

Producing bacterial nano-cellulose and keratin from wastes to synthesize keratin/cellulose nanobiocomposite for removal of dyes and heavy metal ions from waters and wastewaters

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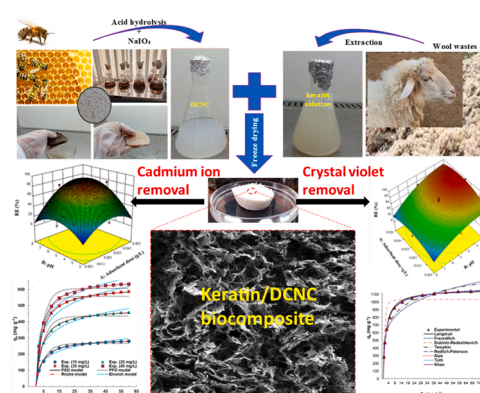
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HIGHLIGHTS

- Beeswax recycling wastewater used as a culture medium to produce bacterial cellulose (BC).
- Keratin/DCNC was fabricated from dialdehyde cellulose nanocrystal (DCNC) and wool keratin.
- The biocomposite was recruited to remove Cd^{+2} and Crystal violet from water media.
- A comprehensive study was carried out on the all aspects of adsorption processes.
- Keratin/DCNC had a high potential for exploitation in treatment of waters and wastewaters.

GRAPHICAL ABSTRACT



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ABSTRACT

Considerable emphasis has been devoted to fabrication of bio-nanocomposites from natural waste resources and recruiting them for low-cost removal of pollutants from water resources. In this research, using dialdehyde cellulose nanocrystal (DCNC) and wool keratin, a highly-beneficial and recyclable biocomposite (Keratin/DCNC) was triumphantly fabricated to remove Cd^{+2} and Crystal violet from water media. Beeswax recycling wastewater, as a culture medium, was exploited to produce bacterial cellulose (BC) at the lowest plausible cost, and keratin was extracted from wool wastes. The adsorption of the adsorbates was optimized and a complete study was carried out on the kinetic, isotherm and thermodynamic aspects of adsorption processes. The adsorbent showed excellent recyclability and maximum adsorption capacity was found to be 695.56 and 1166.67 mg/g for Cd^{+2}

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and Crystal violet, respectively. The results proved the favorability of the processes and indicated that Keratin/DCNC has a high potential for being exploited for treatment of waters and wastewaters.

1. Introduction

Beset with the lack of drinking water, problems associated with the quality of water are of the most important issues of world in the 21st century. Day by day, deterioration of the quality of the water resources is escalating and water pollution has attracted a lot of heed globally, because of increasing trend of industrialization, unplanned urbanization, and endless anthropogenic activities in recent decades. Both organic and inorganic pollutants are emitted into environment from a lot of industries like refining, textile, fertilizer, leather, dyeing, battery, mining, metallurgical, chemical, and many other industries [1]. These pollutions seriously hinder the sustainability and continuity in the development of societies. Heavy metals and organic dyes are two main categories of such pollutions.

The term of heavy metals usually is applied to any metal element that its density exceeds 5 g/cm³ and is toxic or lethal even at low level, therefore a large number of elements, including Cd, Ni, As, Pb, Cu, Hg and Zn, fall into this category. Also, more than 10,000 varieties of dye types are exploited by a large number of industries for coloring. Particularly, during production and dyeing processes, almost twelve percent of dye is lost in the textile industry, and twenty percent of the lost dye enter into water streams as industrial waste [2]. Many dyes and heavy metals threaten the human health and aquatic ecosystems due to non-biodegradable, toxic, carcinogenic, mutagenic and possibly teratogenic character [3]. Consequently, it is of remarkable importance and greatly demanded to eliminate metal ions and dyes from wastewaters.

A large number of technologies, like adsorption, ion-exchange, electrocoagulation, coagulation, ultrafiltration, reverse osmosis [4], chemical precipitation [5], electrodialysis and electrolysis [6], ozonation, photocatalytic degradation, flocculation [7] have been exploited to eliminate metal ions and dyes from aqueous media. Nevertheless, most processes are intensively energy-consuming and uneconomical or impossible, along with low removal effectiveness at high metal concentrations, long processing time and collateral generation of toxic residues which preclude their commercialization [8]. Among various methods mentioned above, adsorption process is the most suitable technology owing to its advantages, like flexibility, simplicity, high uptake capacity, reusability, being cost-effective, easiness of operating, and less consuming of chemicals [9].

Considering the concept of sustainability for the preparation and introduction of new adsorbents, besides being environmental-friendly, cheapness is a principal factor. Therefore, in the construction of efficient adsorbents, usage of waste resources with low cost and high availability has emerged as a prominent method to reduce water and wastewater pollutants [10]. Amongst the utilized adsorbents in the literature, sorbents that are obtained from waste sources or biomasses have attracted a great deal of heed, owing to their easy processing, cost-effectiveness, and abundance, such as straw, rice husk, fly ash, Aloe vera waste biomass and so on. Particularly, solid wastes have been recruited for fabrication of a great number of low-cost sorbents which have been assessed for wastewaters and waters, and some of them have found commercial value. In recent years, among such adsorbents, keratinous waste materials have received great consideration as raw materials from which adequate bioadsorbents for waters and air treatments can be derived, owing to their special traits in terms of capability to adsorb heavy metal ions and other toxic pollutants [11].

Keratin is the principal constituent of wool, hair, feather, horn and nail, and therefore it is one of the most superabundant natural proteins, regarded as one of the most plentiful non-food proteins. Keratin has the potentiality of being influential in the elimination of dyes and heavy metals ions, due to some features like, having good stability, insolubility

in water, having intricate network, and having a surface full of functional moieties such as amino, hydroxyl, carboxyl, and sulfur which are attached to its molecules chain and can serve as adsorption site for both the dyes and heavy metals. Wool is one of the most remarkable sources of keratin. More than 5 million tons of this biomaterial is wasted by the textile industries and slaughterhouse units each year, which is a polluting biowaste for the environment. Because of the keratin content of up to 95% (w/w), wool is a pure and rich resource of intermediate filament protein which has a huge potentiality among the environment-friendly substances [12]. However, the necessity of breaking the disulfide bonds and destroying the keratin molecular structure during the extraction process lead to poor mechanical properties which are of the greatest obstacles for its recruitment in environmental remediations. Hence, many efforts have been focused on the ameliorating and improving of the mechanical features of keratin-based substances [13].

Blending with another polymer or chemical cross-linkage are two eminent strategies which have been used for augmentation of the mechanical properties of keratin-based materials. Usage of usual chemical cross-linkers like formaldehyde or glutaraldehyde brings about some troubles, since they are toxic or even carcinogenic and, thus, are not suitable for largescale applications. Another obstacle is dramatic shrinkage after crosslinking which leads to serious decline of the surface area and porosity of the produced adsorbents. Comparingly, blending with a synthetic polymer often results in confiscation of inherited biodegradability and biocompatibility of keratin product. Lately, composites based on reinforced biopolymers have been used with different types of reinforcing agents, which have received a lot of attention, because of their significant reinforcing effect and easy processing capability [14]. Nanofillers such as functionalized cellulose nanocrystal (CNC) as building blocks for reinforcing is one of the influential options which has the potential to be used for addressing the aforementioned problem. Functional CNC is subjected to an oxidation stage for introducing aldehyde moieties to the surface and formation of dialdehyde cellulose nanocrystals (DCNC). Crosslinking bond betwixt keratin and DCNC can raise mechanical properties of the adsorbent and lead to shape integrity higher stability in water [15].

One of the superabundant biopolymers in the biosphere is cellulose which is principally produced by plants. Nevertheless, separation and purification processes needed for obtaining cellulose from plants need harsh agents like acidic and alkali compounds, for elimination of lignin and hemicellulose structures. Hence, production of purified cellulose from plants is an energy- and water-consuming process which is intensive-demanding for chemicals which lead environmental contamination and damaging the native cellulose structure [16]. Alternatively, highly-pure cellulose with a large degree of polymerization, great tensile strength, and high crystallinity can be produced by employing many bacteria, especially those belonged to *Gluconacetobacter* genus, which deliver a very strange form of cellulose with unique properties, mechanically and structurally. In addition, bacterial cellulose has high water retaining capacity, higher degrees of water adsorption, and good biodegradability, biocompatibility, biological adaptability, and renewability. Therefore, these unique properties result in making this material attractive for an ample range of applications, like recruitment as the ideal nanofiller in polymer nanocomposites [17]. Compared with cellulose obtained from plants, bacterial cellulose (BC) is considered to be free of impurities like lignin and hemicellulose molecules, which are challenging and tedious when it comes to being removed [18]. Nevertheless, the potential needed for BC production, industrialization, and its commercialization at large-scale is a significant defiance, because of high cost of fermentation media. To overcome this problem, in this context, researcher have developed a desire to exploit low-cost

substrates and waste by-products of different industries for BC production [19].

