



OPEN Valorization of textile waste for removal of Cadmium from contaminated water

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The rapid development in agriculture and industrial sectors has raised some serious global issues like heavy metals pollution of water resources. Cadmium (Cd) is amongst the major water pollutants worldwide. In this study, two novel sorbents were prepared by using post-consumer textile waste (PCTW). The waste denim fabric was recycled with environmentally friendly H₂O₂ and Ozone through oxidation under alkaline conditions to produce several functional groups at the surface (named as ODF@H₂O₂ and ODF@O₃ respectively) that could trap the heavy metal cations from contaminated water. The functionalized fabric sorbents were characterized by Fourier transform infrared spectroscopy (FT-IR), X-Ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-Ray (EDX) that revealed the presence of carboxylic acid, hydroxyl, and amine functional groups on their surfaces. The sorption isotherm, sorption kinetics and sorption thermodynamics were carried out to unravel the sorption process mechanism. The ODF@H₂O₂ sorbent was proved more effective by giving maximum adsorption capacity of (238.09 mg g⁻¹) compared to Ozone treatment (175.44 mg g⁻¹) for Cd²⁺ and achieved within just 20 min for both sorbents. Pseudo 2nd order and Langmuir models confirmed the chemisorption as dominant mechanism for the monolayer sorption of Cd²⁺ ions onto ODF@H₂O₂ and ODF@O₃. The sorption thermodynamic revealed the sorption process as endothermic and spontaneous in nature. The results showed that both ODF@H₂O₂ and ODF@O₃ sorbents have an efficient potential for sorbing Cd from contaminated water. Furthermore, both ODF@H₂O₂ and ODF@O₃ sorbents were also tested in a regeneration study to investigate the reuse of these sorbents, and we achieved marvelous results. Both sorbents gave up to 90% of the sorption capacity even after 10 recycles. Conclusively, both sorbents can have their implications for the preparation of filters that can be used for the treatment of wastewater. This study has practical significance by tackling the two environmental problems i.e. heavy metal pollution and denim waste.

Keywords Recycling, Post-consumer textile waste, Functionalization, Carboxylic acid groups, Sorption, Wastewater treatment, Sustainability

Though this is the era of growing technology, still the concentration of heavy metals in water is not within the safe range in many countries as suggested by regulatory authorities¹. Mostly, the water is contaminated with various heavy metals like cadmium, arsenic, mercury, lead, and chromium that are hazardous to human health². These heavy metals pollution of water and soil has become the hotspot of recent studies for environmental researchers due to their non-biodegradable, bioavailable, persistent, and more toxic nature³. Due to increased consumption of these heavy metals through drinking of contaminated water, diseases like diabetes, neuronal damage, cardiovascular disorders, renal injuries, and even cancer have been diagnosed^{3,4}. Cd has been listed as the fifth harmful toxicant for human beings which causes diseases like osteoporosis, hypertension, diabetic renal dysfunction/ complications, pancreas, bladder, kidney, lung and breast cancer^{5,6}. The main reason behind the heavy metal toxicity is the generation of reactive oxygen species that are responsible for oxidative damage and

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health associated disastrous effects⁷. The mortality rate is also increasing due to excessive utilization of various heavy metals⁸.

Another issue of same importance is the post-consumer textile waste (PCTW) due to fast fashion. It is reported that 27 million tons of cotton are being produced per year globally and almost the same number of textiles in the form of PCWT are disposed of every year. About 5% of all worldwide landfills are being taken up by dumping of textile waste which is creating serious environmental and health hazards due to open air dumping^{9,10}. The degradation of textile waste particularly cotton generates greenhouse methane (CH₄) gas and carbon dioxide (CO₂) which are responsible for climate change while, toxic chemicals and dyes have been leached out into soil and groundwater causing soil and freshwater pollution.

Recently, every organization has been trying to achieve sustainability by recycling waste and converting it into useful products that can have minimum environmental impacts¹¹. The denim, which is generally made of cotton, loses its aesthetic and functional value at the end of its lifecycle^{11–13}. Moreover, recycling of post-consumer denim waste into new textile products is also very challenging due to loss of fiber strength and length. Denim fabric is often made from cotton having more than 90% cellulose. Cellulose is made up of several functional groups like hydroxyl, carbonyl and others. Due to the presence of hydroxyl groups on its surface the cellulose can be converted into sorbents having potential to extract positive metal ions from a contaminated medium¹⁴. These functional groups can further be oxidized to convert hydroxyl ion into carboxylic acid groups having more strong potential to sorb heavy metal ions compared to hydroxyl groups^{14–16}.

To address the issues of heavy metals in water and denim waste environmental footprint, the present study is aimed at recycling denim waste and preparing a sustainable and cost-effective sorbent using environmentally safe hydrogen peroxide and ozone for generation of carboxylic acid groups on denim waste. Moreover, the present study also explores the possibility to regenerate sorbent once it is saturated with heavy metals during removal process. This study has a practical significance as it will tackle two environmental problems at the same time. This study is novel as it involves preparing two sustainable sorbents by recycling waste material into useful and reusable sorbents having strong sorption potential for metal ions. Both sorbents are environmentally friendly as no harmful chemicals are used during their synthesis and will have minimum environmental impacts.

Results and discussion

Selection of efficient oxidation treatment

The effect of different oxidation treatments on the removal of Cd was studied by varying the oxidation treatments for H₂O₂ (0, 10, 25, 50, 100, 200, 400 ml/L), and for Ozone (0, 15, 30, 45, 60, 75 min). The adsorbent dose (0.01 g), shaking time (1 h) and Cd concentration (100 ppm) were kept constant and different H₂O₂ and ozone treatments were tested as described above. These samples were run on Atomic Absorption Spectrophotometer (AAS) and Cd removal percentage was calculated (Fig. 1a and b). We achieved maximum Cd removal percentage (96%) with H₂O₂ treatment 200 ml/L (ODF@H₂O₂) and 89% with Ozone treatment of 75 min (ODF@O₃) compared to fabric with untreated denim fabric (UDF) which gave only 29% Cd removal percentage. Both above samples were chosen for further use in the experiment.

