm, C_o = 5 ppm)

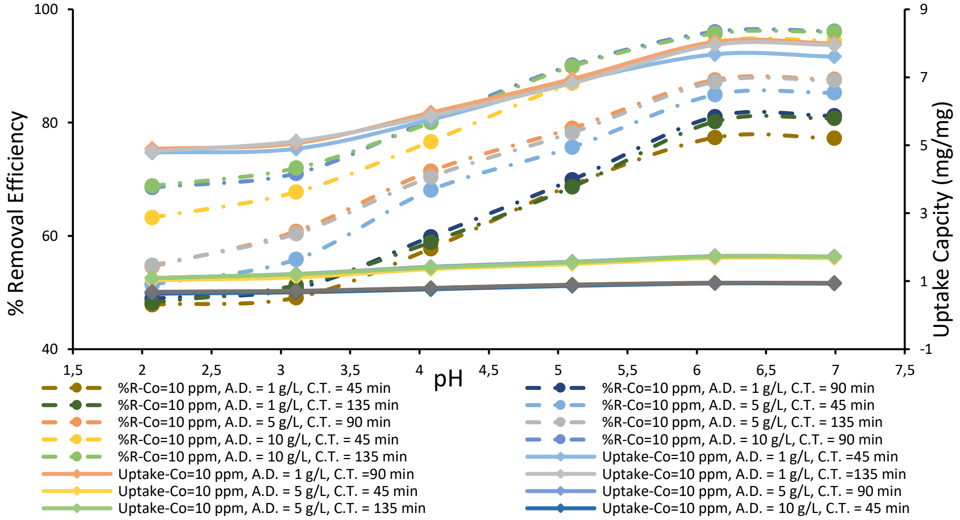


Figure 5 (b): pH influence on adsorption of Cd^{2+} onto STG at room temp. (Optimum pH and contact time, stirring speed = 150 rpm, C_o = 10 ppm)

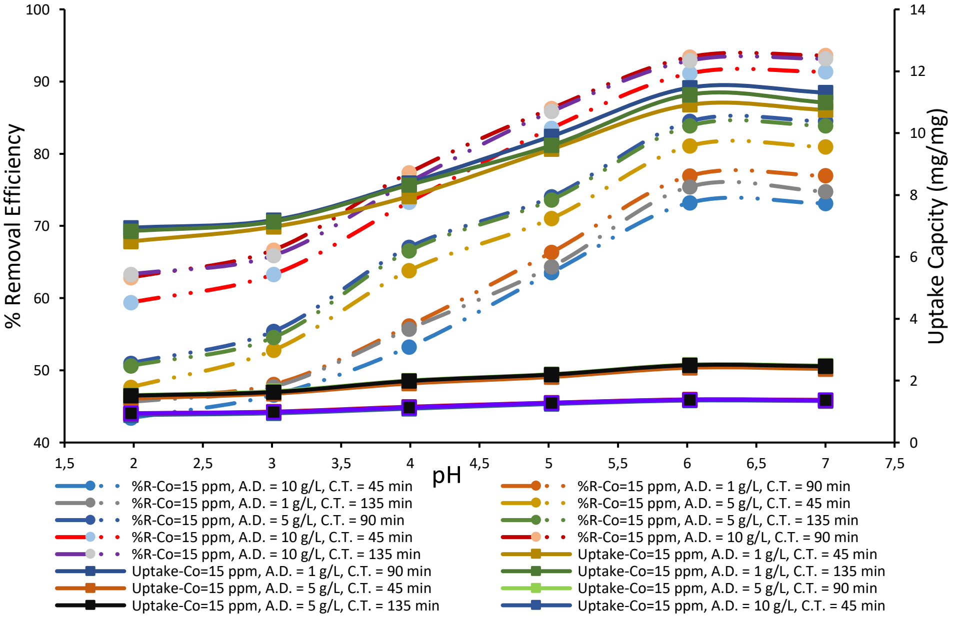


Figure 5 (c): pH influence on adsorption of Cd^{2+} onto STG at room temp. (Optimum pH and contact time, stirring speed = 150 rpm, C_o = 15 ppm)

Beyond the range of 6-7, further elevation of the pH did not yield significant improvements in the results. The optimal pH for Cd was determined to be 6.08 ± 0.06. These findings regarding the pH value align with previous studies that also utilized acidic pH conditions. An important outcome observed in the series of experiments was the attainment of a maximum removal efficiency of up to 98.01% at room temperature. This achievement was accomplished at pH 6.08, with a C_o of 5 ppm, contact time of 90 minutes, dosage of 10 g/L, and shaker speed of 150 revolutions per min.

These findings on pH levels are consistent with several studies using the acidic pH range. Dubey et al. examined the efficacy of dried plant biomass for removing Cd(II) from aqueous solutions. They explored various pH conditions and determined that a pH of 6 yielded optimal results.(Dubey et al., 2014) Cationic heavy metals are usually found in aqueous media and have greater solubility and reactivity at neutral to low pH values. The pH of the environment plays a crucial role in determining the surface charge of the adsorbent. (Çelebi et al., 2020)

Influence of contact time

Determination of the optimum contact time is crucial for efficient adsorption. To measure the optimal contact time, a range of 15 minutes to 180 minutes was tested at the previously determined optimum pH and room temperature. Additional factors taken into account encompassed three distinct adsorbent dosages, two varying initial metal ion concentrations, and a stirring rate of 150 revolutions per minute (rpm). Fig. 6 depicts the trends discerned in the removal efficiencies of Cd(II) ions.