This study has adopted a facile, low-cost, and environmentally-friendly strategy to fabricate a robust composite nanoadsorbent by incorporating wool keratin into bacterial cellulose. First, as a novel agro-industrial waste, beeswax recycling effluent was employed for cost-effective production of a high-value biomaterial, i.e. BC, using *Komagataeibacter xylinus* BPR 2001. CNC was prepared by acid hydrolysis of BC. DCNC, as a cross-linking and reinforcing agent, was prepared from CNC with sodium periodate as an oxidant and, afterward, it was incorporated into keratin sponge to obtain a biocomposite (Keratin/DCNC) with a high performance for organic dye and heavy metals ions elimination from water media. Then, as the model dye and metal ion, adsorption of Crystal violet and cadmium ion on Keratin/DCNC adsorbent was optimized by face-centered central composite design (FCCCD) method to vouchsafe irresistible advantages like saving time, efforts, and resources. Keratin/DCNC adsorbent scrutinized from some aspects such as re-generatability and recyclability, as well as shape integrity which is imperative for its high adsorption capacities. Also, besides to optimizing physicochemical factors, kinetics thermodynamic, and equilibrium properties of adsorption processes were brought underneath close and comprehensive evaluation.

2. Materials and methods

2.1. Materials

Samples of waste wool fibers with an average diameter of 21 μm as keratin source were provided by local farm in Rivash, Khorasan-e Razavi province, Iran. Strain of *Komagataeibacter xylinus* BPR 2001 (Japanese culture collection) were obtained from the Malek-e-Ashtar university of technology, Tehran, Iran. Beeswax recycling effluent as the culture medium were supplied by beeswax recycling industrial unit in Kashmar, Iran. Urea, sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), sodium dodecyl sulfate (SDS), sodium periodate (NaIO_4), sulfuric acid (98%), sodium hydroxide and Crystal violet ($\text{C}_{25}\text{N}_3\text{H}_{30}\text{Cl}$) were of high purity and were supplied by Merck (Germany). Cadmium nitrate was purchased from Fluka, USA. Dialysis tubing (molecular cut of 12–14 kDa) were supplied by Sigma Aldrich.

2.2. Fabrication of Keratin/DCNC adsorbent

2.2.1. Extraction of keratin

To retrieve the fatty residues and other impurities a Soxhlet extraction set was employed for cleaning wool fibers, using an acetone/ethanol mixture 1:1 (v/v) for 48 h. After that, the samples were washed with deionized water, and subjected to a 12-h drying period at 100 °C, in an oven [20]. Keratin was extracted by a slightly-modified sulphitolysis reaction, according to the method proposed in literature [21], and its structural properties were compared with those obtained by other methods. Briefly, in the slightly-modified sulphitolysis, a 5-g portion of dried and defatted wool fibers was cut into snippets and immersed into 100-mL distilled water solution having urea (8.0 M), sodium dodecyl sulfate (SDS, 0.1 M), and sodium metabisulphite (0.5 M), with constant stirring at 65 °C for 12 h. Afterward, the filtered mixture was subjected dialyzing against deionized water, exploiting a dialysis tube (molecular weight cut off 12,000–14,000 Da) for a 3-day period at ambient temperature, while the deionized water was replaced 6 times a day. Eventually, the mixture was lyophilized to generate a powdered keratin extract.

2.2.2. BC production and purification

In this research, the wastewater obtained from the refining and melting of beeswax without adding any other compounds was used as the culture medium of *Komagataeibacter xylinus* BPR 2001 for production of bacterial cellulose, as an alternative to standard Hestrin–Schramm

(HS) medium. The traditional Hestrin–Schramm (HS) culture media which contains 2% (w/v) glucose, 0.27% (w/v) Na_2HPO_4 , 0.115% (w/v) citric acid, and 0.5% (w/v) yeast extract and is exploited as standard medium for producing BC. BC production by *Komagataeibacter xylinus* BPR 2001 in beeswax recycling effluent and that in standard Hestrin–Schramm (HS) medium were compared.

Beeswax is a complex mixture of lipophilic nature composed of fatty acid esters, hydrocarbons, alcohols, free fatty acids and other minor substances [22]. It is a building material for the construction of comb cells, where nectar, honey and pollen are stored. The principal application of beeswax is the production of comb foundation, which is used again in the hive. Beeswax recovery is achieved by melting old, worn and ineffective combs, and the easiest route to homogenize and purify the beeswax samples is melting by boiling water which causes comb impurities including pollen, propolis, nectar, honey and other hive materials to enter the water [23]. The resulting effluent, which contains the above compounds, is released into the environment as wastewater, and its use has not been reported so far. The results obtained for the synthesis of BC in beeswax recycling wastewater (2.60 g/L) was approximately commensurate with that obtained in the HS medium (2.73 g/L). Considering that if pure carbon and nitrogen resources like glucose, peptone and yeast extract are used, the production of BC will be very expensive. Therefore, beeswax recycling wastewater can be used as a suitable and cost-free alternative culture medium for bacterial cellulose production.

Being sure of the efficiency of the novel culture media (beeswax recycling effluent), it was pre-treated by centrifugation at 12,000 rpm for 10 min to isolate solid components and the supernatant was collected. This waste by-product was exploited as culture medium without adding any supplementations. Each media was brought to pH=6 with NaOH or HCl. Prior to inoculation, the medium was autoclaved at 121 °C for 20-min period. After that, ethanol 1% (v/v) was added to each medium, and then main cultures were grown in 100-mL media for a 14-day period at 28 °C in triplicate experiments, under static circumstances.

After the incubation time, all BC samples were taken away from the culture broths, rinsed with deionized water to eliminate the remained nutrition and contacted with NaOH solution (0.1 M) at 90 °C for a 1-h period to remove bacterial cells which were plausibly attached to each BC pellicle. The sample was rinsed repeatedly to gain the complete removal of the alkali, bringing the pH of pellicles to neutral. Then, a 12-h drying period (at 60 °C) was inflicted to the purified cellulose till reaches to a constant weight. The concentration of BC was presented as g/L (dried mass (g) of BC/ volume (L) of original medium) [24].

2.2.3. Preparation of DCNC

Dialdehyde cellulose nanocrystal (DCNC) was synthesized according to the reported literature with minor amelioration [25]. At first, a laboratory blender (at 6000 rpm) was recruited to decompose pellicles of BC for a 30-min period. Afterward, the fabricated BC, using beeswax refining effluent, was hydrolyzed by sulfuric acid to supply cellulose nanocrystal (CNC). Therefore, acid hydrolysis was conducted at 50 °C (40 min) by adding diluted sulfuric acid (50% w/w concentrated sulfuric acid (98%): deionized water) to cellulosic pastes (BC: dilute H_2SO_4 solution ratio was 1:50 g/mL), underneath mechanical agitation. The suspension was diluted by adding about 10 folds of deionized water to cease the reaction and rinsed till neutral condition, by successive centrifugation at 10,000 rpm for 10 min each stage. Finally, mechanical treatment with ultrasonic bath (Hielscher, UP200H, Germany) was performed for 10 min in a 40 kW power, and homogenizing at 18,000 rpm for 30 min was done. At the final stage, a predetermined amount of NaIO_4 was poured into CNC solution to result in the formation of aldehyde groups at C₂ and C₃ of the glucopyranose units of cellulose and preparation of dialdehyde cellulose nanocrystal (DCNC). For this purpose, 35 g wet CNC with 99.4% water content (dried weight 0.6 g) was blended with 100 mL distilled water having 0.8 g NaIO_4 in a conical flask underneath darkness and magnetic stirring at 300 rpm and 40 °C

for 2 h [26]. After that, the excess water was removed by centrifugation. Subsequently, the mixture was dialyzed versus deionized water, utilizing a dialysis tube (molecular weight cut off 12,000–14 000 Da) for a 3-day period at ambient temperature, while the deionized water replaced ever 6 h till achieving the neutrality and complete removing of residual reagents. Afterwards, the suspension was lyophilized utilizing freeze dryer.

2.2.4. Preparation of Keratin/DCNC composites

Keratin solution was extracted from wool waste using sulfitolysis method and, after production of DCNC from BC, a predefined magnitude of DCNC was poured into keratin solution. Then, the mixed solution was dispersed well and was frozen prior to putting into freeze-dryer. Finally, Keratin/DCNC nano bioadsorbent was obtained by crosslinking under 60 °C. In details, 0.25 g DCNC was poured into a 100-mL keratin solution (1 wt%) and the mixture was dispersed using ultrasonic processor. Afterward, the mixture was placed in – 80 °C refrigerator for a 2-h period before freeze-drying for a 36-h period of time. The freeze-dried composite was then put in a 60-°C oven for 2 h to afford the crosslinking reaction and obtaining the final biocomposite [15].