Analysis of samples

Once the samples with the highest capacity to absorb cadmium ions from water have been shortlisted, various analysis of those samples were conducted. Figure 2 shows the FTIR of untreated and treated denim fabrics. The FTIR spectrum of untreated denim fabric exhibits peaks that originated from cellulose macromolecule and indigo dye at 3345 cm⁻¹ attributed to O–H stretching, 2941 cm⁻¹ related to C–H aromatics, 1589 cm⁻¹ for N–H stretching, 1433 cm⁻¹ and 1058 cm⁻¹ was due to C–N and C–O stretching respectively¹⁷. From the FTIR spectrum of (ODF@O₃) and (ODF@H₂O₂), it can be observed that the peak at 1058 cm⁻¹ i.e. the β-glucosidic

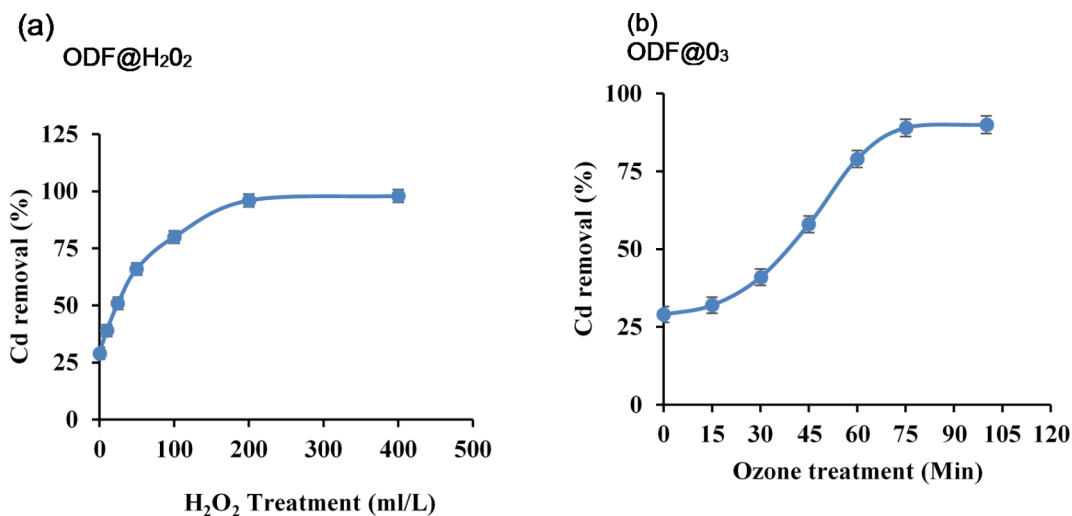


Fig. 1. Cadmium removal percentage achieved with different levels of H₂O₂ (a) and Ozone treatments (b).

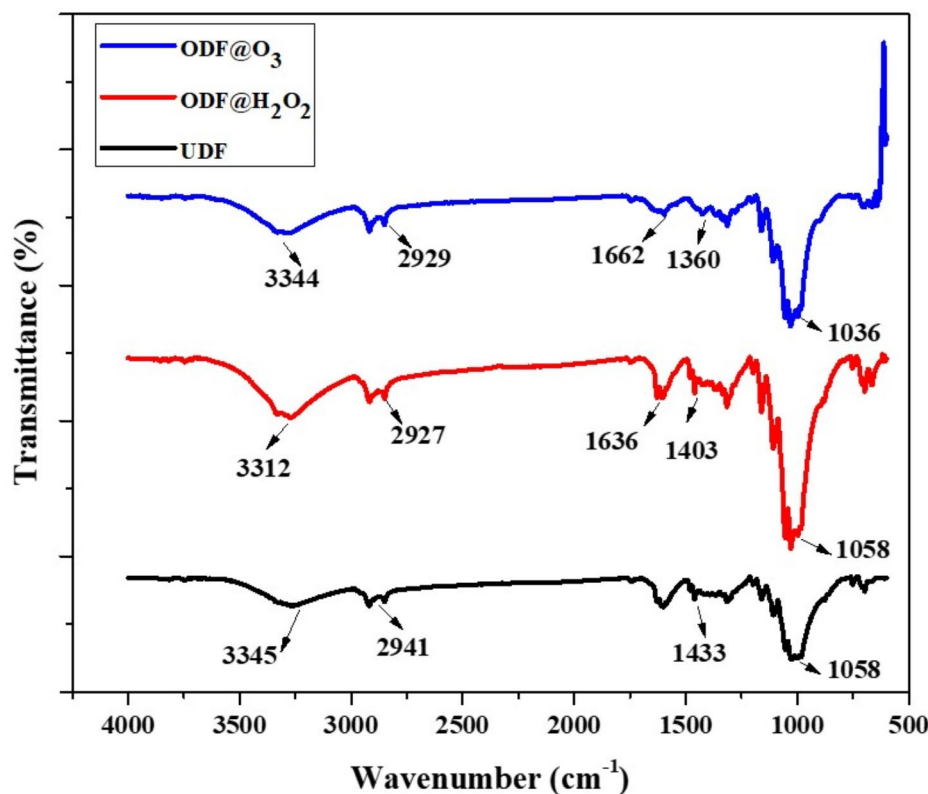


Fig. 2. FTIR spectra of UDF, ODF@H₂O₂, and ODF@O₃.

bond in the cellulose macromolecules do not show any major variation between the untreated and treated fabrics. Furthermore, it was noted that the band at 3345 cm⁻¹ due to OH stretching experienced a minor shift in the position to 3312 cm⁻¹ and 3344 cm⁻¹ after the treatment with ozone and hydrogen peroxide respectively. This slight modification results in a reduction of the hydrogen bonds between the cellulose macromolecules¹⁸.

Figure 3a shows the scanning electron microscopic image of UDF. Figure 3b shows the fabric treated with ODF@O₃ whereas, Fig. 3c is that of ODF@H₂O₂. The ozone treatment made the surface of fibers very rough due to oxidation of cellulosic chains. The treatment with hydrogen peroxide happens to be very drastic. It causes breakage of cellulosic chains due to excessive oxidation which leads to generation of beads on fibers. EDX analysis of UDF, ODF@H₂O₂, and ODF@O₃ was performed to analyze the different elements and their weight percentages. Figure 3d and e, and 3f show the results of treated and untreated denim fabrics. The weight% of oxygen elements enhanced in ODF@O₃ due to the oxidation of denim fabric Fig. 3f while, ODF@H₂O₂ has less weight% of oxygen elements Fig. 3e relative to the UDF Fig. 3d, and ODF@O₃ Fig. 3f. which may be attributed to loss of oxygen due to formation of smaller volatile molecules like carbon dioxide. The exact values of weight% of different elements are represented in Fig. 3d and e, and f.

