



Decontamination of silver ions from aqueous solution using coconut coir

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ABSTRACT

The potential of coconut coir as a low-cost adsorbent was investigated for adsorptive removal of silver ions (Ag^+) from aqueous solution employing batch experiments. The adsorption phenomenon was studied by optimizing various physicochemical parameters such as bio sorbent dose (0.05 to 0.4 g), pH of adsorbing medium (1–13), effect of contact time (1–30 min), adsorbate concentration (4.635×10^{-5} to 6.953×10^{-4} mol·L⁻¹) and temperature (283 to 323 K). The quantification of Ag^+ ions was made by atomic absorption spectrometry. Maximum adsorption of silver ions was observed by shaking 10 mL of 4.635×10^{-5} mol·L⁻¹ of silver ion solution with 0.125 g of coconut coir with contact time of 20 min. Kinetic data preferably followed pseudo-second-order model. The equilibrium adsorption data was fitted to Freundlich, Langmuir and Dubinin–Radushkevich isotherm models over silver concentration range of 4.635×10^{-5} to 3.708×10^{-4} mol·L⁻¹ and the model parameters were evaluated. Determined constants for Freundlich isotherm were $1/n = 0.297$ and $K = 0.103$ mmol·g⁻¹ and for Langmuir isotherm were $Q = 8.99 \times 10^{-2}$ mmol·g⁻¹ and $b = 4,035.64$ dm³·mol⁻¹. The sorption mean-free energy calculated from the Dubinin–Radushkevich isotherm was 13.889 kJ·mol⁻¹ indicated the ion-exchange mechanism of chemisorption. Determined thermodynamic quantities predict that the adsorption process is spontaneous and endothermic in nature.

Keywords: Coconut coir; Silver adsorption; Kinetics; Sorption isotherms; Thermodynamics

1. Introduction

Silver is one of the precious metals [1] and has important roles in life of human beings [2], due to its specific properties such as malleability, ductility [3], antimicrobial [4], corrosion and oxidation resistance [1] and electrical conductivity [5]. Silver and its compounds are being consumed extensively in various industries that include electroplating, batteries, electronics [2], photography, coinage and metal alloy [6] industries and are released in effluents of these industries and ultimately to the aquatic system resulting in its deterioration [7,8]. Monovalent ion, Ag^+ , is known to be the most toxic chemical species in marine environment and its toxicity

to freshwater phytoplankton is directly linked to intracellular accumulation of this ion [9]. The toxic effects of soluble silver compounds include cancer, heart failure, argyria, respiratory disorders and damage to liver and kidney [7,8]. Therefore, it is essential to develop methods for treatment of wastewaters before their safe disposal into water bodies [10].

Various physicochemical methods have been developed for removal of silver ions from aqueous solutions and industrial effluents these include chemical precipitation [11], reduction [12], extraction [13], solid-phase extraction [14], ion-exchange resins [15], coagulation [16] and adsorption [17]. Adsorption process under certain conditions has a definite edge over other methods due to its simplicity, high

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enrichment factor, high recovery, rapid phase separation and low cost [18]. The adsorption of silver on various inorganic materials and organic compounds has been reported. The inorganic sorbents used for silver are activated carbon [19], egg shells [20], titanium dioxide [21], montmorillonite [22], perlite [23], vermiculite [24], Turkish coal [25], silica gel [26], silica nanoparticles [27], whereas the organic sorbents include chelating resins [28], waste coffee grounds [7], chitosan [29], polyurethane foam [30], and polymers [31,32]. However, some of these are either expensive, time consuming or inefficient in reducing the silver ion concentration in effluents. Therefore, there is a need to investigate other inexpensive, rapid, and efficient methods for this purpose.

The use of agricultural waste as substitute to bioadsorbents for replacing traditional adsorbents has been extensively investigated. Among these wastes, coconut residues (such as coir, pith, and shell) have been extensively investigated. Several researchers have reported adsorption of heavy metal ions employing coconut residues such as Zou et al. [33] studied adsorption of silver ions from wastewater by using pre-treated activated carbon coconut shell as an adsorbent. Hasany and Ahmad [34] studied adsorption of silver ions by employing coconut husk. Staroń et al. [9] worked on silver ions adsorption and desorption on coconut fiber as an effective biological adsorbent. Hanafiah et al. [35] investigated the potential of coconut husk for chromium and nickel ions removal from aqueous solution. Aravind et al. [36] used coconut coir for absorptive removal of copper, nickel, and cadmium ions from wastewater. The selection of coconut coir was made for current research since it is abundantly available as a waste product in many countries. Moreover, it contains cellulose, hemicellulose, lignin [37–39], and pectin [40] all of which are good adsorbents for removal of metal ions [41,42] as carboxylic and phenolic groups of lignin are mainly responsible for metal ion adsorption [43].

Main objectives of current work are to investigate/exploit the potential and properties of coconut coir for adsorptive removal of silver ions from aqueous solution. Current research involves determination of sorption capacity of coconut coir in relation to silver metal ions, fitting of a suitable isotherm and kinetic model, thermodynamic parameters, and error analysis of process. Moreover, applicability of developed procedure with tap water will be investigated. Effect of foreign ions on metal ions adsorption will be checked. There are no boundaries to study, and this work establishes a link or relationship between scientific background and the use of coconut coir (adsorbent of biological origin) in removing hazardous silver ions from wastewater and can lead to development of new technologies for removing metal ions from environment or for minimizing their negative impacts on it.

2. Material and methods

2.1. Equipment

The absorption measurements of silver ions were made with a Hitachi Z-2000 (Tokyo, Japan) polarized Zeeman atomic absorption spectrophotometer. The instrument has a strong magnetic field across the burner which provides a double-beam optical correction system. A water cooled,

premix, fish-tail type burner, having a slot of $100 \times 0.5 \text{ mm}^2$, was used for air-acetylene flame. Hollow cathode lamp of silver from Hitachi was used as a radiation source. The instrumental parameters used for quantification of silver were as: lamp current 7.0 mA, width of slit 1.3 nm, wavelength 328.1 nm, burner height 7.5 mm, fuel (C_2H_2) flow $2.0 \text{ L}\cdot\text{min}^{-1}$ and oxidant (air) flow $15.0 \text{ L}\cdot\text{min}^{-1}$.