2.3. Characterization of Keratin/DCNC biocomposite

2.3.1. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectrum of the samples were scrutinized employing a FTIR instrument (AVATAR-370, Thermo Nicolet Corp, USA). All samples were appraised in the range of 400–4000 cm⁻¹ utilizing KBr pellets method at room temperature with a resolution of 4 cm⁻¹.

2.3.2. X-ray diffraction (XRD)

The Crystal structures of as-prepared samples were analyzed utilizing X-ray diffraction (GNR Explorer, Italy) instrument, with CuK α radiation wavelength (λ = 0.15418 nm), generated at a voltage of 40 kV and a filament emission of 30 mA. The crystallinity (Cr) and crystallite size (CrS) were computed according to X-ray diffraction measurements. The index of crystallinity (CrI) was computed by Segal's procedure, utilizing the relation presented below:

$$CrI(\%) = \frac{(I_{110} - I_{am})}{I_{110}} \times 100 \quad (1)$$

where I_{110} is the maximum intensity of diffraction of the (110) lattice peak (2 θ of 22° to 23°) and I_{am} is that of the amorphous material betwixt 2 θ of 18° to 19° where the intensity is minimum [27].

The crystal size was computed utilizing the Scherrer equation:

$$CrS = \frac{K\lambda}{FWHM\cos\theta} \quad (2)$$

where λ is the X-ray wavelength (0.154 nm), β is the Full Width at Half Maximum intensity (FWHM) in radians and θ is the angle of the diffraction peak of the crystalline phase (Bragg's angle), and K is the shape factor which is taken as 0.9.

2.3.3. FE-SEM imaging and EDS analyses

For field emission scanning electron microscopy (FE-SEM) imaging (LMU, TESCAN, BRANO-MIRA3, Czech Republic), the freeze-dried samples were coated with gold. EDS analyses was exploited to characterize the composition of prepared adsorbent.

2.4. Statistical optimization of adsorption of Cd²⁺ and Crystal violet

The process of adsorption of dye and heavy metal by Keratin/DCNC can be influenced by many operation factors like contact time, pH level, adsorbent dose, initial metal and dye concentration. Optimization of operational process variables is very imperative for the adsorption processes. Response surface methodology (RSM) is a collection of

statistical and mathematical techniques beneficial for modeling and has been repeatedly utilized for experimental design and optimization in recent years [28]. Optimization of the adsorption process of Cd²⁺ and Crystal violet has been attained by batch experiments to exploit from the highest removal efficiency. To reach this address, face-centered central composite design (FCCCD) was exploited to design the experiments and model the correlation betwixt the independent variables and the dependent variables (using Design-Expert software; Version 10). Four independent variables were elected, which have been tabulated in [Supplementary data \(Table 1S\)](#). These variables include adsorbent dosage, A (0.001–0.051 g/L); initial pH, B (2 – 8); contact time, C (10 – 150 min); salt (NaCl) concentration, D (0.001 – 0.051 g/L). The residual Crystal violet concentration was determined utilizing a UV/Vis spectrophotometer at 590 nm. The concentrations of Cd²⁺ ions were determined by ICP instrument (SPECTRO ARCOS system, model 76004555). In this study, four different models including Linear, 2FI, Quadratic and Cubic were investigated. Based on FCCCD design, the total number of experiments conducted were 30 runs including factorial points, axial points and replicates at the center point. The correlation betwixt response and independent variables was better estimated by quadratic equation. The goodness of the equation model was assessed by the analyses of variance (ANOVA) at 95% confidence level.

The removal efficiency (RE, %), the adsorption capacities at any time (q_t , mg/g) and the equilibrium adsorption capacities (q_e , mg/g) were respectively computed using the below relations:

$$RE\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3)$$

$$q_e = \frac{(C_0 - C_e)}{W} \times V \quad (4)$$

$$q_t = \frac{(C_0 - C_t)}{W} \times V \quad (5)$$

where C_0 (mg/L) is the initial concentration of Cd²⁺ or Crystal violet, C_t and C_e (mg/L) are respectively the Cd²⁺ or Crystal violet concentrations at a specified time t and at equilibrium, V (L) is the volumes of Cd²⁺ or Crystal violet solution, and w (g) is the weight of Keratin/DCNC biocomposite.

2.5. Isotherm modeling

The adsorption isotherms are invaluable curves that can quantitatively describe the adsorbate distribution betwixt the liquid and solid phases at a constant temperature, and the adsorption capacity depends on the adsorbent affinity for the solute [9]. Isothermal assessments of the adsorption processes are very useful for accurate investigating of the nature and mechanisms of adsorption of Cd²⁺ and Crystal violet from the aqueous solutions on to the surface of Keratin/DCNC. Such assessments were conducted batchwise by exploiting specified proportions of Keratin/DCNC biocomposite and the Cd²⁺ ion concentration, ranging from 5 to 100 mg/L, or Crystal violet concentration, ranging from 5 to 135 mg/L in the shaker incubator at pre-determined optimal conditions. Isotherm studies were carried out at three temperatures (288, 298, and 318 K). The isotherm models usually help in grasping the adsorption mechanisms and revealing the surface features and the adsorbent affinities. In this study, eight adsorption isotherms, including four two-parameter and four three-parameter ones were utilized.

2.6. Kinetic modeling

Analysis of adsorption rate data is essential for gaining insights into kinetics properties of adsorption processes and identifying the best circumstances for designing full-scale adsorption systems. Kinetics help researchers find the rate-controlling stage, by fitting experimental adsorption rate data with models equations [9]. Hence, kinetics of

adsorption was examined to optimize operating conditions for batch adsorption process, by applying different theoretical models such as pseudo-first-order (PFO), pseudo-second-order (PSO), Ritchie, and Elovich. In all these models, nonlinear form of equations was employed to identify the best kinetic model obeyed by the adsorption processes.

2.7. Thermodynamic studies

Assessments of energy changes during the adsorption processes are imperative in practical applications. Therefore, evaluations of thermodynamic parameters are essential and prominent components in adsorption research projects. Thermodynamic assessments do not just indicate the nature of adsorption processes, but also mainly inform us from the nature of the physical or chemical interactions. Though there are several approaches and theories for computing thermodynamic parameters in adsorbate-adsorbent systems, the usage of isotherm studies and equilibrium constants is the most correct way for approaching computation of thermodynamic parameters [10].

The following equations can be employed to derive a useful thermodynamic equilibrium constant [10]:

$$Adsorbate_{(aq)} + Adsorbent = Adsorbate.Adsorbent \quad (6)$$

The thermodynamic equilibrium constant (K_{eq}) can be computed from the following equation.

$$K_{eq} = \frac{a_{Adsorbate.Adsorbent,e}}{a_{Adsorbent,e} \times a_{Adsorbate,e}} \quad (7)$$

$$K_{eq} = \frac{\theta}{(1-\theta) \times a_{Adsorbate,e}} = \frac{\theta}{(1-\theta) \times \left(\frac{a_{Adsorbate,e}}{a}\right)} = \frac{\theta}{(1-\theta) \times \left(\frac{\gamma_e C_{Adsorbate,e}}{a}\right)} \quad (8)$$

In this relation, $\theta/(1-\theta)$ is replaceable with q_e/q_{max} from the Langmuir isotherms and the above relation is transformed to the below one:

$$K_{eq}^0 = \frac{K_{L,M} C_e}{(1 + K_{L,M} C_e) \times \left(\frac{\gamma_e C_e}{a}\right)} = \frac{K_{L,M} \times \left(1 \frac{mol}{L}\right)}{(1 + K_{L,M} C_e) \times \gamma_e} = K_{L,M} \times \left(1 \frac{mol}{L}\right) \quad (9)$$

where $K_{L,M}$ (L/mol) is the equilibrium constant of Langmuir model, and the amount of K_{eq}^0 (dimensionless) is numerically identical to the constant of Langmuir model. Therefore, to compute the Langmuir constants (in L/mol at different temperatures), equilibrium data at 288, 298 and 318 K were exploited, and thermodynamic parameters were computed by following form of the van't Hoff relation:

$$\ln(\text{numerical value of } K_{L,M}) = -\frac{\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (10)$$

ΔG° at each temperature was computed by the following equation:

$$\Delta G^\circ = -RT \ln(\text{numerical value of } K_{L,M}) \quad (11)$$

where ΔG° (kJ/mol) is the change in Gibbs energy of the processes, R (8.314 J/mol.K) is the universal gas constant, T (in Kelvin) is the temperature of aqueous phase, ΔH° (kJ/mol) is the enthalpy change, and ΔS° (J/mol.K) is the entropy change. The amounts of ΔH° and ΔS° were respectively measured from the intercept and slope of the plot of $\ln(K_{L,M} \times 1 \text{ L/mol})$ against $1/T$. Also, alternatively, ΔG° of the processes can be computed from the relation presented below.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

2.8. Recyclability and reusability studies

Recyclability and regeneration of Keratin/DCNC biocomposite were put into test by using 0.015-g and 0.03-g dosage of adsorbent, for Crystal violet and Cd^{+2} ion respectively. The nanobiocomposite was added into

a 200-mL portion of 15-mg/L Crystal violet dye solution (or cadmium ion solution) and stirred for 100 min, then the bioadsorbent was isolated from the solution. The desorption and regeneration of the utilized bioadsorbent was conducted by immersing the adsorbent into 50-mL portion of 1% v/v HCl solution, stirring for a 60-min period and subsequently washing with distilled water till neutrality to get ready for the next adsorption cycle. The regenerated bioadsorbent was applied for another adsorption experiment in the subsequent cycle.