The XRD spectrum of prepared sorbents are represented in Fig. 4. XRD pattern of UDF exhibits peaks at 14.9, 16.9, 22.9, and 34.8° which correspond to (1-10), (110), (200) and (004) crystalline planes respectively (Fig. 4a) which are associated with the crystalline structure of cellulose¹⁸. The XRD pattern of ODF@H₂O₂ is presented in Fig. 4b which shows that the peak intensity of peaks at 14.9° and 16.9° is very low whereas, there is no significant change in case of ozone treatment (ODF@O₃) Fig. 4c. This might be due to the oxidation of cellulose fibers in the denim fabric by hydrogen peroxide due to high concentration causing slight disintegration of crystalline structure, while the ozone treatment was just a surface treatment. However, the peak at 34.8° remained unaffected during hydrogen peroxide treatment which corresponds to plane (004) and is characteristic peak of cellulose (II). This plane is formed during mercerization (caustic treatment) due to staking of crystallographic layers and has very strong hydrogen bonding which resists disintegration of structure due to hydrogen peroxide treatment in ODF@H₂O₂.

Sorption experiment Sorption isotherm

The effect of different initial Cd concentrations (5, 25, 50, 100, 200 and 400 ppm) on the removal of Cd from water was tested using 0.01 g of both sorbents dose, at normal pH and optimum shaking time. The plot of equilibrium metal concentration against experimental sorption capacities is presented in supplementary Fig. 1a and 1b. It was noticed that by increasing the initial concentration, the sorption capacity rapidly increased. Figure shows

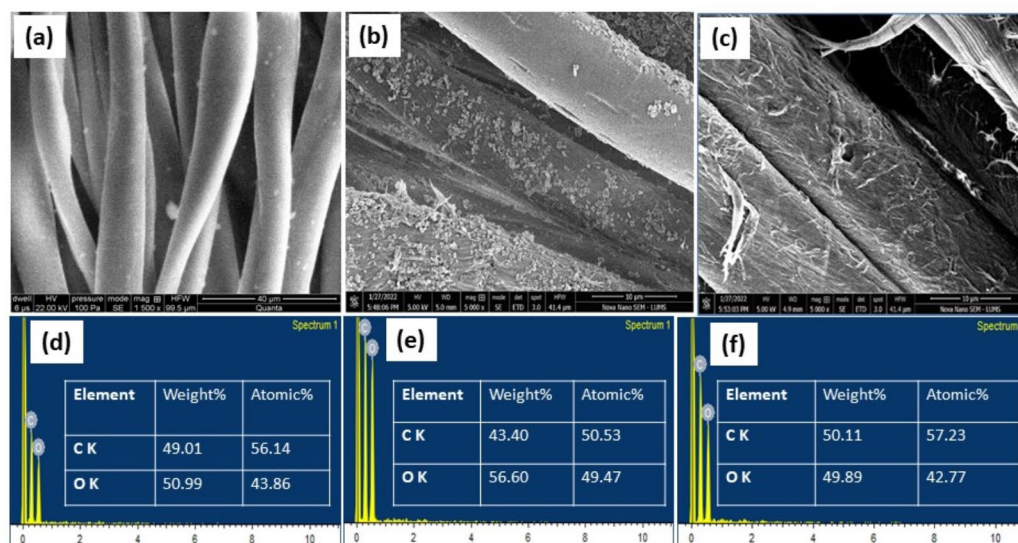


Fig. 3. SEM images of UDF (a), ODF@H₂O₂ (b) ODF@O₃ (c) and EDX analysis of UDF (d), ODF@H₂O₂ (e) ODF@O₃ (f).

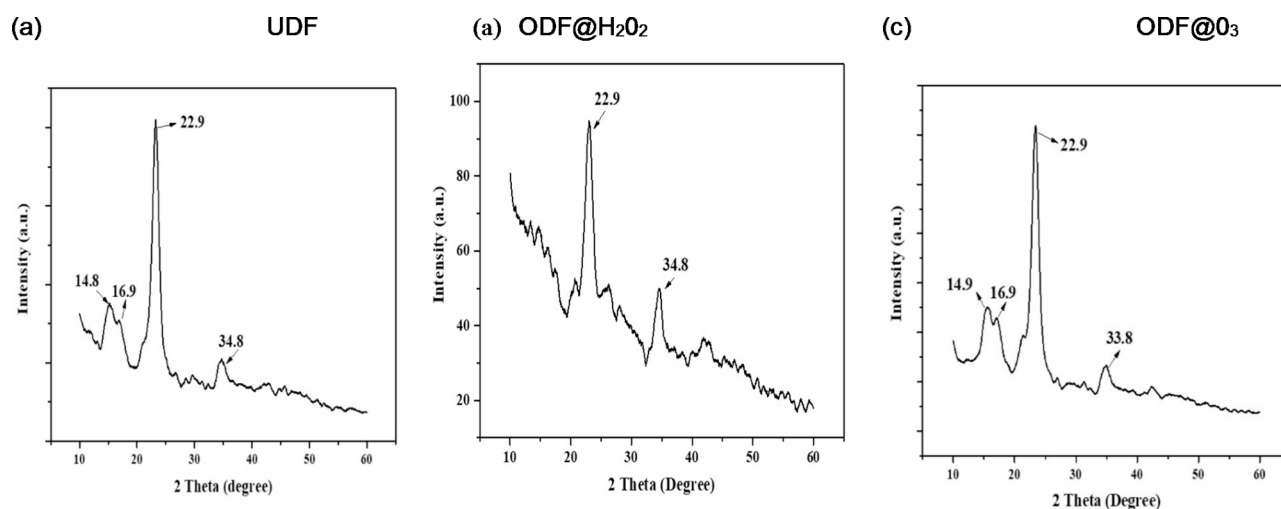


Fig. 4. XRD analysis of UDF (a), ODF@H₂O₂ (b) and ODF@O₃ (c).