Initially, there is a rapid escalation in the removal efficiencies and adsorption uptake capacity, culminating in a peak at approximately 75 minutes, following which they attain a state of equilibrium and remain stable. Around the 90-minute time point, employing a higher adsorbent dose of 10 g/L and a lower initial metal ion concentration of 5 mg/L resulted in achieving a maximum removal efficiency of 98.02%. It is noteworthy that in all experimental sets, the uptake of the metal exhibited an increase up to 75 minutes, after which it remained relatively stable in terms of both the percentage removal and adsorption uptake capacity.

Comparable results have been documented in studies investigating the removal of heavy metal ions through the utilization of tea wastes.(Vilayatkar et al., 2016) Furthermore, various studies have reported similar outcomes for heavy metal removal using diverse agricultural waste materials.(Hidalgo vazquez, A.R.; Alfaro cuevas villanueva et al., 2011) Ghasemi et al. used tea waste as an adsorbent to remove Cd from aqueous solutions. The experimental findings revealed that the maximum removal efficiency of Cd using tea waste reached 99.5% within 90 minutes.(Ghasemi et al., 2016)

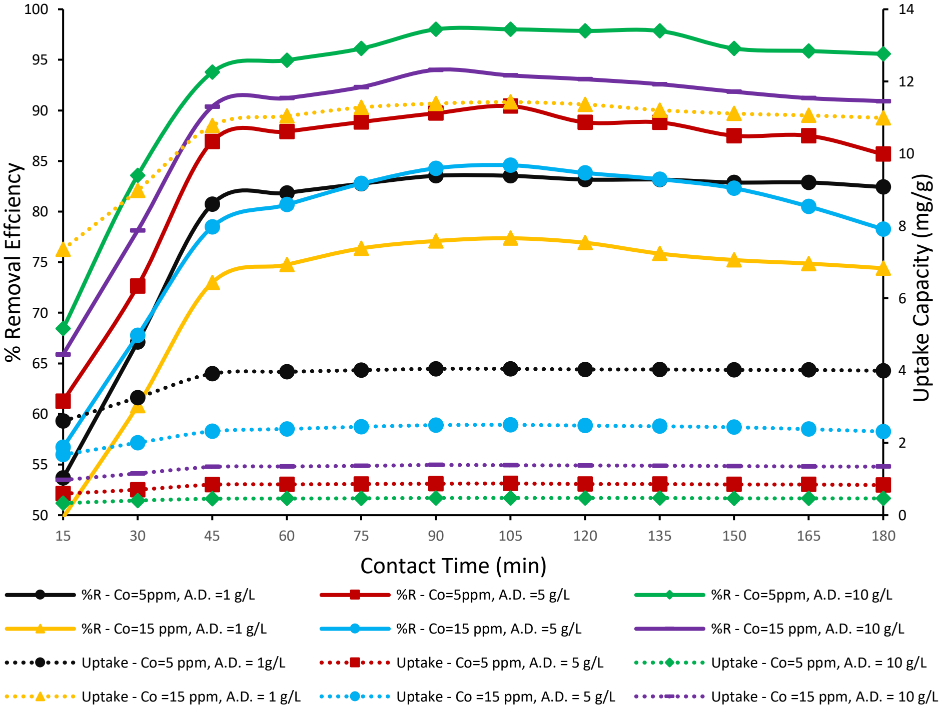


Figure 6: Contact time influence on adsorption of Cd^{2+} onto STG at room temp. (Optimum pH, shaker rotational speed = 150 rpm)

Influence of concentration C_o

To explore the influence of the initial metal ion concentration, batch study experiments were carried out under ambient temperature conditions. The initial metal ion concentration was systematically manipulated across a range of 2 mg/L to 16 mg/L in a methodical manner. The other parameters taken into account included the previously determined optimal pH and contact time, three different adsorbent doses, and a rotational shaker speed of 150 revolutions per min.

The impact of C_o on the adsorption performance and sorption capacity is depicted in Fig. 7. As the concentration (C_o) of Cd(II) increases from 2 mg/L to 16 mg/L, a marginal decline in the removal efficiency is observed, while the adsorption capacity exhibits a substantial augmentation. In the case of a dosage of 1 g/L STG, an increase in the initial Cd(II) ion concentration from 2 mg/L to 16 mg/L resulted in a decrease in removal efficiency from 84.73% to 76.61%. However, the adsorption uptake exhibited an increase from 1.64 mg/g to 12.16 mg/g. Similar trends were observed for other variations as well.