2.2. Reagents

Coconut coir was collected from Rawalpindi market, washed with de-ionized water to remove dust particles, dried in an oven at 60°C till constant weight, manually cut into small pieces and stored in air tight jar. Stock solution of silver ($1,000 \text{ mg}\cdot\text{L}^{-1}$) was prepared by dissolving 0.1 g of Specure metal (Johnson Matthey, UK) in a minimum amount of distilled nitric acid. The resultant solution was diluted to 100 mL with water. Fresh working standard solutions in the range of $1\text{--}5 \text{ mg}\cdot\text{L}^{-1}$, were prepared by appropriate dilution of this stock solution immediately before use. All the reagents used were of analytical grade and used as such distilled water was used in all experiments.

2.3. Adsorption procedure

Adsorption measurements were performed using a batch technique for optimization of operational parameters such as solution pH (1–13), adsorbent amount (0.05–0.4 g), contact time (1–30 min), metal ion concentration ($4.635 \times 10^{-5} - 6.953 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$), and temperature (283 to 333 K). For each experiment, one parameter is taken as a variable while keeping other parameters as constant and metal ion concentration of 10 mL was used. An orbital shaker was employed for shaking mixture for 5 min. When equilibrium was attained then mixture was centrifuged at speed of 3,000 rpm for 3 min. After phase separation (i.e., after adsorption), concentration of silver ions in liquid phase (C_f) was determined by atomic absorption spectrophotometer using optimized instrumental parameters. Experiments were performed at room temperature except where otherwise specified by shaking 0.125 g of coconut coir in a 10 mL of an aqueous solution of known concentration of silver ions in $0.0001 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ solution in 35 cm^3 culture tubes for a given time. Percentage adsorption of silver ions from solution was calculated using following expression:

$$\% \text{Adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i = initial concentration of silver ions in solution ($\text{mg}\cdot\text{L}^{-1}$); C_f = concentration of silver ions in solution after equilibrium ($\text{mg}\cdot\text{L}^{-1}$)

All the experiments were conducted at $298 \pm 1 \text{ K}$ and reported values are the average of at least two independent measurements with an average relative standard deviation of $\pm 2.8\%$ unless otherwise specified.

2.4. Desorption studies and effect of foreign ions

Desorption study was carried out to investigate metal releasing capacity of coconut coir with silver ions. For this,

0.125 g of adsorbent was used for adsorption of metal ion solution having concentration $4.635 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ at pH value of 7 for 20 min. The adsorbent was then washed with distilled water to remove any unabsorbed silver. For desorption, experiment was carried out using 1.0 M HNO_3 as desorption medium for 20 min. The desorption ratio was calculated by following equation:

$$\text{Desorption ratio} = \frac{\text{amount of metal ion desorbed}}{\text{amount of metal ion adsorbed}} \times 100 \quad (2)$$

Effect of various cations and anions were investigated at optimized conditions such as 10 mL of $4.635 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ of silver ion solution with 0.125 g of coconut coir and contact time of 20 min using $25 \text{ mg}\cdot\text{L}^{-1}$ concentration of cations and anions.

2.5. Characterization of adsorbent

Brunauer–Emmett–Teller (BET), Fourier-transform infrared (FTIR), scanning electron microscope (SEM), and energy-dispersive X-ray analysis (EDX) was employed to determine value of surface area of adsorbent, various functional groups present on exterior of adsorbent, to study morphological properties and for elemental analysis of adsorbent, respectively. Adsorbent was characterized both before and after adsorption.

3. Result and discussions

3.1. BET studies

The surface area of coconut coir sample was measured according to BET method by nitrogen adsorption at 77 K using Quantachrome S1 BET surface area analyzer. Before nitrogen adsorption the sample was degassed for 2 h at final pressure of $133.32 \times 10^{-4} \text{ pa}$. The determined value of surface area was found to be $1.18 \text{ m}^2\cdot\text{g}^{-1}$. The bulk density, percent porosity and pH_{ZPC} of adsorbent were determined

by using the reported methods [44,45] and were found to be $0.88 \text{ g}\cdot\text{mL}^{-1}$, 60% and 5.6, respectively.

3.2. FTIR studies

The verification of adsorption of silver ions was made by observing the variation in the absorption peaks in FTIR spectra of samples of coconut coir and silver loaded coconut coir. The characteristic absorption bands at $3,400\text{--}3,200$ and $2,921\text{--}2,851 \text{ cm}^{-1}$ are assigned to for the stretching of surface O–H and aliphatic C–H groups, respectively [46]. The peaks at $1,740$ and $1,367\text{--}1,371 \text{ cm}^{-1}$ is associated with COO^{-1} anion and around $1,029$ due to CO group. The peaks around $1,595 \text{ cm}^{-1}$ is due to OH bending of adsorbed H_2O [47,48]. FTIR spectrum of silver loaded coconut coir exhibited changes in peak positions. The shifting of peaks to $2,921.7$; $1,365$ and $1,019 \text{ cm}^{-1}$, clearly indicate the binding of silver ions with carboxylic group in coconut coir. Adsorption of Cr on coconut coir with similar minor shifting of FTIR peaks have been reported Gonzalez et al. [49].

3.3. SEM and EDX analysis

The morphology of coconut coir was evaluated using scanning electron microscopic (SEM) technique at different magnifications from 500 to 20,000 and those at 20,000 have been shown in Fig. 1. It is clear from Fig. 1A that initially the surface of coconut coir was rough and irregular with many loops and humps. The determined pore size present on surface of coconut coir was in range of $121\text{--}354 \text{ nm}$, indicating the macroporous structure of adsorbent [50].

Fig. 1B illustrates the SEM image of coconut coir after adsorption of silver, with changed surface morphology of adsorbent, that is, decrease in surface heterogeneity resulting in smoother surface. The ionic diameter of silver ions is 0.115 nm , which is much smaller than pore size present in coconut coir ($121\text{--}354 \text{ nm}$), enabling adsorption of silver ions through pore diffusion mechanism. The EDX graph (Fig. 2) shows the presence of three energy peaks of silver