the high sorption efficiency at low initial concentration by exhibiting a sharp slope, while exhibiting a flat slope at higher concentration which indicates saturation of sorption at higher concentration of metal. The increment in metal sorption potential may be due to diffusion-based mechanism on both sorbents¹⁹ and the higher metal concentration also increases the contact opportunities and provides a strong driving force to react with the functional groups present on the surface of sorbents ODF@H₂O₂ and ODF@O₃. The maximum sorption capacity was achieved at 100 ppm metal concentration. After that a decrease in removal % was recorded. This decrease in sorption rate after 100 ppm metal concentration may be due to the insufficient binding sites pertaining to saturation at very high metal concentrations²⁰. To further understand the sorption mechanism on ODF@H₂O₂ and ODF@O₃, the obtained experimental sorption results were fitted with Freundlich, Langmuir and Temkin

models. The Langmuir model assumes the monolayer sorption of adsorbate on the surface of adsorbent²¹. The Langmuir equation can be represented as

$$\frac{1}{q_e} = \frac{1}{q_{max} \cdot K_L} \frac{1}{C_e} + \frac{1}{q_{max}} \quad (1)$$

where, q_e (mg g^{-1}) represents the equilibrium sorption capacity of metal ions on surface, q_{max} (mg g^{-1}) represents the maximum sorption capacity of metal ions at complete monolayer coverage. C_e (mg L^{-1}) is the concentration of metal ions at equilibrium. K_L (L mg^{-1}) is the Langmuir constant related to the heat of sorption²¹.

The Freundlich model describes the sorption behavior for sorbents having heterogeneous surfaces and assumes multilayer sorption of adsorbate on the heterogeneous surface of adsorbent. The Freundlich equation can be represented as:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (2)$$

where, q_e (mg g^{-1}) represents the equilibrium sorption capacity of metal ions on surface. C_e (mg L^{-1}) is the concentration of metal ions at equilibrium. K_f (mg g^{-1}) is the Freundlich sorption isotherm constant related to sorption capacity. $1/n$ represents the magnitude of driving force for sorption and indicates the heterogeneity of the data distribution.

The Temkin equation can be represented as

$$q_e = \frac{RT}{b_T} \ln K_t + \frac{RT}{b_T} \ln C_e \quad (3)$$

where, q_e (mg g^{-1}) represents the equilibrium sorption capacity of metal ions on surface. K_t (L g^{-1}) is the Temkin sorption isotherm constant. T is the absolute temperature (K). R represents the ideal gas constant 8.314 ($\text{J mol}^{-1}\text{K}$). b_T is the constant related to the heat of sorption (J mol^{-1}).

The fitting results for three models have been presented in Fig. 5a and f, and the model's calculated parameters have been presented in Table 1. It is clear from Fig. 5c and d, and Table 1 that Langmuir model best fitted with the sorption of Cd on ODF@H₂O₂ and ODF@0₃ as compared to Freundlich (Fig. 5a and b) and Temkin model (Fig. 5e and f) as indicated by the higher correlation coefficients values (Table 1). This indicates that the sorption of Cd on ODF@H₂O₂ and ODF@0₃ is monolayer and homogenous^{22–24}. The maximum sorption capacities for Cd calculated from Langmuir model were 238.1 and 175.4 mg g^{-1} for ODF@H₂O₂ and ODF@0₃ respectively indicating that ODF@H₂O₂ has 36% more sorption potential for Cd compared to ODF@0₃. The separation factor R_L was calculated for Langmuir model to estimate the extent of sorption using the following Eq.

$$R_L = \frac{1}{1 + K_L C_o} \quad (4)$$

When the value of R_L is 0 the sorption is irreversible, beneficial when $0 < R_L < 1$ and adverse when $R_L > 1$ ²⁵. The R_L values we achieved for both ODF@H₂O₂ and ODF@0₃ were between 0 and 1, so the sorption of Cd on both sorbents is beneficial. Furthermore, both of our sorbents exhibited more sorption capacities compared to most of the previously reported sorbents. The comparison of maximum sorption capacities of ODF@H₂O₂ and ODF@0₃ for Cd metal with other reported sorbents has been presented in supplementary Table 1.

Sorption kinetics

The effect of contact time on the sorption of Cd on ODF@H₂O₂ and ODF@0₃ was investigated using different shaking times (0, 5, 10, 20, 40, 60 and 120 min). Figure 6a shows the sorption capacities (q_t) achieved as a function of time at three different initial concentrations 5, 50, and 100 mg L^{-1} . It is clear from the figure that the sorption capacities rapidly increased with increasing contact time reaching to maximum at 20 min of contact time, after that became constant for both ODF@H₂O₂ and ODF@0₃ by reaching at equilibrium time²². The very

short equilibrium time (20 min) as we achieved in this study for heavy metal removal by both ODF@H₂O₂ and ODF@0₃ is beneficial for practical application of these sorbents for wastewater treatment. To further explore the sorption mechanism the experimental results were modeled by Pseudo first and Pseudo second order kinetic models. The equations for both models are given as under

$$\ln (q_e - q_t) = \ln (q_e) - K_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t} \quad (6)$$

Where K_1 (min^{-1}) and K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) represent the constants of reaction rate for Pseudo first and Pseudo second order models respectively. The plots between time (min) and $\ln(q_e - q_t)$ for pseudo first order and between time (min) and t/q_t for pseudo second order have been presented in (supplementary Fig. 2a and 2b (ODF@H₂O₂) and Fig. 2b and c (ODF@0₃)). The calculated parameters for these models are given in Table 2. It is clear from Table 2 that Pseudo second order gave best fit for the sorption of Cd on both ODF@H₂O₂ and ODF@0₃, exhibiting correlation coefficients (R^2) values 0.9997 and 0.9993 for ODF@H₂O₂ and ODF@0₃ respectively compared to Pseudo first order R^2 (0.6278 and 0.5674) respectively^{26,27}. Furthermore, the q_e values calculated from Pseudo second order (181.8 and 161.3 mg g^{-1}) for ODF@H₂O₂ and ODF@0₃ respectively at initial concentration 100 mg