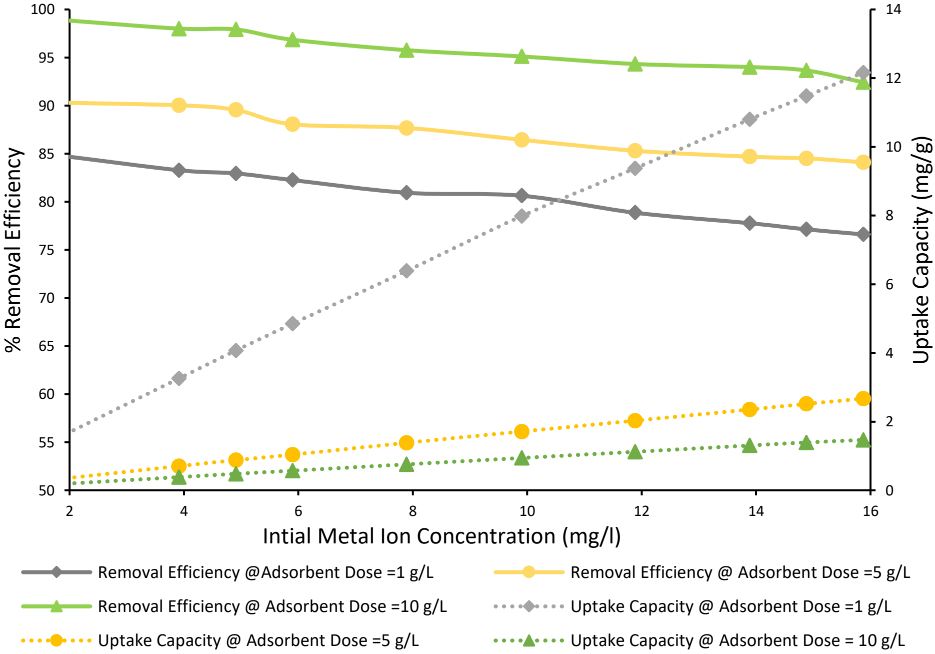


Figure 7: Influence of IMC on Cd^{2+} adsorption - % removal and adsorption capacity at room temp. (optimum pH, stirring speed = 150 rpm)

Ali et al. also obtained similar results in their study regarding the adsorption of Cd(II) using natural adsorbents.(Ali F et al., 2015) In their study, Al-Masri et al. examined the removal of Cd(II), lead, and uranium from wastewater using poplar leaves and branches through a batch adsorption process. Their findings exhibited a similar pattern. (Al-Masri et al., 2010)

Influence of Adsorbent dose

To examine the impact of adsorbent dose on the removal efficiency and adsorption uptake capacity, a series of batch experiments were conducted at room temperature using varying adsorbent doses ranging from 1 g/L to 10 g/L. During the aforementioned series of experiments, the supplementary parameters considered encompassed the optimized pH and contact duration ascertained in prior phases, concentrations (C_o) of 5 mg/L and 15 mg/L, and an agitation rate of 150 rpm.

Fig. 8 illustrates the relationship between the STG dosage and the removal efficiency of Cd(II) ions. It is evident that as the STG dosage increased from 1 g/L to 10 g/L, the removal efficiency of Cd(II) ions also increased from 83.36% to 98.51% when the initial metal ion concentration was 5 mg/L. These results were obtained under the other optimal conditions, including a pH of approximately 6, a contact time of 90 minutes, a stirring speed of 150 rpm, and room temperature. The observed pattern of increased elimination efficacy can be attributed to the heightened adsorption capacity of the active surface of STG, particularly for the specific heavy metal of interest, Cd(II). The experimental studies carried out in this study align with the findings of relevant studies in the literature (Mondal et al., 2015; Mahvi et al., 2005)

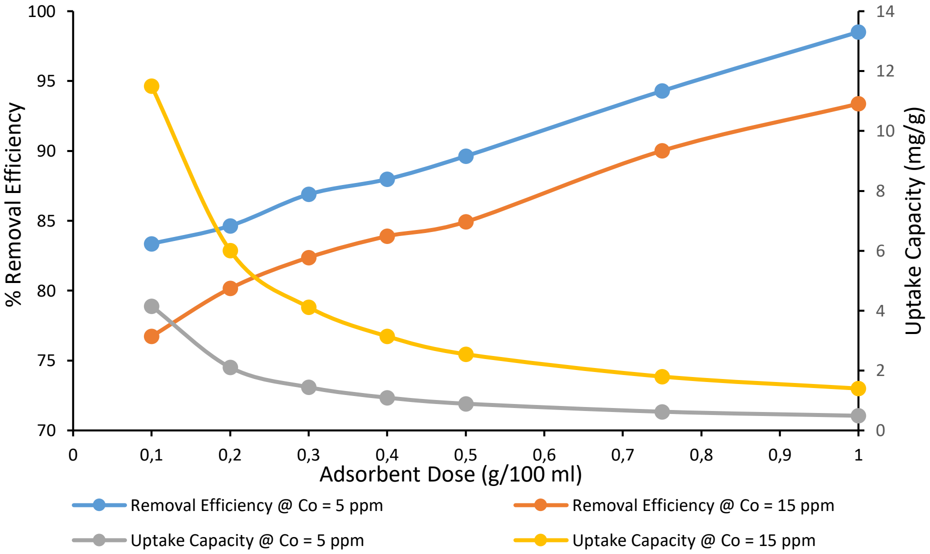


Figure 8: Influence of A.D. on Cd^{2+} adsorption - % removal and adsorption capacity at room temp. (optimum pH, C.T. = 90 min, shaker Speed = 150 rpm)

Influence of particle size

The available surface area for adsorption plays a pivotal role in determining the efficiency of the adsorption process. To evaluate the influence of particle size on the performance of the adsorbent (STG), experiments were carried out at room temperature, employing particle sizes within the range of 75 µm to 1.18 mm. In the aforementioned series of experiments, the following factors were considered: the optimized pH and contact time determined in prior stages, an initial concentration of metal ions at either 5 mg/L or 15 mg/L, a dosage of 5 g/L for the adsorbent, and a stirring rate of 150 rpm.