3. Results and discussion

3.1. Synthesis and characterization of Keratin/DCNC biocomposite

In this work, an innovative waste biomass (nanobiadsorbent) was produced by wool keratin and bacterial cellulose (BC). The preparation process of the Keratin/DCNC bioadsorbent is schematically presented in [Supplementary data \(Fig. 1S\)](#).

3.1.1. FTIR studies

Fourier-transform infrared spectroscopy (FTIR) analyses were conducted to indicate the functional groups of different samples used in this study. The FTIR spectra of the CNC and DCNC are displayed in [Supplementary data \(Fig. 2Sa\)](#). FTIR spectroscopy was adopted to confirm the introduction of aldehyde groups in DCNC. Compared with CNC spectrum, a new absorption shoulder at around 1730 cm^{-1} emerged in the DCNC spectrum which is attributable to the stretching vibration of aldehyde group in DCNC. Such result indicates that the hydroxyl moieties in the CNC molecular chain where partially oxidized to aldehyde groups that could serve as crosslinking and reinforcing agent [29].

Various extraction routs and chemicals are used for extracting the keratin from wool, and they elicit impacts on the properties and the structure of extracted keratin [30]. The spectra of keratin samples usually display characteristic absorption bands ascribed to the peptide bonds ($-\text{CONH}$) and vibrations of peptide bonds called amide A, amide I, amide II and amide III bands. The amide A band, located at $3400\text{--}3300 \text{ cm}^{-1}$ range is assigned to N-H stretching, and usually is a wide bond, owing to the hydrogen bond formed betwixt the hydroxyl and amino functional moieties. Amide I band at $1700\text{--}1600 \text{ cm}^{-1}$ is principally associated with C=O stretching, amide II is caused by the N-H bending and C-N stretching vibrations with an absorption range of $1540\text{--}1520 \text{ cm}^{-1}$, and amide III band lies in the range of $1300\text{--}1220 \text{ cm}^{-1}$ and is related to the combination of C-N and C-O stretching vibrations along with N-H and O=C-N bending vibrations [31].

Although, finally, the keratin extracted by sulfitolysis method (KS) was used for fabrication of biocomposite in this study, one can see and compare the FTIR spectra of keratins samples examined for extraction of keratin ([Supplementary data; Fig. 2Sb](#)). [Fig. 2Sb](#) shows and compares the FTIR spectra of keratin extracted by sulfitolysis method (KS) and those extracted by alkali hydrolysis (KA) and reduction (KR) methods. As shown in this figure, absorption bands at aforementioned wave-number ranges have been appeared for all amides, i.e. A, I, II, III, indicating that all the examined methods for production of wool keratin samples do not affect the peptide bonds. However, because of the higher efficiency of keratin production by KS method, this method was recruited for producing keratin for fabrication of biocomposite.

[Fig. 2Sc](#) shows the FT-IR spectrum of the Keratin / DCNC nanobiadsorbent and compare it with those of its constituents, i.e. keratin (KS) and DCNC. Keratin/DCNC composite, which was formed by cross-linking of keratin and DCNC, possesses an FT-IR spectrum which is very similar to a spectrum that could obtained from integration of the spectra of these two compounds, confirming the presence of their functional groups in the composite nanobiocomposite. The vibrations of amide A, amide I, amide II, amide III in keratin (KS), which were discussed in detail in the FT-IR studies, were perfectly present and observed in the composite adsorbent. The aldehyde group (C=O bond) of DCNC located

at around 1730 cm^{-1} has disappeared and cannot be seen in the Keratin/DCNC composite due to covalent bond formation between KS and DCNC. Nevertheless, the band at $\sim 1660\text{ cm}^{-1}$ for imine stretching vibration ($\text{C}=\text{N}$, Schiff's base) cannot be identified, maybe because of being masked by the strong amide I band of KS. Additionally, the amide A band showed a blue shift upon the addition of DCNC, plausibly because of hydrogen bonding interaction between KS and DCNC. Therefore, hydrogen bonding and crosslinking occurred between KS and DCNC which definitely lead to improvement in the properties of the bio-composite adsorbent [32].

3.1.2. XRD studies

The crystal structures of wool and keratin extracted by different methods were scrutinized by X-ray diffractometry results which can be seen in both Fig. 1a and Supplementary data (Fig. 3S). In Fig. 1a, the results of characterization of the keratin sample acquired by sulfitolysis method has shown and compared with that of natural wool. For both regenerated natural wools, two crystalline structures are commonly observed. The structure of the α -helix is displayed at the peaks $2\theta = 9^\circ$ and 17.8° , while the β -sheet structure displays peaks at $2\theta = 9^\circ$ and 19° [20]. According to research conducted on the keratin structure, the peak at $2\theta = 9^\circ$ is always attributed to the α -helical structure, whereas the peak at $2\theta = 20^\circ$ always shows the presence of β -sheet structure [33]. In this work, the pattern obtained from XRD analysis for natural wool with characteristic diffraction peaks at $2\theta = 9.36^\circ$, $2\theta = 19.56^\circ$ shows the existence of both α -helix and β -sheet structures. In comparison to the natural wool, the XRD pattern for the keratin (KS) displayed a decline in intensity for the peak existing at $2\theta = 9^\circ$ and an enlargement of the peak at around 20° . This is due to the augmentation in the content of the β -sheet structure which occurs during the dissolving process (keratin extraction).

Bacterial cellulose (BC) is a semi-crystalline biopolymer principally composed of cellulose I, which contains polymorphs I_α and I_β in certain proportions, varying based on the production state [34]. It shows properties like tiny crystallite sizes, high I_α cellulose content, and high crystallinity. In this research, XRD analysis of BC produced in beeswax recycling effluent and DCNC was accomplished to appraise the crystallite structure of acquired cellulose and the changes in the crystallite nature of bacterial cellulose oxidation and transformation to DCNC (Fig. 1b). The XRD patterns of BC displayed three 2θ diffraction peaks at 14.5° , 16.7° , and 22.7° , which are commonly assigned to crystallographic planes of 100, 010 and 110 respectively. The existence of these three diffraction peaks characterizes cellulose type I_α (triclinic), which is common in bacterial cellulose, or (1–10), (110), and (200) planes of cellulose I_β [27]. The XRD patterns of BC produced in beeswax recycling effluent medium showed three principal diffraction peaks at $2\theta = 14.75^\circ$, 17.05° and 23° . The XRD patterns of DCNC showed three 2θ diffraction peaks at 14.78° , 16.93° , and 22.83° , is similar to cellulose produced in HS and beeswax recycling effluent media (cellulose type I), indicating the structure of cellulose has not changed during the oxidation process. However, the crystallite size (CrS nm) and crystallinity index (CrI%) for BC and DCNC were computed based on X-ray diffraction measurements, using Segal method and Scherrer's equation, respectively. The results of these calculations are summarized in Supplementary data (Table 2S).

Based on the data obtained from the XRD spectra, the crystallinity index and crystallite size of DCNC were calculated 82% and 5.35 nm, respectively, in which the crystallinity index vouchsafe a slight decrease, compared to CNC. On the other hand, altogether, crystallinity of BC slightly increases after acid hydrolysis reaction, which is assigned to deduction of the amorphous contents, because this area is more available to acid attack. Also, it should be noted that this effect is in competition with decrease elicited in the crystallinity of the DCNC structure which is brought about by opening of the glucopyranose ring during the oxidation process and DCNC formation [35].