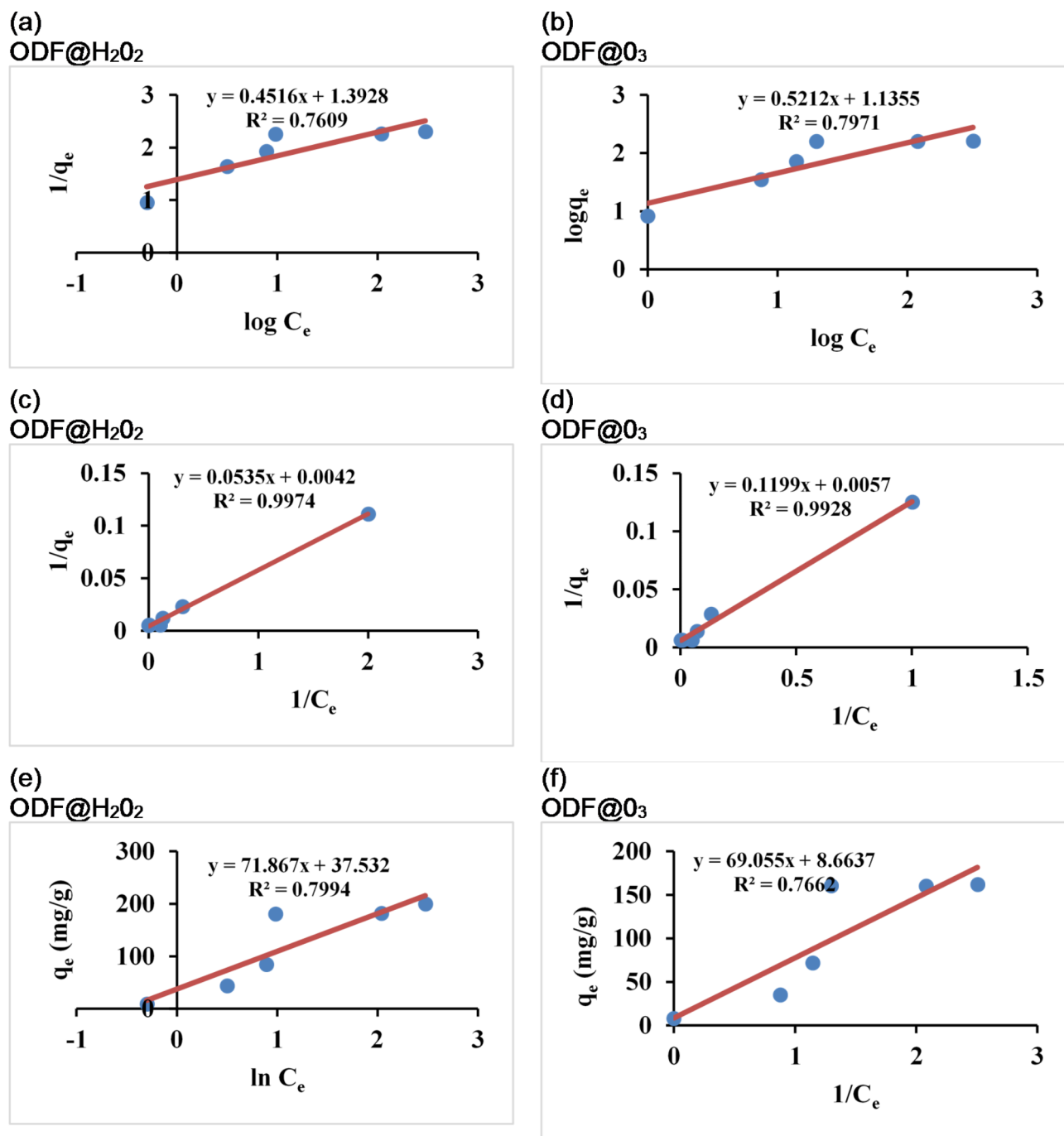


Fig. 5. Sorption isotherms for Freundlich (a and b) Langmuir (c and d) and Temkin (e and f) for the sorption of Cd on ODF@H₂O₂ and ODF@O₃ respectively.

Adsorbent	Freundlich					Langmuir					Temkin					
	<i>n</i>	<i>K_f</i> (mg g ⁻¹)	<i>R</i> ²	RMSE	<i>P</i> value	<i>Q_m</i> (mg g ⁻¹)	<i>b_L</i>	<i>R_L</i> (Lmg ⁻¹)	<i>R</i> ²	RMSE	<i>p</i> value	<i>b_T</i> (J mol ⁻¹)	<i>K_T</i> (L g ⁻¹)	<i>R</i> ²	RMSE	<i>p</i> value
ODF@H ₂ O ₂	2.21	4.03	0.761	0.28	0.005	238.09	0.08	0.33	0.997	0.002	0.02	34.49	1.68	0.799	40.8	0.22
ODF@O ₃	1.92	3.11	0.797	0.26	0.005	175.44	0.05	0.50	0.993	0.004	0.04	35.89	1.13	0.766	37.8	0.78

Table 1. Parameters for Freundlich, Langmuir and Temkin models.