Valuable insights regarding the influence of particle size of STG on the efficiency of metal removal and the capacity for metal uptake can be gleaned from the data depicted in Fig. 9. The evidence from the results indicates that smaller particle sizes of STG demonstrate higher efficiency in removing Cd(II) ions from the aqueous solution. By decreasing the particle size from >1180 microns to 150-75 microns while keeping other parameters at their optimum values at room temperature, the removal efficiency of Cd(II) ions shows an increase from 76.11% to 91.95%. Analogous trends can be discerned when the initial concentration of metal ions in the aqueous solution is increased. Consistent trends and patterns have been observed in the literature, which supports and reinforces the findings documented in this study (Eze et al., 2013; Gora et al., 2022).

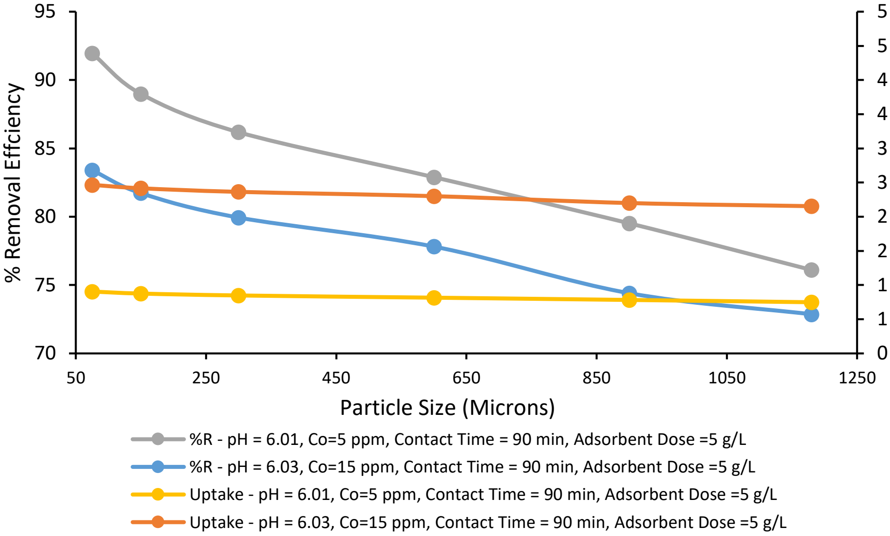


Figure 9: Impact of particle size on Cd^{2+} adsorption onto tea waste adsorbent

Influence of stirring speed

According to the findings depicted in Fig. 10, augmenting the agitation rate of the rotary shaker in the batch study experiments led to a discernible enhancement in the removal efficiency of STG in the context of Cd(II) ion removal from the aqueous solution. During our various batch study experiments, the maximum removal efficiency was observed at a stirring speed of 150 rpm, which was consistent with the optimal conditions.

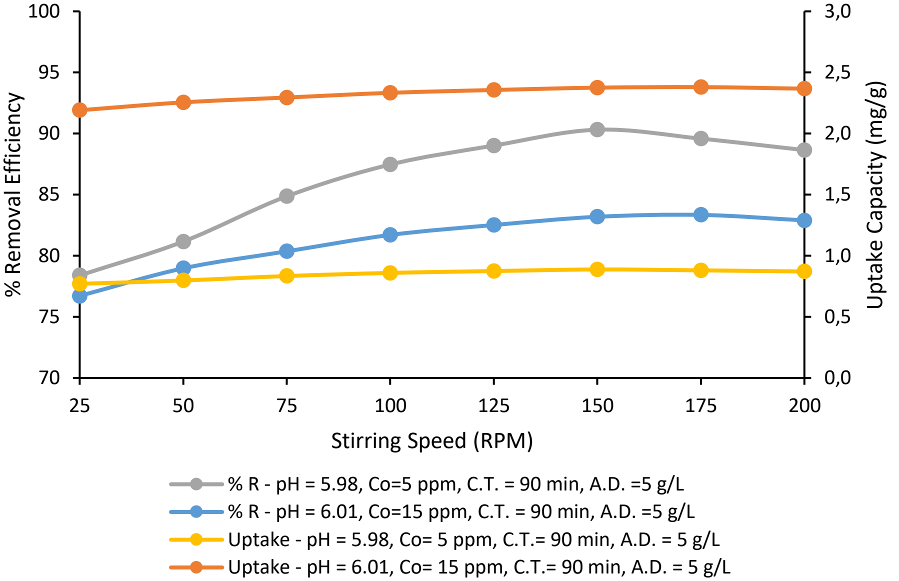


Figure 10: Impact of shaker speed on heavy metal % removal and adsorption capacity.

Adsorption isotherm models

In the present study, we investigated four commonly applied isotherms to understand the adsorption mechanism and various relationships between Cd(II) ions in the adsorbate and Cd(II) ions on the adsorbent surface (STG). Fig. 11 (a-d) illustrates the plots depicting the initial optimum conditions of a pH of approximately 6, exposure time of 90 minutes, and shaker rotational speed of 150 rpm at room temperature. The relationship between the Cd(II) ion concentration in the adsorbate and the removal efficiency of the adsorbent (STG) was examined. This analysis was conducted using different STG dosages of 1 g/L, 5 g/L, and 10 g/L.