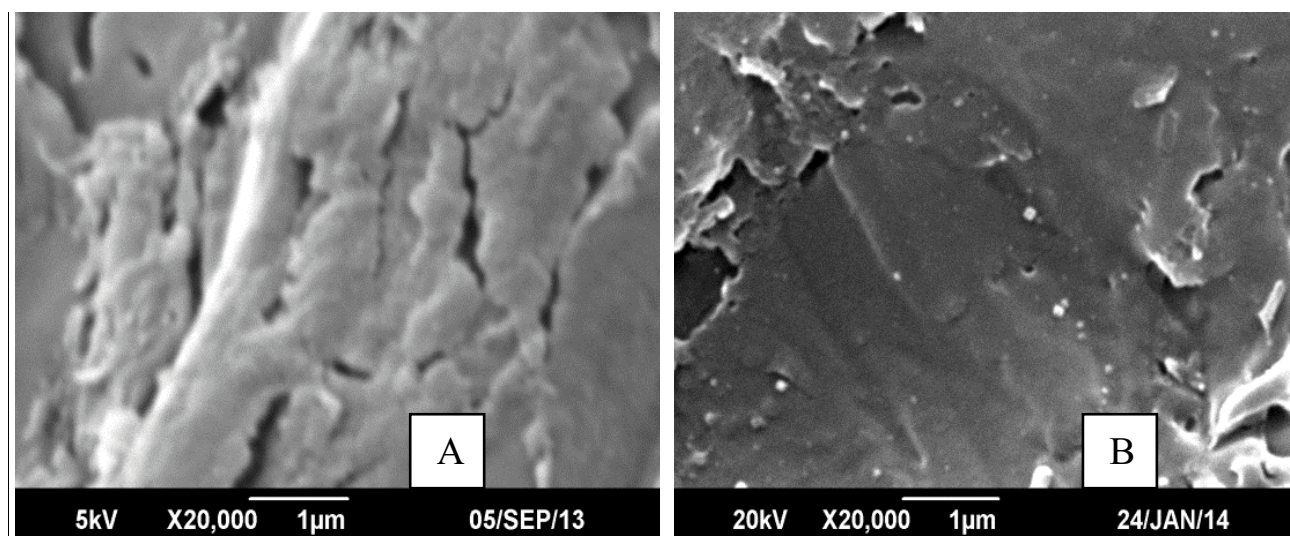


Fig. 1. SEM images of the coal before (A) and after (B) silver decontamination.

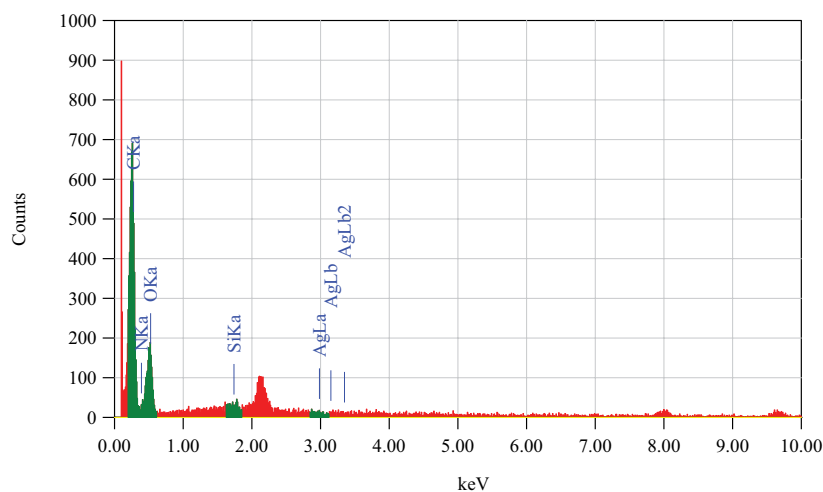
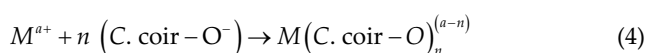
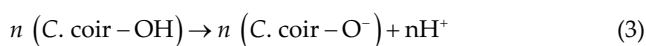


Fig. 2. EDX graph of silver loaded coconut coir.

in range of 2.95 to 3.35 keV. Thus, revealing the presence of silver ions on coconut coir surface because of adsorption.

3.4. Optimization of pH

The pH of adsorption medium plays important role in adsorption efficiency of adsorbate ions. Therefore, the effect of pH on adsorption of silver ions ($4.635 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) was studied over the pH range of 1–13 using arbitrarily selected 0.125 g of coconut coir and shaking time of 20 min and results are shown in Fig. 3, which depicts that the adsorption of silver ions first increases from 1 to 8. Maximum adsorption was observed at pH value of 7.0 that remains almost constant up to pH value of 13.0 because at low pH values, functional groups present at surface of adsorbent were un-dissociated or protonated resulting in decrease in percentage removal of silver ions while at higher pH values, deprotonation of adsorbent’s functional groups lead to greater interactions between negatively charged adsorbent surface and positively charged silver ions resulting in greater percentage removal [51] up to pH 7 after which it become constant. Hence, optimum pH for next experiments was selected to be 7. The low adsorption ability of silver ions at lower pH could be attributed to competition for binding sites between H^+ ions and silver ions. The attachment of silver ions on surface of coconut coir may be explained based on surface complex formation model. In this model the hydrolysed coconut surface possesses negative charge, that is, $(\text{C. coir}-\text{O}^-)$, where cations exchange reaction can occur in aqueous solutions as follows:



The overall reaction could be represented as:

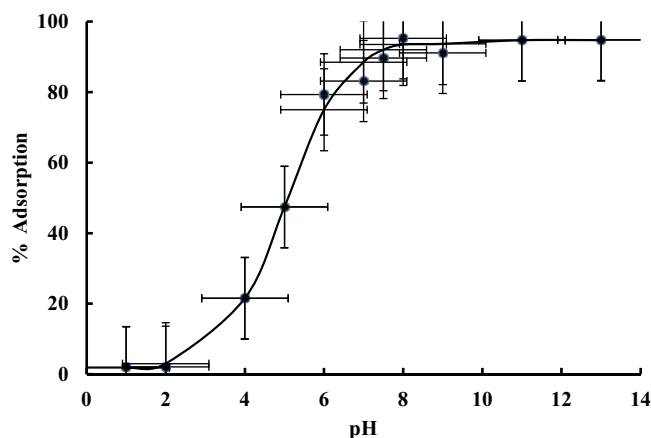
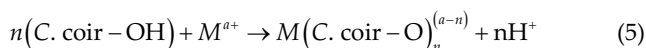


Fig. 3. Variation of adsorption of silver ions on coconut coir as a function of pH.

where $(\text{C. coir}-\text{OH})$ = hydroxyl group on the surface of coconut coir; $(\text{C. coir}-\text{O}^-)$ = hydrolyzed surface of coconut coir; M^{a+} = metal ions with $a+$ charge; $n\text{H}^+$ = number of protons released.

Reaction (5) is reversible in acidic solutions.