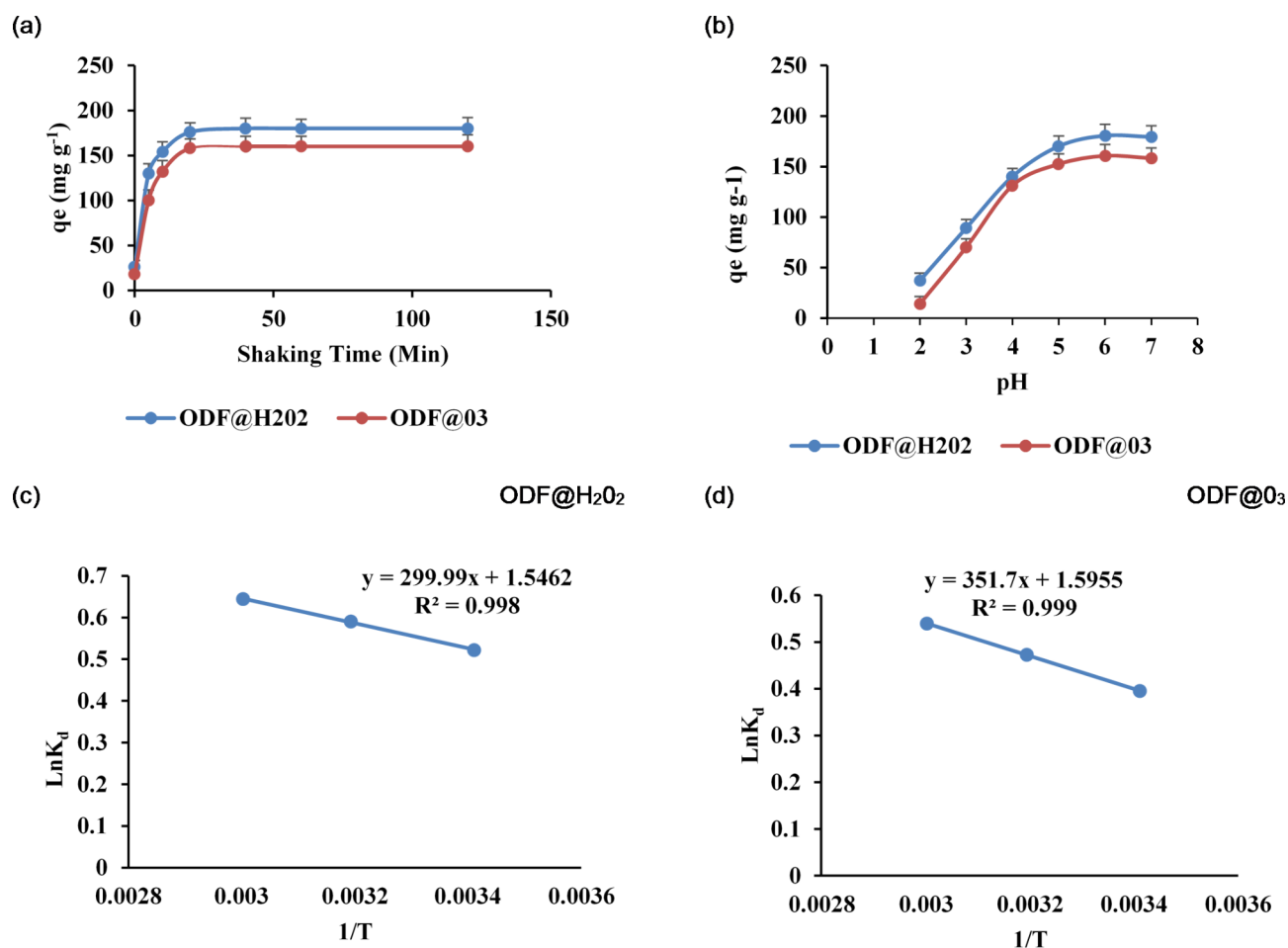


Fig. 6. Effect of different shaking times (a) and effect of different pH (b) on the equilibrium sorption capacity of Cd by ODF@H₂O₂ and ODF@O₃. The plot of (1/T) versus LnK_d for ODF@H₂O₂ (c) and ODF@O₃ (d).

Adsorbent	Pseudo first order					Pseudo second order				
	q _e (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²	RMSE	p value	q _e (mg g ⁻¹)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²	RMSE	p value
ODF@H ₂ O ₂	28.99	0.0003	0.627	1.65	0.01	181.8	0.005	0.999	0.004	0.06
ODF@O ₃	20.40	0.0004	0.567	1.73	0.01	161.3	0.006	0.999	0.007	0.07

Table 2. Calculated parameters for Pseudo first and Pseudo second order models.

L⁻¹ are very close to the experimental values i.e. (180.5 and 160.5 mg g⁻¹) respectively indicating best fitting of Pseudo second order model for the Cd sorption. These findings can be supported by previous published work for Pb sorption²² and Cd sorption²³. So, the Cd sorption kinetics in our study followed pseudo second order kinetics and is governed by chemical interactions between metal ions and the abundance of COOH groups present (Fig. 2) on the surfaces of ODF@H₂O₂ and ODF@O₃.

Effect of pH

The solution pH is an important factor affecting the sorption of Cd by ODF@H₂O₂ and ODF@O₃ sorbents. The surface electrical properties of ODF@H₂O₂ and ODF@O₃ as well as the forms of Cd in the solution can vary with the change in solution pH. To investigate the effect of different solution pH on the sorption of Cd by ODF@H₂O₂ and ODF@O₃, we changed the pH from 2 to 7 while other batch conditions were kept constant as in previous sections and the results are shown in Fig. 6b. The minimum Cd sorption capacities were recorded at pH 2 i.e. 37 and 14 mg g⁻¹ by ODF@H₂O₂ and ODF@O₃ respectively. As at low pH the surface of both sorbents is positively charged and Cd is least sorbed on these surfaces due to electrostatic repulsion²⁸. A sharp increase in the sorption capacities was noted with increasing solution pH and maximum sorption capacities (180.5 and 160.5 mg kg⁻¹) for both ODF@H₂O₂ and ODF@O₃ were recorded at Ph 6. When we increase the pH the surface functional groups of both ODF@H₂O₂ and ODF@O₃ are deprotonated making their surfaces gradually negatively charged

and at high pH due to electrostatic attraction the positively charged Cd ions are more sorbed on the surfaces of both sorbents. These findings can be supported by^{23,26}.

Sorption thermodynamics

To investigate the effect of different temperatures on the sorption of Cd ions from contaminated water by ODF@H₂O₂ and ODF@O₃ we conducted a thermodynamic study at three different temperatures i.e. 293.15, 313.15 and 333.15 K under optimized pH conditions. For both sorbents a significant increase in equilibrium sorption capacities was recorded with increasing temperature. The thermodynamic parameters like Entropy change, Enthalpy change, and Gibbs free energy can provide the better information regarding spontaneity and thermodynamic changes during sorption processes²⁹. The equations being used are as under

$$\Delta G^{\circ} = -RT \ln K_d \quad (7)$$

$$\Delta G = \Delta H^{\circ} - T \Delta S^{\circ} \quad (8)$$

Where, ΔS° is the entropy change, ΔH° is the enthalpy change, ΔG° represents the Gibbs free energy related to sorption process, K_d is the distribution coefficient calculated by dividing equilibrium sorption capacity (Q_e) over initial Cd concentration (C°). The calculated thermodynamic parameters have been presented in Table 3.

The plot of (1/T) versus $\ln K_d$ for both sorbents ODF@H₂O₂ and ODF@O₃ have been shown in Fig. 6c and d. The ΔH° and ΔS° were calculated from the slope and intercept respectively Table 3. As we increased the temperature the distribution ratio K_d was also increased. A direct proportion between K_d values and temperature indicates that the sorption process is endothermic³⁰. We obtained negative values of Gibbs free energy (ΔG°) at all temperatures indicating the spontaneous sorption of Cd²⁺ ions onto both ODF@H₂O₂ and ODF@O₃. Furthermore, the ΔG° negative values decreased with increasing temperature which suggests that at high temperatures a stronger adsorptive force exists between sorbents and Cd²⁺ metal cations. These findings can be supported by²². The positive values of entropy change (ΔS°) confirmed the structural changes in sorbents ODF@H₂O₂ and ODF@O₃ and affinity of both sorbents for Cd²⁺ metal cations^{22,30}. The positive values of entropy change ΔS° also confirmed the occurrence of ion replacement reaction and enhanced randomness at solid-solution interface during sorption of Cd²⁺ onto ODF@H₂O₂ and ODF@O₃. Gubbuk, (2011) results for the sorption of Cu²⁺ ions onto sporopollenin surface supports our findings for Cd²⁺ ions sorption on ODF@H₂O₂ and ODF@O₃³¹.