Fig. 11 (a) displays the linear Langmuir isotherm plot for STG, with an R^2 value exceeding 0.9, highlighting its favorable adsorption affinity. Analyzing equilibrium data through the Langmuir isotherm, we found q_{max} to be 28.17 mg/g, which is very significant. The R_L value carries significant importance, as it signifies the adsorption conditions on the adsorbate-adsorbent relationship. R_L values exceeding 1 signify adsorption that is unfavorable and suboptimal, whereas an R_L value of 1 indicates linear adsorption. When R_L values fall within the range of 0 to 1, favorable and optimal adsorption conditions are indicated. In the present case scenario, the determined R_L value of 0.2379 signifies the optimal adsorption of Cd(II) onto STG.

The Freundlich isotherm model demonstrates a linear relationship with a high correlation coefficient ($R^2 = 99.33$), indicating that STG exhibits a strong affinity and high adsorption capacity. The value of 1/n (i.e., 1/n = 1.93), which is greater than 1, suggests cooperative adsorption and implies multilayer adsorption on a heterogeneous surface.

After analyzing the data, it becomes clear that the Temkin isotherm model exhibits a strong correlation coefficient ($R^2 > 0.9$), further validating its adsorption process reliability. The corresponding parameters of the Temkin model are tabulated alongside other isotherm parameters in Table 1. Based on the data obtained from the Temkin model, the heat of sorption is determined to be less than 1 kcal/mol, implying physical adsorption. However, the Dubinin–Radushkevich isotherm model demonstrates a relatively low correlation coefficient ($R^2 < 0.9$) compared to the other models. This suggests that the data do not conform well to the Dubinin–Radushkevich isotherm model in this study. Additionally, there is a notable discrepancy between the maximum adsorption capacity calculated using the Dubinin–Radushkevich isotherm model and the value obtained through the Langmuir isotherm model in this study. Previous studies in the literature that focused on the adsorption of diverse heavy metals using agricultural waste adsorbents have consistently shown that the removal of heavy metal ions aligns with the Langmuir isotherm.(Alalwan et al., 2020)(Simón et al., 2022) The findings of the present study are in agreement with the literature in this regard.