3.1.3. FE-SEM and EDS analyses

The micrography of keratin (KS), BC, DCNC and keratin/DCNC bioadsorbent were assessed by field emission scanning electron microscopy (FE-SEM) and are exhibited in Fig. 1c–g, as well as in Supplementary data (Fig. 4S). The morphology of the extracted keratin by sulfitolysis method exhibited a porous structure with three-dimensional interconnections (Fig. 1c), owing to the freeze-drying operation [36]. Such a porous structure for the keratin seems to be beneficial for pollution absorption, since it makes interior surfaces of the solid support accessible for interaction with adsorbates.

The morphological features of the BC produced by *Komagataeibacter xylinus* BPR 2001 in beeswax recycling effluent medium and the obtained DCNC were also examined utilizing FE-SEM. The diameter of the nanofibers was computed with ImageJ software. The surface micrographs of BC and DCNC can be observed in Fig. 1d and f. FE-SEM images clearly show that these nanostructures were composed of network-like three-dimensional structure which has a high porosity. The BC nanofibers showed a diameter in the range of 18–35 nm, with average 28.70 ± 3.5 nm. The average fiber width of DCNC was estimated to be 17.17 ± 3.0 nm. The oxidation of nanocellulose is imperative to maintain a certain morphology and crystallinity for applying as a filler. Therefore, according to the morphology and crystallinity properties of DCNC, the obtained nanocrystals can be used as reinforcing and crosslinking nanofillers in Keratin/DCNC composite nanobioadsorbents [37].

It is identified that filler dispersion and interfacial interaction are the utmost important parameters that affects the eventual mechanical features of nanocomposite. For attaining better reinforcement effects, the nanofillers must be dispersed homogeneously in the base matrix to form a penetrating network-like structure [14]. FE-SEM images show that DCNC was homogeneously dispersed in the keratin matrix (Fig. 1e and g). Also, photo of Keratin/DCNC bioadsorbent approves excellent interconnected pore structure (Fig. 1h). The incorporated DCNC assists as a crosslinking and reinforcement agent and helps the integrity of the shape and improvement in mechanical properties of the bioadsorbent.

In addition, EDS analyses were performed on DCNC and Keratin/DCNC adsorbent (Fig. 1i and j). The EDS analyses exhibited the distinct peaks for C and oxygen elements with an atomic percentage of 62.32% and 37.68% for DCNC and 69.18% and 19.19% for Keratin/DCNC, respectively. The Au peak was originated from the gold coating of the samples for recording micrographs. The N and S peaks with an atomic percentage of 11.13% and 0.51%, respectively, were identified for Keratin/DCNC which could be assigned to the existence of keratin in the bioadsorbent structure. These peaks did not exist for DCNC.

3.1.4. pH_{ZPC} of biocomposite

The pH of zero-point of charges was measured, utilizing the drift procedure and following the course adopted elsewhere [10]. The obtained value for pH_{ZPC} of Keratin/DCNC biocomposite was 5.5.

3.2. FCCCD experimental design and optimization

The adsorption of Cd^{+2} ion and Crystal violet dye by Keratin/DCNC was appraised underneath diverse circumstances, based upon the experimental runs, as proposed by RSM (FCCCD) Methodology. According to the RSM, batchwise study of 30 experiments designed by FCCCD was conducted to verify the influence of four independent process variables, viz adsorbent dose (A), initial pH (B), contact time (C), and salt concentration (D) on the efficiencies of Crystal violet and Cd^{+2} ion removal (R%). The values of removal efficiency (R%) were calculated from obtained experimental results, given in Supplementary data (Tables 3S and 4S).

The results and fit summaries, given in Supplementary data (Tables 5S and 6S), were exploited to elect the optimal highly significant polynomial model out of linear, 2FI, quadratic and cubic models which were fitted with the FCCCD experimental data. The adequate model, which would bestow the experimental results close to the predicted

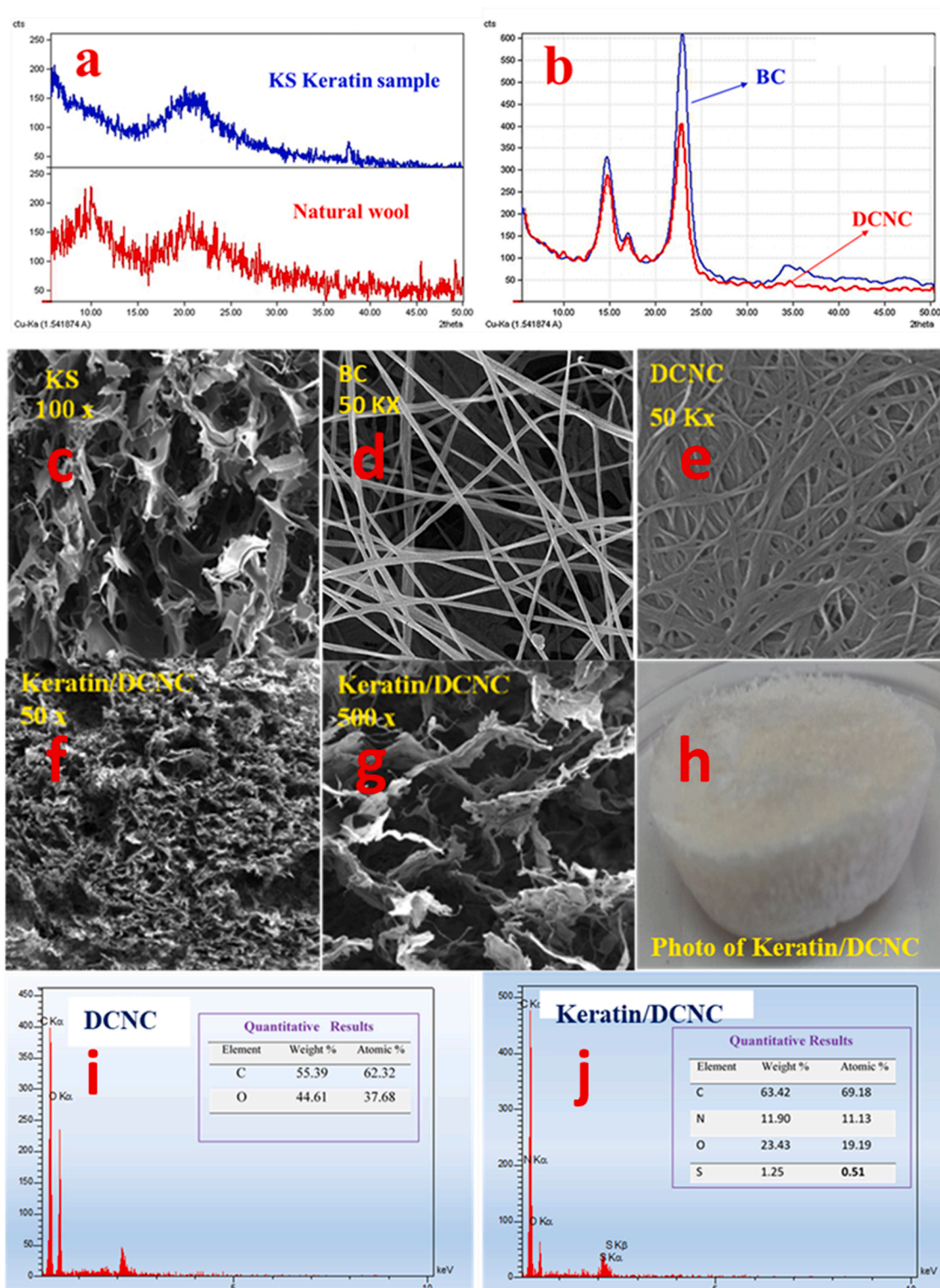


Fig. 1. X-ray diffraction patterns of keratin (KS) and natural wool (a) and X-ray diffraction patterns of BC and DCNC (b); FESEM images (different magnifications) of keratin (KS), BC, DCNC, and Keratin/DCNC; photo of Keratin/DCNC; and EDS analyses of DCNC and Keratin/DCNC biocomposite.

values by the model with the lowest residual values, was chosen based on an insignificant lack of fitness test and significant model parameters. The adequate model for removal of both Cd^{+2} ion and Crystal violet was the quadratic model, as reported in [Supplementary data \(Tables 5S and 6S\)](#). For Cd^{+2} removal, the quadratic model's summary statistics vouchsafed the highest adjusted (0.9554) and predicted (0.9068) R^2 values. Additionally, the quadratic model's summary statistics for

Crystal violet dye removal had the highest adjusted (0.9515) and predicted (0.8902) R^2 values. These results vouchsafe that the predicted- R^2 values are very close to adjusted R^2 ones, indicating that the mentioned model is important amid the experimental range of parameters.