3.5. Effect of coconut coir weight

Effect of weight of coconut coir on adsorption of silver ions was studied by varying the weight of coconut coir from 0.05 to 0.4 g using $4.635 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ of silver solution at $0.0001 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ for time interval of 20 min. The results are shown in Fig. 4, which shows the variation of percentage adsorption vs. adsorbent weight. Fig. 4 shows that the percentage adsorption increases with an increase in adsorbent weight up to 0.125 g beyond which almost constant adsorption was observed and was sufficient for removal of silver ions. This amount of coconut coir, that is, 0.125 g was selected for all further experiments. The increase in percent adsorption of silver ions with an increase in weight of coconut coir could be attributed to availability of more

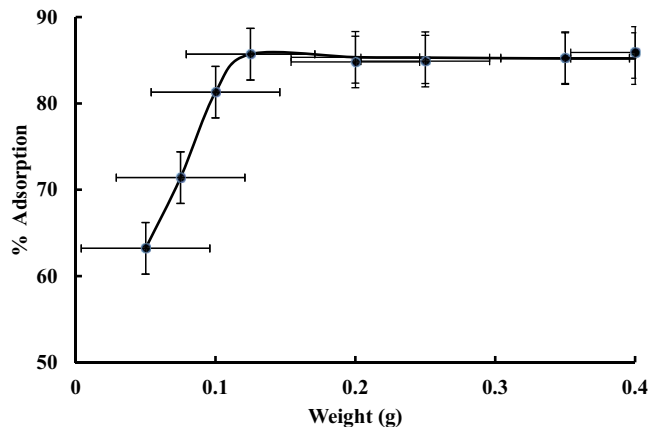


Fig. 4. Effect of coconut coir weight on the adsorption of silver.

active sites with increase in adsorbent weight [1] which become constant after certain point owing to saturation of all active sites of adsorbent resulting in no further increase in metal ion removal [51]. Hence, optimum adsorbent dose for silver ions adsorption was selected to be 0.125 g.

3.6. Influence of equilibration time

The influence of equilibration time on adsorption of silver ions was studied by varying the shaking time from 1–30 min using $4.635 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ of silver ion solution in $0.0001 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ with 0.125 g of coconut coir and the results are shown in Fig. 5.

Fig. 5 shows that adsorption of silver ions gradually increases with increase in contact time up to 20 min, where percentage removal was 83%, but after 20 min no significant increase in adsorption was observed up to 30 min. Therefore, 20 min was optimized equilibration time for maximum adsorption of silver ions and was selected for further experimentation. The increase in percentage adsorption with increase in shaking time is due to more contact time for $\text{Ag}(\text{I})$ ions using fixed amount of coconut coir. The initial rapid adsorption of silver ions could probably be due to availability of more vacant active sites on surface of adsorbent [52], and it was controlled by diffusion process from bulk to adsorbent surface, however, in latter stage the adsorption process became slow due to availability of lesser number of active sites for binding the silver ions on adsorbent surface and sorption is likely an attachment-controlled process due to less available active sites [53].

3.6.1. Kinetic studies

The time dependent adsorption data was utilized to verify the Morris–Weber [54] Eq. (6):

$$q_t = K_{\text{int}} t^{0.5} \quad (6)$$

where q_t = adsorbed concentration ($\text{mg}\cdot\text{g}^{-1}$) at time t ; K_{int} = intraparticle diffusion coefficient.

Plot of q_t vs. $t^{0.5}$ is shown in Fig. 6, which clearly shows that initially the adsorption was rapid up to 15 min and

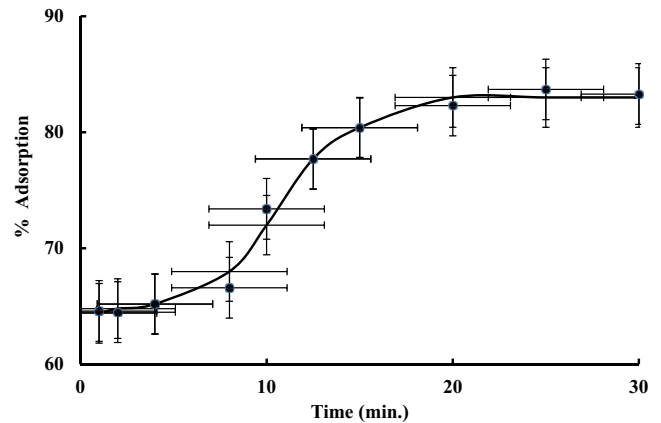


Fig. 5. Effect of equilibration time on the adsorption of silver on coconut coir.

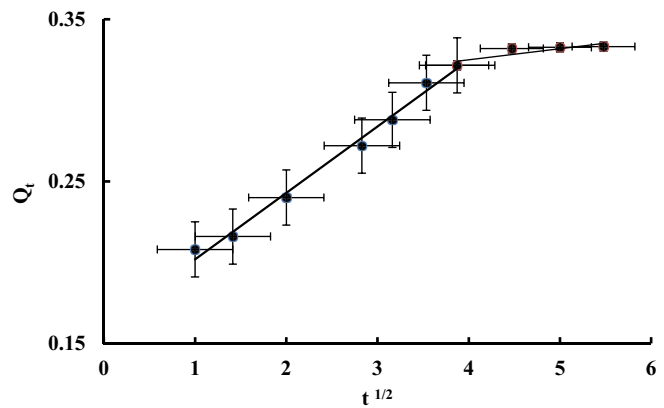


Fig. 6. Morris–Weber plot of silver ions adsorption on coconut coir.

was then slowed down from 15 to 30 min, which were depicted from two distinct slopes of 0.041 and 0.006 for first 15 min and 15–30 min, respectively.

The nature of adsorption either by film diffusion or intraparticle diffusion mechanism was verified by using data in Reichenberg [55] Eq. (7):

$$X = \left(1 - \frac{6}{\pi^2}\right) e^{-\beta_i} \quad (7)$$

$$\text{where } X = \frac{Q_t}{Q_c} = \frac{\text{Amount of metal adsorbed at time "t"}}{\text{Amount of metal adsorbed at equilibrium}}$$

The value of “ β_i ” is a mathematical function of X that can be calculated for each value of X by using following equation:

$$\beta_i = -0.4977 \ln(1 - X) \quad (8)$$

When we plot β_i vs. time, then we get a straight-line graph (as shown in Fig. 7) with a correlation coefficient of 0.941 which indicates that the sorption is controlled by film

diffusion, that is, current adsorption data was fit to intra-particle diffusion model.