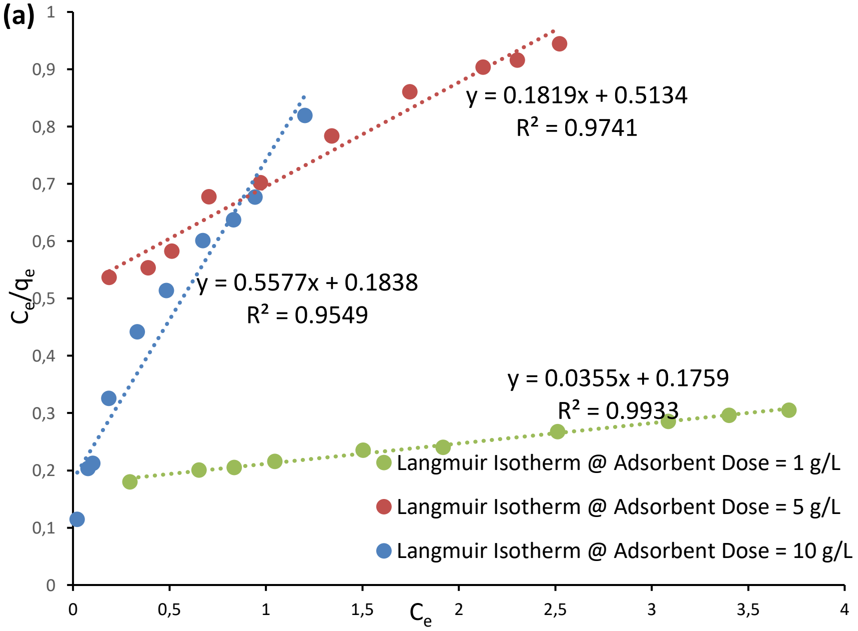


Figure 11 (a): Isotherm plot - Langmuir equilibrium

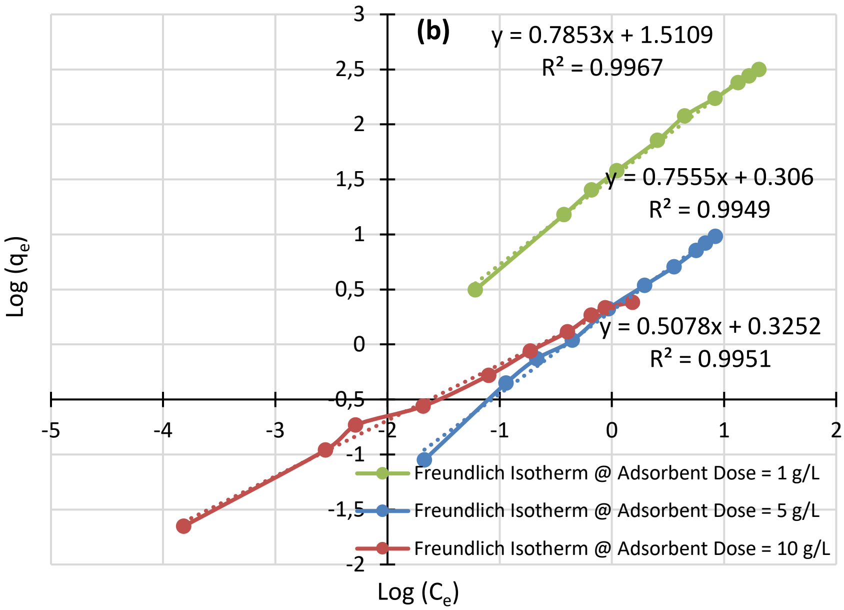


Figure 11 (b): Isotherm plot - Freundlich equilibrium

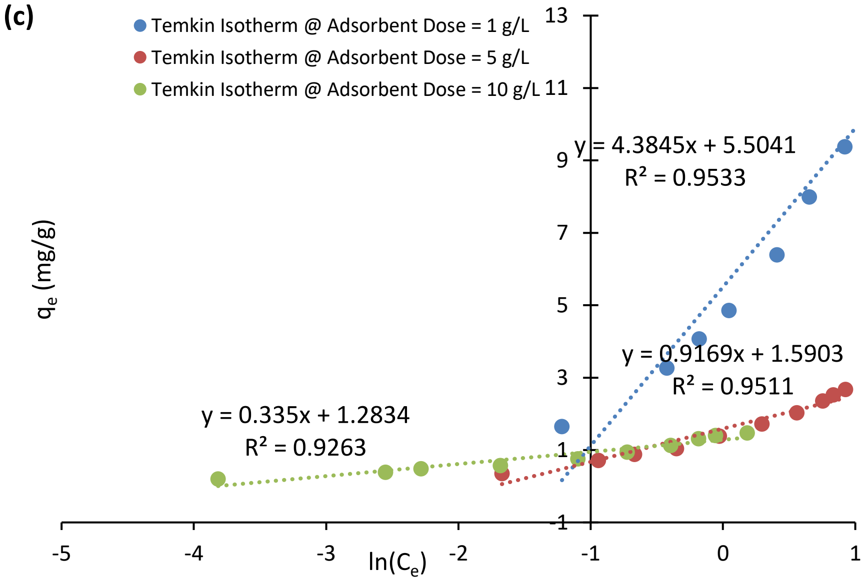


Figure 11 (c): Isotherm plot - Temkin

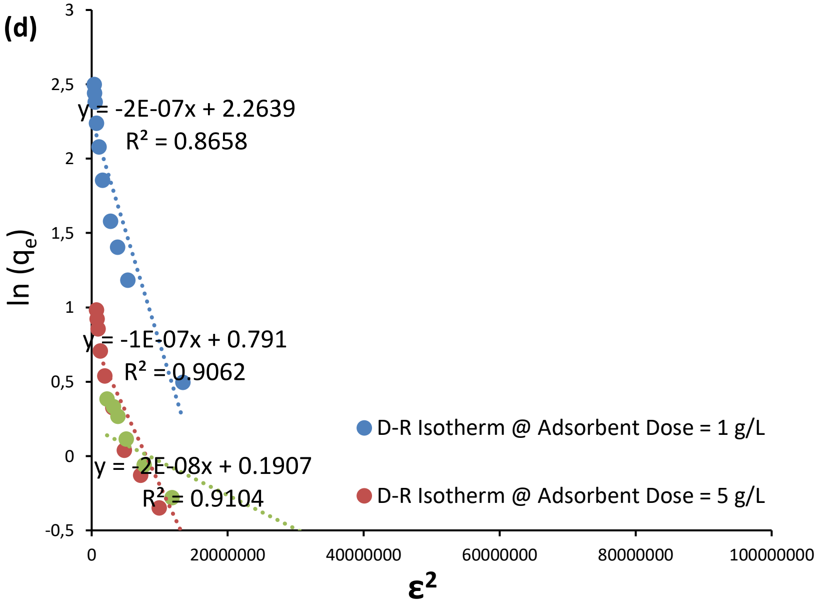


Figure 11 (d): Isotherm plot - Dubinin–Radushkevich

Table 1: Equilibrium isotherm parameters of Cd^{2+} adsorption onto STG at optimum factors (A.D. = 1 g/L)

Equilibrium Model	Isotherm	Model Parameters	Model Values	Equilibrium
Langmuir	Equilibrium	q_m (mg/g)	28.17	
Isotherm		K_L (L g^{-1})	0.2018	
		R^2	0.9933	
R_L			0.2327	
Freundlich	Equilibrium	K_F (mg/g)	4.53	
Isotherm		n	0.5530	
		1/n	1.9295	
		R^2	0.9967	
Temkin	Equilibrium	A_T	18.0033	
Isotherm		b_T	565.36	
		R^2	0.9533	
D-R Equilibrium Isotherm		q_m (mg/g)	9.621	
		K (mol^2/K^2J^2)	0.0000002	
		R^2	0.8434	
		E (KJ/mol)	1581.14	

Adsorption kinetics models

To assess the rate of adsorption, a crucial factor for process design, the rate kinetics of Cd(II) adsorption onto STG were thoroughly examined. Several kinetics models, namely, PFO, PSO, IPD, and Elovich kinetics, were employed to analyze the adsorption behavior of Cd(II) onto STG.