The analysis of obtained experimental data was carried out by ANOVA to appraise the statistical significance of the FCCCD model, and the results were reported in [Supplementary data \(Tables 7S and 8S\)](#),

showing ANOVA data for the removal efficiency (RE%) of both studied pollutants. An F-value higher than the critical value in ANOVA implies that the model is significant for dependent variable. As can be seen in Tables 7S and 8S, F-values are 45.38 and 41.67 for removal efficiency of Cd^{+2} and Crystal violet, respectively, indicating that the model is significant. Also, the p-values and other factors proved the goodness-of-fit of quadratic model for adsorption of both Cd^{+2} and Crystal violet.

The adsorption processes of the studied pollutants are explained by the quadratic polynomial functions as follows:

$$\text{RE\% (cadmium)} = 70.44 + 18.77 \text{ A} + 15.18 \text{ B} - 0.10 \text{ C} - 3.10 \text{ D} + 13.46 \text{ AB} + 1.35 \text{ AC} - 1.04 \text{ CE} + 0.14 \text{ BCE} + 0.13 \text{ BD} + 0.30 \text{ CD} - 22.14 \text{ A}^2 - 26.93 \text{ B}^2 - 0.66 \text{ C}^2 + 1.50 \text{ D}^2$$

$$\text{RE\% (Crystal violet)} = 81.08 + 6.65 \text{ A} - 30.04 \text{ B} + 4.65 \text{ C} - 6.06 \text{ D} - 4.24 \text{ AB} - 0.22 \text{ AC} - 2.26 \text{ CE} - 3.65 \text{ BCE} + 1.83 \text{ BD} + 0.32 \text{ CD} - 18.27 \text{ A}^2 - 16.68 \text{ B}^2 - 11.09 \text{ C}^2 + 5.84 \text{ D}^2$$

Moreover, the model adequacy was assessed for Cd^{+2} and Crystal violet dye removal by data analysis, using normal probability plot (NPP) which is a critical aspect in assessing the model's adequacy. The normal % probability versus externally studentized residuals have been displayed in Fig. 2. These plots demonstrated that error variances were uniform, the points were not scattered too much, and the residuals of the model fitted are typically scattered along the standard distribution's diagonal line, proving that the model is appropriate and adequate.

The 3D plots were generated to demonstrate the correlation between the responses, i.e. Cd^{+2} or Crystal violet removal efficiency (%), and the four surveyed independent factors (Fig. 3 and Fig. 5S in Supplementary data). They were exploited to appraise changes in the responses and to discover the best levels of the independent variables for maximum Cd^{+2} or Crystal violet dye removal from solution.

Assessment by the software vouchsafed that, for maximal removal of Cd^{+2} , the optimum pH value was about pH 6.28. Keratin/DCNC adsorbent exhibited electric neutrality at pH about 5.5 which is the zero point of charge (pH_{ZPC}). At lower pHs, electrostatic repulsion was against the adsorption process, since lesser acidic pHs lead to protonation (positive charge) of adsorbent. At pH above pH_{ZPC} , deprotonation of the Keratin/DCNC bioadsorbent led to negative charge of the sorbent surface and, hence, electrostatic attraction can facilitate the sorption of Cd^{2+} ions. Also, increasing contact time increases the removal efficiency of Cd^{2+} , and a 72-min time was sufficient for optimum sorption. Investigation of effect of salt concentration vouchsafed that the presence of alkali metal ion, Na^+ , exhibited a little influence on the adsorption, by competing with Cd^{2+} adsorption ions and causing a reduction in the removal efficiency of Cd^{2+} ion. The salt concentration of 0.0036 g/L was an optimum value for obtaining the highest efficiency. In addition, the increase of adsorbent dose up to about 0.04 g/L increased the percentage of removal. The optimum values of pH, contact time, salt concentration, and biocomposite dosage for the dye adsorption were 2.39, 90 min, 0.02 g/L, and 0.028 g/L. Such results imply that the removal of the cationic dye proceeds via replacement of hydronium ions by the dye cations.

3.3. Kinetic studies

In this research, the experimental kinetic adsorption data were scrutinized by their fitting with four kinetic models including pseudo first order (PFO), pseudo second order (PSO), Ritchie second order and Elovich models to find the rate of adsorption as well as its limiting step and to scrutinize the mechanism engaged in adsorption processes. Fitness of kinetic data implies that the external diffusion or the internal diffusion is the rate controlling step, and such situations occur when the adsorbate concentration is very high and/or the number of active sites of the adsorbent is very low. On the other hand, obeying the PSO by the experimental kinetic data means that interaction between adsorption sites and adsorbate controls the process, and such mechanism happens

when the adsorbate concentration is low and/or there are abundant active sites on the adsorbent surface. Ritchie second order model was firstly exploited to model the kinetic data of gas adsorption on solid supports. As PSO model, Ritchie second order model also implies that the process is controlled by the adsorption of adsorbates on active sites. The Elovich model is an empirical equation with no definite physical meaning. It is usually exploited for modeling the chemisorption of gases onto solids. It assumes that the activation energy increases with adsorption time and the adsorbent surface is heterogeneous.

The goodness-of-fit of experimental findings with the exploited kinetic models was appraised, recruiting non-linear regressions and some statistical indices. The kinetic model recruited in the present work have been introduced in the following:

$$q_t = q_e \cdot [1 - \exp(-K_1 t)] \text{ PFO model} \quad (13)$$

$$q_t = \frac{q_e^2 \cdot K_2 \cdot t}{[K_2 \cdot (q_e) \cdot t + 1]} \text{ PSO model} \quad (14)$$

$$q_t = \frac{q_e K_R t}{1 + \frac{q_e K_R t}{K_R}} \text{ Ritchie model} \quad (15)$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \text{ Elovich model} \quad (16)$$

where q_t is the adsorption capacities (mg/g) at any time (t), K_1 (min^{-1}) and K_2 ($\text{g/mg} \cdot \text{min}$) are respectively the rate constants of pseudo-first order and pseudo-second order equations, q_e (mg/g) is the equilibrium adsorption capacities, K_R is the constants of Ritchie (min^{-1}), and α and β are the initial rate constant ($\text{mg/g} \cdot \text{min}$) and desorption constant during each experiment (mg/g) in Elovich model, respectively.

The relations used for the calculation of R^2 value and those used for computing different statistical indices are as follows:

$$R^2 = 1 - \frac{\sum (q_{e, \text{exp}} - q_{e, \text{cal}})^2}{\sum (q_{e, \text{exp}} - q_{e, \text{mean}})^2} \quad (17)$$

$$\chi^2 = \sum_{i=1}^N \left(\frac{(q_{e, \text{exp}} - q_{e, \text{cal}})^2}{q_{e, \text{cal}}} \right) \quad (18)$$

$$\text{HYBRID} = \frac{100}{N - P} \sum_{i=1}^N \left[\frac{q_{e, \text{exp}} - q_{e, \text{cal}}}{q_{e, \text{exp}}} \right] \quad (19)$$

$$\Delta q (\%) = 100 \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{q_{\text{exp}} - q_{\text{cal}}}{q_{\text{exp}}} \right)^2} \quad (20)$$

$$\text{ARE} (\%) = \frac{100}{N-1} \sum_{i=1}^N \left(\frac{q_{\text{exp}} - q_{\text{cal}}}{q_{\text{exp}}} \right)^2 \quad (21)$$

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N (q_{\text{exp}} - q_{\text{cal}})_i^2} \quad (22)$$

where $q_{e, \text{exp}}$ and $q_{e, \text{cal}}$ are the experimental adsorption capacities (mg/g) and the amount of the adsorption capacities anticipated by the models, respectively, and $q_{e, \text{mean}}$ is the average value of the experimental adsorption capacity (mg/g) for each pollutant.

Based on the lowness of statistical indices and highness of the correlation coefficients (R^2) the kinetics modeling for the Cd^{+2} ion and Crystal violet dye exhibited that a better fitting is attained with the Ritchie and pseudo-second-order kinetic models (Fig. 4a and b). In data analysis and comparison, if the experimental findings are analogous to the data anticipated by the model relation, the statistical indices are near to zero and the R^2 values are large and close to one, and vice versa. The parameters and statistical indices for all models were computed and

listed in Tables 1 and 2). Such results show that, at the studied conditions, the stage of interaction between adsorption active sites and adsorbate is the rate-controlling step. Also, these results reveals that the adsorbent has copious adsorption sites which are readily accessible for removal of the studied heavy metal and organic dye from the aqueous solutions.

3.4. Isotherm studies

The experimental equilibrium adsorption data were scrutinized by their fitting with four two-parameter isotherm models including Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and four three-parameter models including Sips, Toth, Redlich-Peterson and Khan. In fact, the three-parameter isotherm models were used to cover the shortcomings of the two-parameter isotherm models. The isotherm recruited in this study has been introduced in the following.