The kinetic adsorption parameters were also evaluated by fitting the time dependent adsorption data of silver ions on to the coconut coir to first order Lagergren [Eq. (9)] and pseudo-second-order [Eq. (10)] rate equations using the linearized forms as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{9}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

where q_e = amount of silver ions adsorbed at equilibrium ($\text{mg}\cdot\text{g}^{-1}$); q_t = amount of silver ions adsorbed at time “ t ” ($\text{mg}\cdot\text{g}^{-1}$); t = time in min; k_1 = rate constant of first-order model (min^{-1}); k_2 = rate constant of pseudo-second-order model ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$).

The straight lines were obtained by plotting $\log(q_e - q_t)$ vs. “ t ” and t/q_t vs. “ t ” with correlation coefficients (R^2) of 0.941 and 0.997, for pseudo-first-order and pseudo-second-order kinetic models, respectively (Fig. 8). The determined kinetic parameters for pseudo-first-order and pseudo-second-order models are given in Table 1. From results, it was found that R^2 value for pseudo-first-order kinetic model was 0.941 (less than 1). Additionally, there was greater difference between calculated (i.e., $0.274 \text{ mg}\cdot\text{g}^{-1}$) and experimental (i.e., $0.333 \text{ mg}\cdot\text{g}^{-1}$) q_e values showing that current adsorption process does not follow pseudo-first-order kinetic model. The higher R^2 value, that is, 0.997 (greater

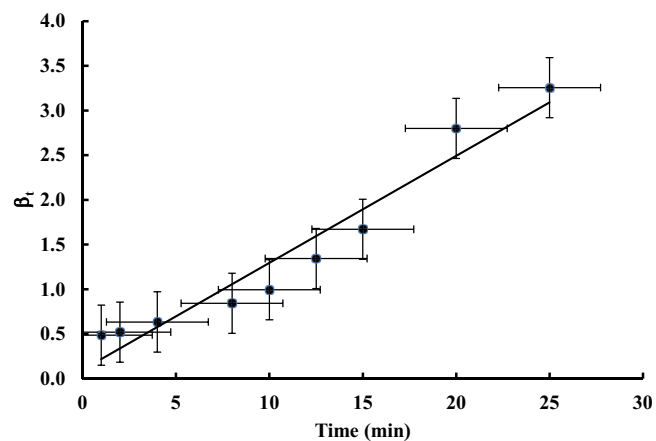


Fig. 7. Reichenberg plot of silver adsorption on coconut coir.

Table 1
Kinetic data for the adsorption of silver ions on coconut coir

Pseudo-first-order			Pseudo-second-order		
q_e ($\text{mg}\cdot\text{g}^{-1}$)	k_1 (min^{-1})	R^2	q_e ($\text{mg}\cdot\text{g}^{-1}$)	k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	R^2
0.274	0.239	0.941	0.351	1.862	0.997

Experimentally calculated $q_e = 0.333 \text{ mg}\cdot\text{g}^{-1}$

than that of pseudo-first-order model) and good correspondence between graphically calculated ($0.351 \text{ mg}\cdot\text{g}^{-1}$) and experimental ($0.333 \text{ mg}\cdot\text{g}^{-1}$) values of adsorption capacity confirm that experimental kinetic data agrees with pseudo-second-order rate equation, that is, some chemical interactions are also involved in complex adsorption process of silver ions on coconut coir. Similar results have been reported by Jintakosol and Nitayaphat [1].

3.7. Effect of initial silver ion concentration

The effect of initial silver ion concentration on efficiency of adsorption was investigated under optimized conditions, that is, contact time 20 min, adsorbent weight 0.125 g and $0.0001 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 solution. The initial concentration of silver was varied from 4.635×10^{-5} to $6.953 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$. It was observed that percentage adsorption decreases gradually with an increase in concentration of silver ions (Fig. 9) which could be explained based on availability of relatively lesser number of active sites in a fixed amount of coconut coir at higher concentrations of silver ions.

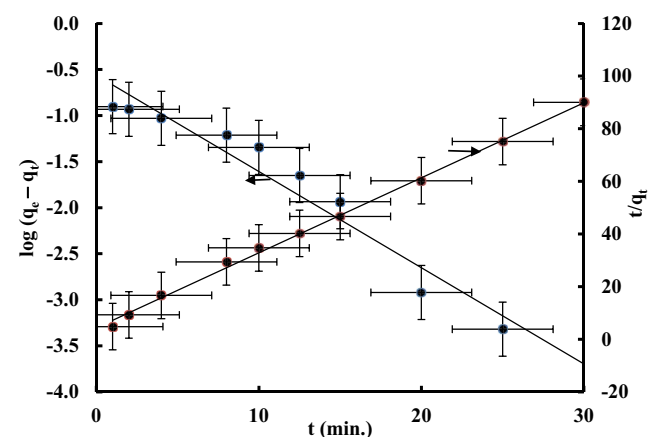


Fig. 8. Pseudo-first-order and pseudo-second-order plots of silver ions adsorption on coconut coir.

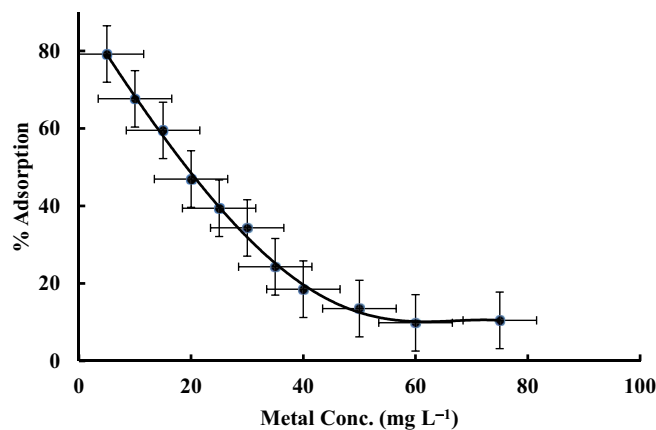


Fig. 9. Adsorption of silver ions as a function of its own concentration on coconut coir.

3.7.1. Adsorption isotherms

It is important to study the most appropriate expressions for equilibrium plots, to optimize the design of an adsorption process. Freundlich, Langmuir and Dubinin–Radushkevich isotherm models were used to describe adsorption equilibrium using optimized parameters.