Upon evaluating the various kinetics models, it becomes apparent that the removal rate and adsorption uptake of STG exhibited a rapid initial increase for Cd(II) within the first few minutes. Subsequently, the adsorption continued to increase gradually and consistently until reaching equilibrium, which took approximately 90 minutes. As represented in Fig. 12 (a) to (d)

The obtained parameters from the analysis of various rate kinetic equations analyzed for the removal of Cd(II) onto STG are presented in Table 2. Notably, the pseudosecond-order kinetics demonstrated a high correlation coefficient value exceeding 0.99. Upon scrutinizing the parameters derived from the four kinetic models, it can be inferred that the experimental data align most accurately with the PSO rate kinetics model when describing the adsorption of Cd(II) onto STG, surpassing the other kinetic models. Based on prior studies that explored different methods for Cd(II) ion adsorption, the kinetics of Cd(II) ion removal are well suited for PSO modeling. The results of the current study concerning Cd(II) ions exhibit a notable correlation with the outcomes reported in previous studies conducted in the field.(Garg et al., 2008)(Kwikima et al., 2021)

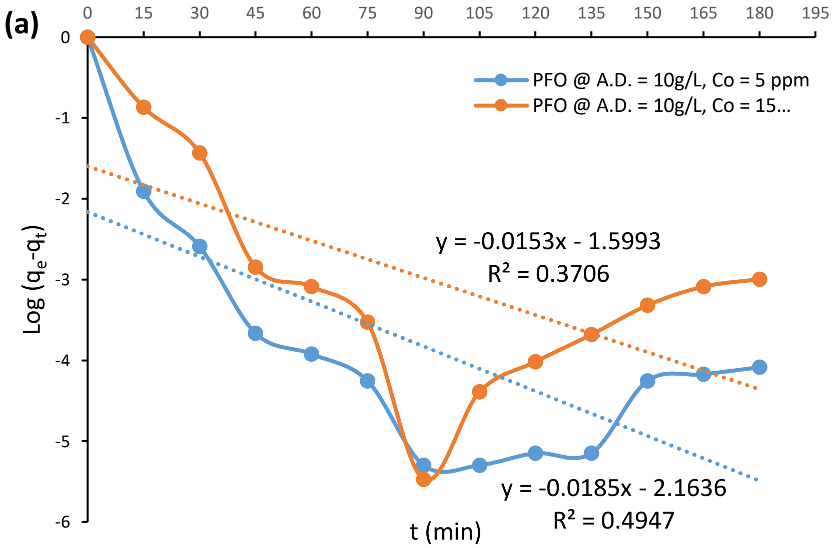


Figure 12 (a): PFO kinetics model

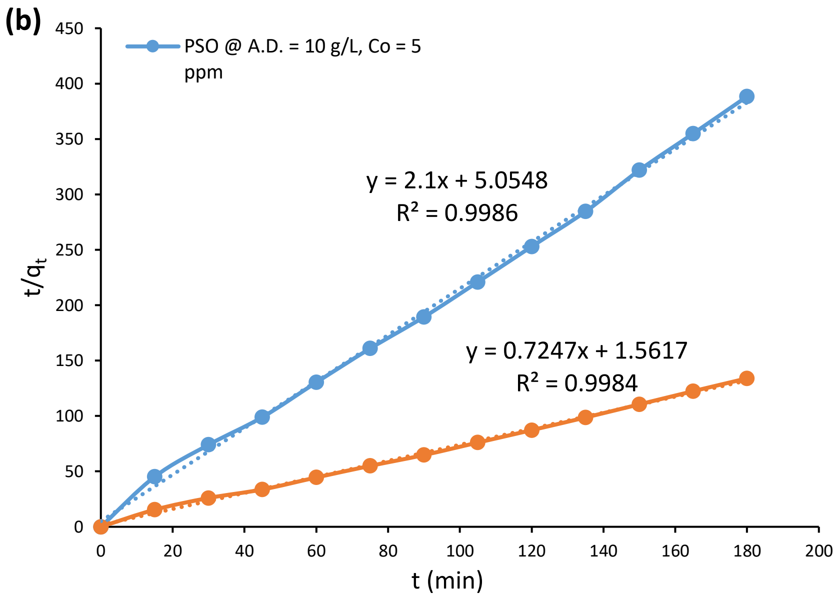


Figure 12 (b): PSO kinetics model

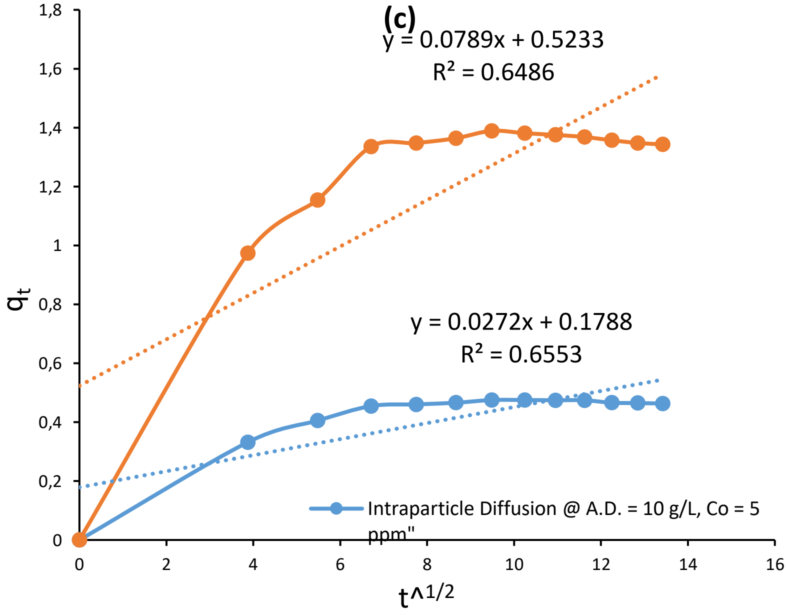


Figure 12 (c): Intraparticle diffusion kinetics model

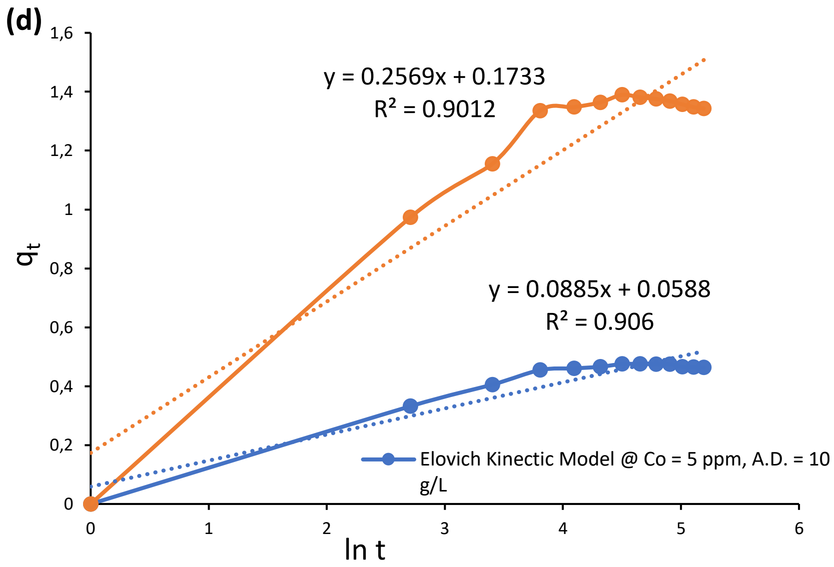


Figure 12 (d): Elovich kinetics model

Table 2: Various kinetics parameters of Cd^{2+} adsorption

Kinetics Model	Model Parameters	Model Values
PFO kinetics	Q_e (mg/g)	0.9582
	K_1 (min^{-1})	0.0120
	R^2	0.4947
PSO kinetics	K_2 (g mg^{-1} min^{-1})	0.0448
	Q_e (mg/g)	0.4761
	R^2	0.9986
Intraparticle Diffusion kinetics	K_{int} (mg g^{-1} s^2)	0.0272
	C	0.1788
	R^2	0.6553
Elovich kinetics	α	11.294
	β	0.1719
	R^2	0.906

CONCLUSION

The release of heavy metals into wastewater has substantial consequences for the environment and human health. The process of adsorption plays a vital role in eliminating heavy metals from wastewater.