3.4.1. Langmuir isotherm model

The theoretical Langmuir equation was introduced utilizing the following assumptions: (1) a constant number of accessible sites are on the surface of adsorbent and all of them are energetically equivalent and independent; (2) when an adsorbate is adsorbed on a site, no further adsorbate can be adsorbed on that site; (3) adsorption is reversible; and (4) there is no interaction between adsorbate molecules which have occupied neighboring sites [38].

$$q_e = \frac{Q_{\max}^0 + K_L C_e}{1 + K_L C_e} \text{Langmuir model} \quad (23)$$

where $Q_{\max}^0$ (mg/g) represents the maximum saturated monolayer adsorption capacities of adsorbent (Keratin/DCNC), C_e (mg/L) represents the concentrations of adsorbates (dye or metal ion) at equilibrium, q_e (mg/g) represents the amount of adsorbates uptakes at equilibrium, and K_L (L/mg) is a constant related to the affinity between the biocomposite and pollutants.

3.4.2. Freundlich isotherm model

Freundlich adsorption isotherm model is one of the primary empirical mathematical relations utilized to explain equilibrium data and adsorption features for heterogeneous surfaces. This model is utilized to model non-ideal and reversible adsorption processes [39]. In contradiction with the Langmuir model, this model is not restricted to the formation of monolayer and its exploitation to the multilayer adsorption

is plausible with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. This isotherm is not able to explain the linearity range at too low levels nor the saturation effects at too high pollutant levels. Therefore, the saturation behavior of an adsorbent cannot be described by the Freundlich isotherm [40]. The nonlinear form of the Freundlich equation (Eq. (24)) was provided as follows [41].

$$q_e = K_f C_e^{\frac{1}{n}} \text{Freundlich model} \quad (24)$$

where K_f ($\text{mg}^{1-(1/n)} \cdot \text{L}^{1/n}/\text{g}$) represents the Freundlich constant, and n (dimensionless) represents the Freundlich intensity parameter, indicating the surface heterogeneities or the amount of the adsorption driving forces.

3.4.3. Dubinin-Radushkevich isotherm model

Dubinin-Radushkevich model generally is recruited for expressing the sorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. This model is a fundamental equation for the quantitative description of adsorption of subcritical vapors onto micropore solid adsorbents like activated carbon and synthetic zeolite. The nonlinear form of the Dubinin-Radushkevich equation (Eq. (25)) is expressed as follows [42]:

$$q_e = q_{DR} e^{-K_{DR} \mathcal{E}^2} \text{Dubinin-Radushkevich model} \quad (25)$$

$$\mathcal{E} = RT \left(1 + \frac{1}{C_e} \right) \quad (26)$$

where K_{DR} (mol^2/kJ^2) is a constant related to the adsorption energies or Dubinin-Radushkevich constant, $\mathcal{E}$ (kJ/mol) is the adsorption potential (Polanyi Potential energy), T (K) represents the absolute temperature, and R (J/mol.K) represents the universal gas constant.

3.4.4. Temkin isotherm model

The interactions of adsorbent-adsorbate and heat of surface adsorption were studied by Temkin and Pyzhev. Temkin isotherm model explains the behavior of adsorption on heterogeneous surfaces. This isothermal model is based on the following assumptions: (i) Due to the interactions between the adsorbent and the adsorbent, the adsorption heat of all molecules decreases linearly by covering the adsorbent surface. In fact, the adsorption heat (ΔH_{ads}), as a function of temperature, for all molecules existing in the layer declines linearly rather than

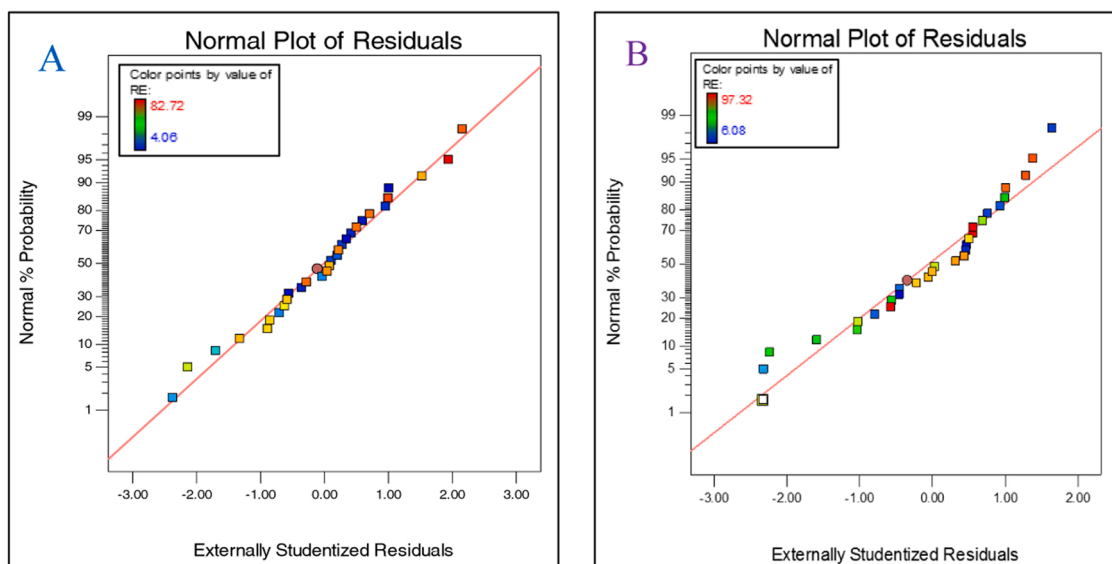


Fig. 2. Normal probability plot of externally studentized residuals of Cd^{+2} (A) and crystal violet dye (B).

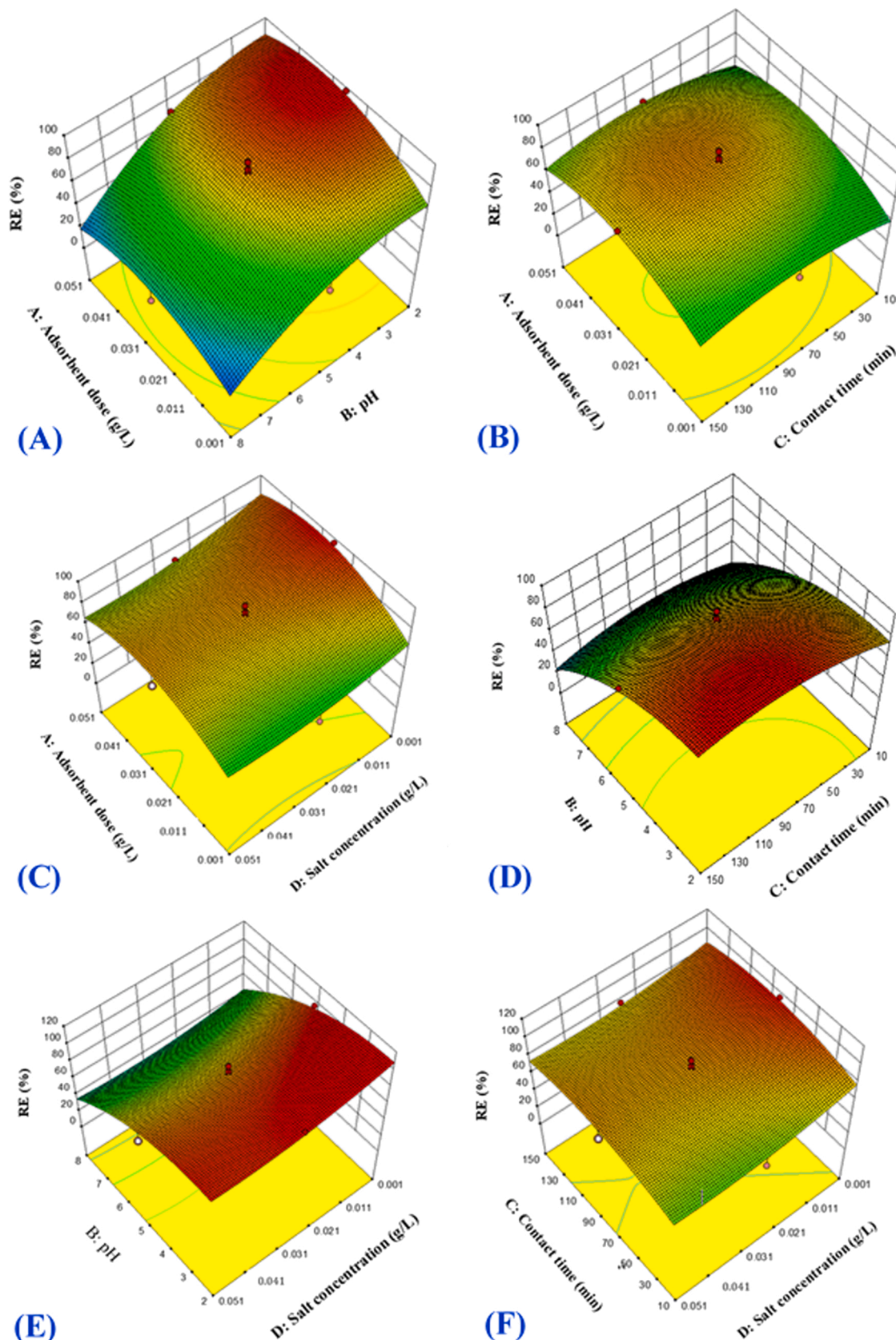


Fig. 3. The 3D plots of the correlation between the responses, Crystal violet removal, and the surveyed independent factors.

logarithmically because of the surface coverage augmentation. (iii) Adsorption is determined by the uniform distribution of bond energies until some of these energies are maximized [40,41].