The Freundlich adsorption isotherm is the relationship between the concentration of the metal uptake per unit mass of an adsorbent (C_{Ad}) and the concentration of metal at equilibrium (C_E).

$$\log C_{Ad} = \log K + \frac{1}{n} \log C_E \quad (11)$$

where C_{Ad} = amount of silver adsorbed ($\text{mol}\cdot\text{g}^{-1}$); C_E = equilibrium concentration of silver in solution ($\text{mol}\cdot\text{L}^{-1}$); $1/n$ and K = Freundlich constants

A plot of $\log C_{Ad}$ vs. $\log C_E$ yields a straight line with a correlation coefficient " R^2 " value of 0.932. The linear plot (Fig. 10) supports the applicability of Freundlich adsorption model in the present study. Obtained adsorption isotherm showed that current process of adsorption of silver ion adsorption on coconut husk powder is favourable [56]. From intercept and slope of graph KF and " $1/n$ " (value ranges from $1-10^{19}$) can be determined [57,58] and were found to be $0.103 \text{ mmol}\cdot\text{g}^{-1}$, and 0.297 , respectively. The fractional value of the adsorption affinity ($1/n$) corresponds to a heterogeneous surface of coconut coir.

The determined adsorption capacity of silver ions on coconut coir (11.114 mg g^{-1}) was compared with reported values for different adsorbents and the results are represented in Table 2. The determined adsorption capacity is lower than that of waste coffee grounds and polyurethane foam, almost equal to titanium dioxide but is higher than the reported values for montmorillonite, perlite, Turkish coal, silica gel and polymer which showed that coconut coir is an excellent adsorbent for adsorption of silver ions from wastewater.

The Langmuir adsorption isotherm model assumes that all adsorption sites have equal affinity for metal ions. This linear equation is given by Irving Langmuir [59] and its linear form may be represented as

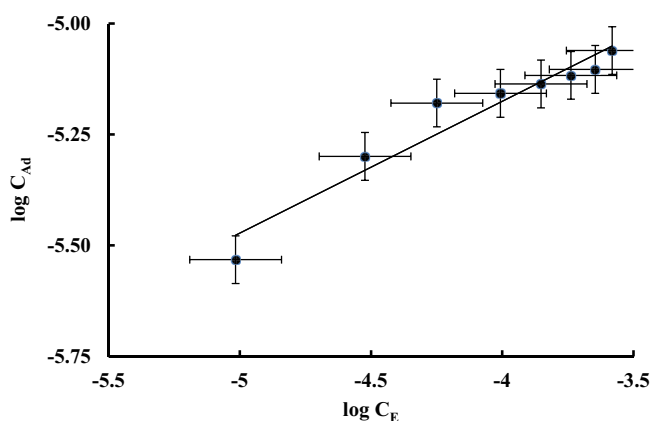


Fig. 10. Freundlich plot for the adsorption of silver on coconut coir.

$$\frac{C_E}{C_{Ad}} = \frac{1}{Qb} + \frac{C_E}{Q} \quad (12)$$

where C_{Ad} = concentration of silver adsorbed at equilibrium ($\text{mol}\cdot\text{g}^{-1}$); C_E = equilibrium concentration of silver in solution ($\text{mol}\cdot\text{L}^{-1}$); Q and b = Langmuir isotherm constants.

A plot of C_E/C_{Ad} vs. C_E yields a straight line (Fig. 11), with a correlation coefficient " R^2 " of 0.992, indicating the applicability of the Langmuir model for the data of silver ions adsorption on coconut coir. The values of Langmuir constants " Q " and " b " were determined from the slope and intercept of the plot and were found to be $8.99 \times 10^{-2} \text{ mmol}\cdot\text{g}^{-1}$ and $4,035.64 \text{ dm}^3\cdot\text{mol}^{-1}$, respectively. Separation factor parameter, that is, R_L was used to determine whether process of silver ion adsorption on coconut coir was favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). Formula of R_L is given as follows:

$$R_L = \frac{1}{1 + bc_{in}} \quad (13)$$

Table 2
Adsorption capacities of silver for different adsorbents

Adsorbent	Capacity ($\text{mg}\cdot\text{g}^{-1}$)	References
Titanium dioxide	14.06	[13]
Montmorillonite	1.31	[14]
Perlite	8.46	[15]
Turkish coal	1.87	[17]
Silica gel	0.38	[18]
Waste coffee grounds	49.5	[21]
Polyurethane foam	16.18	[23]
Rice husk	1.62	[40]
Peat	10.8	[41]
Polymers	2.41	[42]
Coconut coir	11.11	Present work

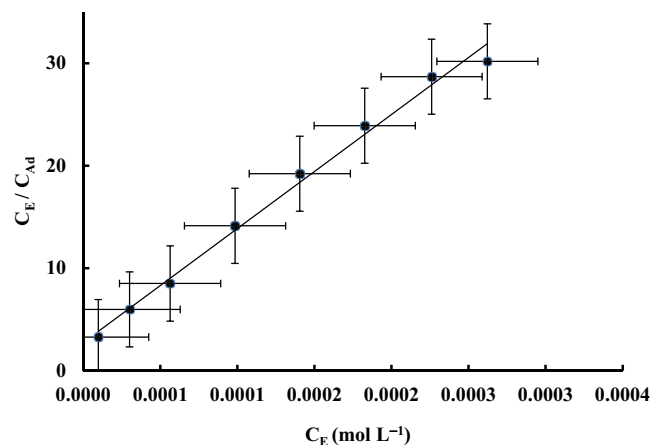


Fig. 11. Langmuir plot for the adsorption of silver on coconut coir.

where b = Langmuir adsorption equilibrium constant ($L \cdot mol^{-1}$), C_{in} = initial dye concentration ($mol \cdot L^{-1}$). From b and C_{in} we can determine R_L [59,60] which in current case comes out to be 1, that is, $R_L = 1.00$ confirming that current process of silver ion adsorption on coconut coir was of linear type. The higher value of sorption capacity (K_f) calculated from Freundlich isotherm as compared to the Langmuir isotherm model may be attributed to the multilayer and mono-layer adsorption of silver ions, respectively.

To verify the physical or chemical adsorption, the Dubinin–Radushkevich isotherm was also checked. The Dubinin–Radushkevich isotherm is temperature dependent [59]. The linear form of Dubinin–Radushkevich isotherm may be expressed as:

$$\ln C_{Ad} = \ln C_m - \beta \varepsilon^2 \quad (14)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_E} \right) \quad (15)$$

where b = a constant with a dimension of energy; e = Polanyi potential; R = ideal gas constant; T = absolute temperature; C_E = equilibrium concentration of silver ions in solution.