The analysis of the prepared adsorbent characterization suggests its potential for effectively adsorbing Cd^{2+} ions from aqueous solutions. Upon considering various isotherm models, it was determined that the equilibrium process, as explained by the Langmuir isotherm, showed a monolayer maximum adsorption capacity of 28.17 mg/g. However, further analysis revealed that the adsorption process exhibited heterogeneity and could be more accurately described by the Freundlich isotherm model. The kinetic studies revealed that the adsorption of Cd^{2+} ions onto the adsorbent prepared from agricultural waste was most accurately described by the pseudosecond-order kinetics model. A stronger conformity to the Elovich model suggested that the rate of adsorption exhibited greater variation in the initial stages but gradually slowed down in the later stages. The intraparticle kinetics model findings provide clear evidence that the boundary layer effect significantly influenced the sorption of Cd(II) onto STG. Furthermore, the nonpassing of the plotted line through the origin suggests that intraparticle diffusion alone was not the sole rate-controlling step, and it is likely that boundary layer diffusion played a role in governing the adsorption process to some extent. The adsorption rate and capacity of STG are greatly affected by the pH of the solution, with an increase in pH resulting in a corresponding increase in adsorption rate and capacity. A pH value of approximately 6.0 was determined to be the ideal condition for maximizing the adsorption uptake of Cd^{2+} ions. The removal efficiency of Cd(II) ions into STG was observed to increase with a higher dosage of the adsorbent, while a decrease was observed with an increase in the initial metal ion concentration.

Under the optimal conditions, the maximum observed removal rate of 98.52% was achieved for Cd^{2+} ion adsorption with an adsorbent dose of 10 g/L. Various parameters, including particle size of the adsorbent, adsorbent dosage, rotary shaker stirring speed, pH of the adsorbate, initial concentration of metal ions, and contact time, exerted an influence on the adsorption rate and metal uptake capacity. Through this study, we found that tea residue, which is easily accessible and frequently discarded as waste from tea shops to restaurants, has the potential to be transformed into an adsorbent material for the removal of Cd^{2+} ions from various industrial effluents. This approach provides an affordable and easily accessible means of mitigating the contamination caused by Cd^{2+} ions in wastewater.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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