Regeneration study

A regeneration study was conducted to check the recycling ability of both ODF@H₂O₂ and ODF@O₃ sorbents. The results of the regeneration study have been presented in Fig. 7. which shows that both sorbents exhibit minimal changes in the sorption efficiency during all 10 cycles. The sorbents ODF@H₂O₂ and ODF@O₃ gave adsorption efficiency of 99 and 96% after 1 cycle of desorption. Whereas, after 10 recycles the ODF@H₂O₂ and ODF@O₃ sorbents gave sorption efficiencies of 90 and 84% respectively. The efficient regeneration abilities of both sorbents indicate their suitability for their practical applications in wastewater treatment. Moreover, the cost of sorbent preparation from waste denim is nominal. The waste denim was collected from the local waste Collection Centre for free of cost. The treatment costs include hydrogen peroxide, sodium hydroxide and ozone treatment which is just a few cents per kilogram of sorbent.

Conclusion

The present research work is designed to convert the challenge of landfill with waste denim into an opportunity to address the problem of heavy metal contamination of water. The waste denim fabric was oxidized with H₂O₂ and ozone under alkaline conditions using two simple techniques yielding ODF@H₂O₂ and ODF@O₃. The spectroscopic and microscopic analysis confirmed the generation of new carboxylic groups on the surfaces and complete change in the surface morphology of both functionalized sorbents. The sorption efficiency of both sorbents was evaluated in a batch laboratory experiment. Both sorbents showed excellent sorption capacities for Cd from contaminated water. The ODF@H₂O₂ sorbent was found to be more effective by giving 36% more sorption capacity compared to ODF@O₃. The Langmuir and pseudo second order model best fitted with the experimental sorption results. The sorption isotherm, sorption kinetics and sorption thermodynamics revealed the sorption process as spontaneous and endothermic with chemisorption as a dominant process governing the sorption process. The present work addresses a practical approach as both sorbents can effectively be implied for wastewater treatment due to having efficient sorption capacities and recycling ability of 90% even after 10

Sorbents	Temperature (K)	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
ODF@H ₂ O ₂	293.15	-1272.8605	2494.12	12.85
	313.15	-1529.8605		
	333.15	-1786.8605		
ODF@O ₃	293.15	-964.60075	2924.03	13.27
	313.15	-1229.90075		
	333.15	-1495.20075		

Table 3. Thermodynamic parameters for the sorption of cd on ODF@H₂O₂ and ODF@O₃.

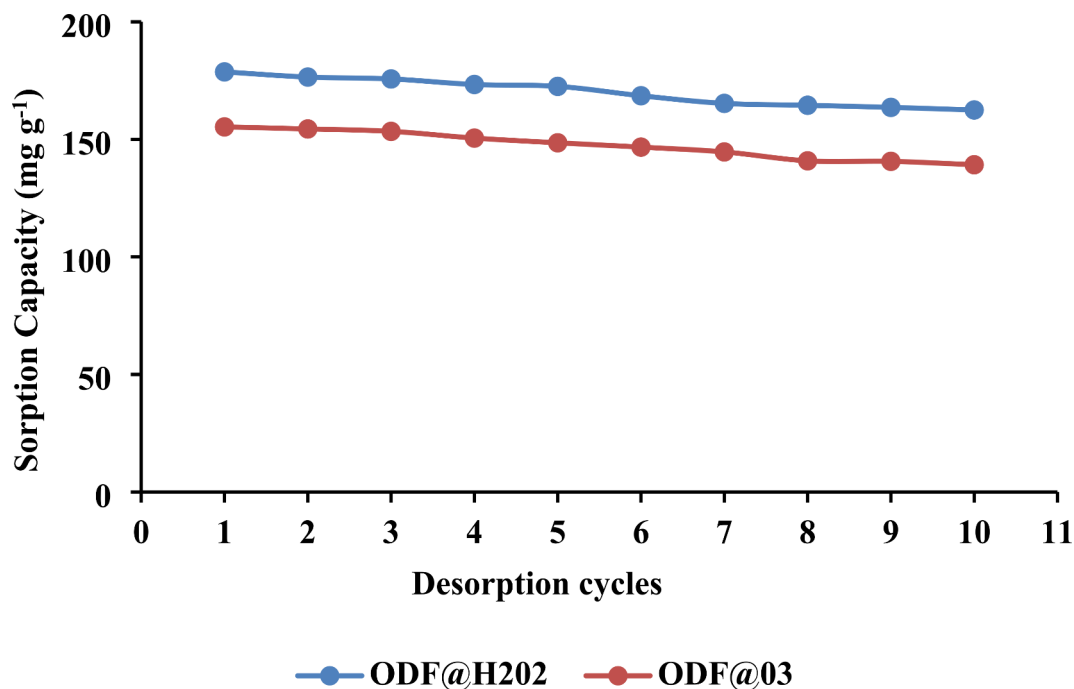


Fig. 7. Desorption cycles of both sorbents.

recycles. Furthermore, our findings present a cost-effective and very simple technique where a waste is converted into a sustainable material having strong potential to address heavy metal contamination of water with minimum environmental impacts.

Materials and methods

Chemicals and materials

Hydrogen peroxide, sodium hydroxide (NaOH), sodium meta bisulfite and cadmium nitrate were procured from Merck Germany and were of analytical grade. The Cd stock and sub stock solutions were prepared in deionized water. The waste denim fabric was collected from disposed garments. All the glassware, centrifuge tubes, and laboratory consumables used in the experiment were dipped in nitric acid solution (20%) and then thoroughly washed three times with deionized water before use for quality assurance.

Preparation of sorbent

The oxidation of denim fabric with hydrogen peroxide (H₂O₂) (named as ODF@H₂O₂) was done in the presence of a base in a beaker with stirrer and thermometer. A 10 cm² piece of denim fabric was treated with different levels of H₂O₂ (5, 25, 50, 100, 200 and 400 ml/L) with 6 g of NaOH (sodium hydroxide) dissolved in distilled water. Continuous stirring was done on medium flame using Bunsen burner. When the temperature of the solution reached 85 °C the flame was slowed down, and further stirring was done for 30 min. After that, the fabric was removed and rinsed with distilled water. After washing it was placed on aluminum foil and dried in oven at 80 °C for 15 min.