A straight line was obtained when $\ln C_{Ad}$ was plotted against e^2 with $R^2 = 0.952$ (Fig. 12), indicating that silver ions adsorption on coconut coir also obeys Dubinin–Radushkevich equation. From the linear plot the determined value of “ b ” was $-2.6 \times 10^{-3} \text{ kJ}^2 \cdot \text{mol}^{-2}$. By using the value of “ b ” the mean adsorption energy (E_{Ad}) was calculated using Eq. (16) as:

$$E_{Ad} = \frac{1}{(-2\beta)^{1/2}} \quad (16)$$

The determined value of “ E_{Ad} ” from Eq. (17) was $13.867 \text{ kJ} \cdot \text{mol}^{-1}$, indicating chemisorption or ion-exchange process between functional groups of adsorbent and silver ions of aqueous solution [61]. Similar results have been reported by Nemeş and Bulgariu [51].

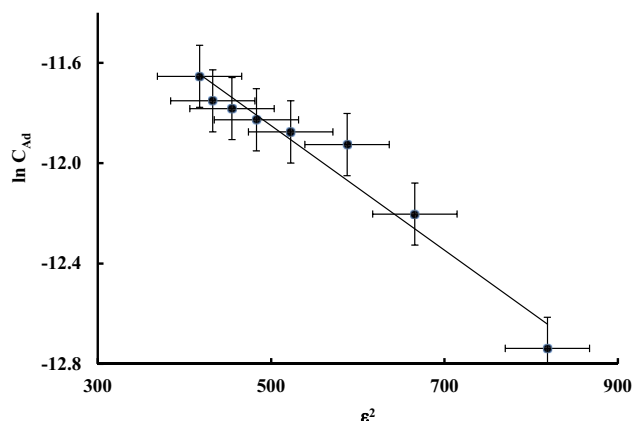


Fig. 12. Dubinin–Radushkevich plot for the adsorption of silver on coconut coir.

3.8. Effect of temperature

The adsorption of $4.635 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of silver ions on coconut coir was carried out using optimized adsorption parameters at different temperatures. The temperature was varied from 283 to 333 K and the results are shown in Table 3 which showed that the silver ions adsorption increases with rise in temperature. Van’t Hoff plot, that is, $\ln K_c$ vs. $1/T$ was a straight line (Fig. 13) and was used to determine ΔH and ΔS from slope and intercept, respectively, by using following equation:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (17)$$

where K_c , ΔS , ΔH , R and T are equilibrium constant, change in entropy, enthalpy change, gas constant and absolute temperature, respectively, for adsorption process. Equilibrium constant (K_c) was calculated by using the equation:

$$K_c = \frac{C_{EqS}}{C_{EqL}} \quad (18)$$

where C_{EqS} is concentration of silver adsorbed at equilibrium ($mg \cdot L^{-1}$) and C_{EqL} is concentration of silver in solution at equilibrium ($mg \cdot L^{-1}$). ΔG and ΔS for specific adsorption process have also been calculated using the equations:

$$\Delta G = -RT \ln K_c \quad (19)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (20)$$

The calculated values of ΔG , ΔH and ΔS have been summarized in Table 4. The negative values of ΔG represent that adsorption of silver on coconut coir is a spontaneous process. The increase in numerical value of $-\Delta G$ with rise in temperature indicates that adsorption process of silver ions on coconut coir is more favourable at higher temperatures. The positive values of enthalpy change indicate the endothermic nature of adsorption process, whereas

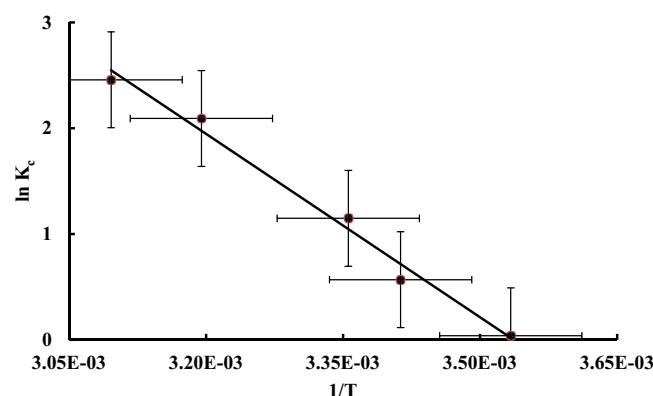


Fig. 13. Van’t Hoff plot for the adsorption of silver ions on coconut coir.

Table 3
Adsorption behavior of silver ions on coconut coir as a function of temperature

		Dose of coconut coir	0.125 g		
		Contact time	20 min		
		Volume equilibrated	10 cm ³		
		HNO ₃ concentration	0.0001 mol·L ⁻¹		
		Silver ions concentration	4.635 × 10 ⁻⁵ mol·L ⁻¹		
Temp. (K)	1/T (K ⁻¹)	Concentration adsorbed (mol·L ⁻¹)	Concentration in bulk (mol·L ⁻¹)	K _c	lnK _c
283	3.597 × 10 ⁻³	2.364 × 10 ⁻⁵	2.276 × 10 ⁻⁵	1.039	0.038
293	3.413 × 10 ⁻³	2.962 × 10 ⁻⁵	1.678 × 10 ⁻⁵	1.765	0.568
298	3.356 × 10 ⁻³	3.523 × 10 ⁻⁵	1.117 × 10 ⁻⁵	3.154	1.149
313	3.195 × 10 ⁻³	4.130 × 10 ⁻⁵	5.099 × 10 ⁻⁶	8.000	2.092
323	3.096 × 10 ⁻³	4.274 × 10 ⁻⁵	3.662 × 10 ⁻⁶	11.671	2.457
333	3.003 × 10 ⁻³	4.586 × 10 ⁻⁵	2.543 × 10 ⁻⁶	18.034	2.892

Average relative standard deviation is ±2.8%.

Table 4
Thermodynamic parameters for the adsorption of silver ions on coconut coir

Temperature (K)	ΔG (kJ·mol ⁻¹)	ΔH (kJ·mol ⁻¹)	ΔS (J·K ⁻¹ ·mol ⁻¹)
283	-0.089		170.12
293	-1.384		168.74
298	-2.847	48.057	170.82
313	-5.444		170.93
323	-6.598		169.21
333	-8.007		168.36

Average relative standard deviation is ±2.8%.

positive value of ΔS represents increase in randomness during adsorption process.

3.9. Influence of foreign ions

The presence of other cations and anions in adsorptive medium may affect the environment and solution chemistry of concern metal, which influences the adsorption efficiency of an adsorbent. Therefore, using optimized conditions the adsorption of 4.635 × 10⁻⁵ mol·L⁻¹ of silver ions on coconut coir was also examined in presence of highway concentration (25 mg·L⁻¹) of various cations and anions. The anions used were as their sodium salts, while for cations the nitrate salts were used. The results are summarized in Table 5.

The results show that adsorption efficiency of silver on coconut coir was decreased in the presence of cations [62]. Since radius of manganese is the smallest of all studied cations (i.e., 0.082 nm) hence its effect on silver ion adsorption is the greatest of all studied cations. While the adsorption of silver on coconut coir was almost constant in the presence of all the anions studied except F⁻, Br⁻ and S²⁻ which decreased the adsorption significantly because their radius are the smallest of all studied anions (i.e., 0.133, 0.196, and 0.184 nm, respectively) thus causing a significant decrease in percentage adsorption. This decrease in adsorption

efficiency of silver may be due to competitive action of cations or the formation of stable compounds/complexes with anions under experimental conditions. Similar results have been reported by Tariq et al. [44].

3.10. Desorption

To be useful in silver ion recycling processes, adsorbed silver ions should be easily desorbed under suitable conditions. Desorption experiments were carried out by using 1.0 M HNO₃ as the desorption medium. The coconut coir adsorbed with the maximum concentration of silver ions was placed within the desorption medium and shaken for 20 min. It was observed that at least 93% of adsorbed silver was desorbed. The desorbed adsorbent was then further used again for the adsorption of silver ions. This exercise was repeated for three times, and it was found that the observed adsorption efficiency was 79.5% ± 0.3%. This clearly indicates that coconut coir can be reused for adsorptive removal of silver ions from aqueous solutions without significant loss in adsorption efficiency.

3.11. Applicability of the developed procedure

The applicability of the developed method was checked by the removal of silver ions from a real tap water sample using optimized parameters. The tap water sample was spiked with 4.635 × 10⁻⁴ mol·L⁻¹ of silver ions in 1.0 × 10⁻⁴ mol·L⁻¹ of nitric acid. The solution was equilibrated with 0.125 g of coconut coir for 20 min. The determined components of tap water sample are shown in Table 6. The observed removal efficiency of silver ion was 84.6% in a single step, indicating that the developed procedure can be utilized for decontamination/removal of silver ions from such matrices.

4. Conclusions

Coconut coir has effective and suitable adsorption characteristics for adsorptive removal of toxic silver ions from wastewater. Adsorbent was characterized by BET, FTIR, SEM, and EDX techniques. Experiments were performed in

Table 5
Effect of diverse ions on the adsorption of 4.635×10^{-5} mol·L⁻¹ of silver ions on coconut coir

Cations			Anions		
Ion	Concentration (mol·L ⁻¹)	% Adsorption	Ion	Concentration (mol·L ⁻¹)	% Adsorption
No ion	–	80	No ion	–	80
Na ⁺	1.088×10^{-3}	37	F ⁻	1.316×10^{-3}	52
K ⁺	6.410×10^{-4}	16	Br ⁻	3.129×10^{-4}	2
Mg ⁺²	1.029×10^{-3}	41	SO ₄ ⁻²	2.604×10^{-4}	77
Ca ⁺²	6.250×10^{-4}	36	S ⁻²	7.798×10^{-4}	21
Al ⁺³	9.266×10^{-4}	51	NO ₂ ⁻	5.435×10^{-4}	79
Cr ⁺⁶	4.808×10^{-4}	76	PO ₄ ⁻³	2.632×10^{-4}	81
Fe ⁺³	4.477×10^{-4}	58	CN ⁻	9.615×10^{-4}	75
Sb ⁺³	2.053×10^{-4}	22	HCO ₃ ⁻	4.098×10^{-4}	85
Co ⁺²	4.242×10^{-4}	32	ClO ₄ ⁻	2.514×10^{-4}	76
Zn ⁺²	3.824×10^{-4}	23	NO ₃ ⁻	4.032×10^{-4}	75
Ni ⁺²	4.258×10^{-4}	39	Citrate ⁻³	2.514×10^{-4}	84
Mn ⁺²	4.551×10^{-4}	13	EDTA	6.721×10^{-5}	74

Average relative standard deviation is $\pm 2.8\%$.

Table 6
Determined composition of tap water sample

Cations/anions	(mg·L ⁻¹)
Ca	25.52
Mg	13.92
Na	15.92
K	1.03
Fe	0.01
Mn	0.01
Zn	0.07
Cu	0.01
Pb	0.01
CO ₃ ²⁻	9.00
HCO ₃ ²⁻	123.20
NO ₃ ⁻	1.50
SO ₄ ²⁻	6.20
Cl ⁻	3.40
Ag ^{**}	5.00*
Ag ^{**}	0.77**

Average relative standard deviation is $\pm 2.8\%$;

*Concentration after spiking;

**Concentration after decontamination.

batch mode to investigate the effect of various operational parameters on silver ion adsorption and results showed that maximum amount of silver ions, that is, 93% was removed under optimized conditions such as 4.635×10^{-5} mol·L⁻¹ of silver ion concentration solution having pH 7, with 0.125 g of coconut coir, contact time of 20 min at 333 K temperature. Kinetic studies confirmed that process of adsorption of silver on coconut coir followed pseudo-second-order rate equation having co-efficient of determination $R^2 = 0.997$ with intraparticle diffusion process. Adsorption data followed

Freundlich, Langmuir and Dubinin–Radushkevich isotherms over the silver concentration range studied. The adsorption mean free energy from Dubinin–Radushkevich isotherm was 13.889 kJ·mol⁻¹ indicating ion-exchange mechanism of chemisorption. Process was spontaneous and endothermic in nature as confirmed by thermodynamic studies. Foreign ions (cations or anions) with the smallest radius affect silver ions adsorption on a greater extent as compared to ions with larger radius. Applicability of developed procedure with tap water was 84.6% and the desorption experiment resulted in 93% regeneration of adsorbent. Based on this study, it was concluded that efficient, inexpensive, and eco-friendly coconut coir has great silver removal potential from contaminated environmental aqueous media which will be helpful for environmental protection.

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