A second piece of fabric was treated with ozone to generate carboxylic acid groups (named as ODF@O₃). For this, an A4 size piece of moistened fabric was placed in the ozone treatment machine from Tonello (denim fading machine) that contains (O₃ 48 g/h with 100% moisture) in air. Five samples of fabrics were run separately on ozonation machine with different spinning times (15, 30, 45, 60 and 75 min). To neutralize the fabric, sodium meta bisulfite (2 g/L) was used for 8 min. Adjusted the rotation at 27 rpm for 4 min. Then the first Drain was done by filling water 5 L/kg for 2 min. After the second drain, spinning was done at 200 rpm for 4 min, and then fabric was taken out from machine. The fabric was Squeezed and placed on aluminum foil and dried in the oven at 80 °C for 15 min. the schematics for the preparation of both sorbents has been presented in the Fig. 8a and b.

Batch sorption experiment

A batch sorption experiment was conducted in the laboratory to optimize the different factors affecting Cd sorption on ODF@H₂O₂ and ODF@O₃. A stock solution (1000 ppm) of Cd was prepared in deionized water using Cd (NO₃)₂·4H₂O from which further sub stocks of 5, 25, 50, 100, 200, and 400 ppm concentrations were prepared. A sorbent sample of 0.01 g of both ODF@H₂O₂ and ODF@O₃ was inserted in the 20 ml Cd solutions of different concentrations as stated above in 50 ml centrifuge tubes. The centrifuge tubes were shaken on an orbital shaker for 1 h at 180 rpm at 25 °C. Then the sorbent material was removed from the solution and the solution mixture was filtered by filter paper. The atomic absorption spectrophotometer (AAS) was used to examine the remaining metal ion concentration after sorption. The sorption experiment was repeated 3 times and results

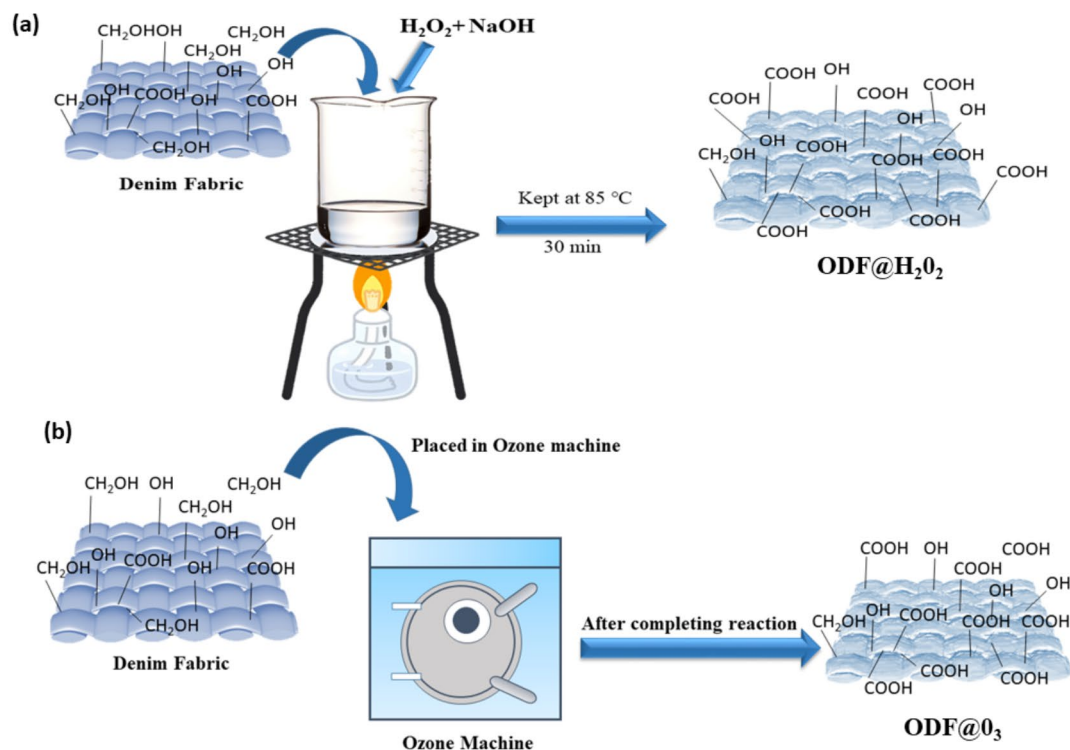


Fig. 8. Schematic diagram for the preparation of sorbents.

were taken as an average of three replicates. The sorption trial was further performed using different shaking times of (0, 5, 10, 20, 40, 60, 120) min, different pH (2, 3, 4, 5, 6, and 7) different temperatures (293.15, 313.15 333.15) K while keeping the other batch conditions constant. The experimental sorption capacities (mg g^{-1}) and metal removal % were calculated using the following Eq.

$$q_e = \left(\frac{C_o - C_e}{m} \right) V \quad (9)$$

$$R = \left(\frac{C_o - C_e}{C_o} \right) 100 \quad (10)$$

Where C_o is the initial concentration and C_e is the equilibrium concentration of the cadmium, V is the volume in (L) and m is the quantity of sorbent in (g). The experimental results obtained allowed the determination of the sorption isotherm in the system $Q = f(C_e)$ and Cd removal curves in the system of $R = f(C_o)$.

Regeneration study

To check the sustainability of the two prepared sorbents a series of desorption steps were conducted using the same treated fabrics for all cycles. The sorbents were treated with nitric acid to remove Cd ions from fabric. For this purpose, both sorbents removed from batch study from 100 ppm Cd solution were thoroughly washed with deionized water and placed in 15 ml HNO_3 (1 mol/L) for 1 h. After that the sorbents were dried in oven and reused to check the sorption capacity in new 100 ppm Cd solution. The batch conditions were kept the same as mentioned above. This desorption process was repeated for 10 cycles using the same sorbents and sorption capacity was calculated for each cycle.

Data availability

The datasets used or analyzed during this research work are available from the corresponding author upon request.

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H.A. and M.A. : Writing- Original draft preparation, conceptualization, conducted research, M.R. and U.R. : Methodology, Software. Data curation, validation, S.A., A.R. and J.W. H.Y. Visualization, Investigation, validation.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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