The nonlinear form of Temkin equation (Eq. (27)) is expressed as follows [43]:

$$q_e = \frac{RT}{b} \left(\ln K_T C_e \right) \text{Temkin model} \quad (27)$$

where C_e (mg L⁻¹) represents the equilibrium concentrations, q_e (mg g⁻¹) represents the adsorption capacities at equilibrium, K_T (L g⁻¹) is the equilibrium binding constant corresponding to the maximum binding energy, b (kJ/mol) is the adsorption heat of surface and B is the Temkin constant related to the heat of adsorption ($B = RT/b$).

3.4.5. Sips isotherm model

Sips isotherm combines Langmuir and Freundlich relations [44]. At low adsorbates levels, this model is collapsed to Freundlich relation, whilst at high levels, it anticipates the monolayer adsorption capacities for pollutants, which are characteristic of the Langmuir relation.

Generally, the isotherm parameters are principally controlled by operating circumstances like changes in pH, temperature, and concentrations [45]. The nonlinear form of Sips equation (Eq. (28)) is expressed as follows [46]:

$$q_e = \frac{q_{\max} (K_S \cdot C_e)^{1/n}}{1 + (K_S \cdot C_e)^{1/n}} \text{Sips model} \quad (28)$$

where K_S (L/g) represents the Sips model constant and n represents the Sips equation exponent.

Toth isotherm model:

Toth isotherm model [47] is another empirical relation aiming to improve Langmuir isotherm fitting [48]. This model is adequate for describing the estimation of heterogeneous adsorption processes and brings about satisfaction when both the low and high concentrations of adsorbate are brought into account. This model presupposes that an asymmetrical quasi-Gaussian distribution of energy is at work, in which most sites have less adsorption energy than the mean or peak value [41, 49]. The nonlinear form of Toth equation can be represented as the

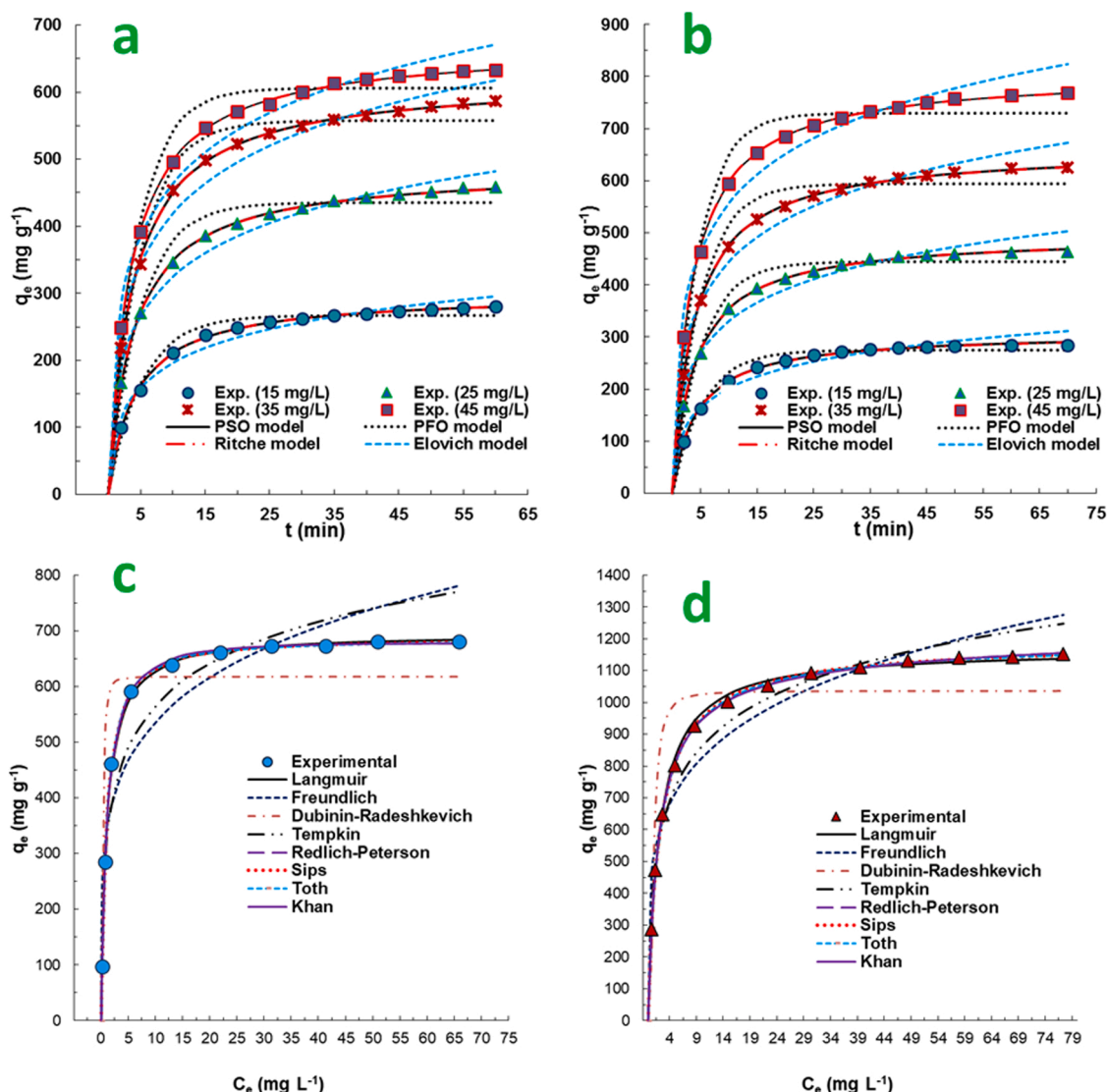


Fig. 4. Kinetic plots for adsorption Cd^{2+} (a) and Crystal violet (b) onto Keratin/DCNC bioadsorbent at ambient temperature, and isothermal plots for adsorption Cd^{2+} (c) and Crystal violet (d) onto Keratin/DCNC bioadsorbent at ambient temperature. Both kinetic and isothermal experiments were conducted at optimum values of pH (6.3 for Cd^{2+} and 2.4 for CV) and NaCl concentration (3.6 mg/L for Cd^{2+} and 20.0 mg/L for CV), using 0.01 g adsorbent and a 200-mL portion of adsorbate solution. The adsorbate concentrations studied for kinetic studies were 15, 25, 35, and 45 mg/L. The concentration ranges for isothermal studies were 5–100 mg/L for Cd^{2+} and 15–135 mg/L for CV.

Table 1
Results of kinetic parameters and statistical indices of different models for cadmium (Cd²⁺) adsorption by Keratin/DCNC adsorbent.

Pseudo-first order model								
C ₀	k ₁ (min ⁻¹)	q _{el} (mg g ⁻¹)	R ²	χ ²	Δq (%)	RMSE	ARE (%)	HYBRID
15	1.90 × 10 ¹	266.93	0.9621	7.22	5.96	10.18	0.36	0.23
25	2.02 × 10 ⁻¹	435.29	0.9883	13.36	6.03	18.88	0.36	0.14
35	2.07 × 10 ⁻¹	558.02	0.9938	15.44	5.81	22.43	0.34	0.16
45	2.22 × 10 ⁻¹	606.21	0.9942	17.34	5.78	25.37	0.33	0.09
Pseudo-second order model								
C ₀	k ₂ (g/mg.min)	q _{e2} (mg/g)	R ²	χ ²	Δq (%)	RMSE 2.44	ARE(%) 0.03	HYBRID 0.01
15	7.96 × 10 ⁻⁴	299.32	0.9978	0.46	1.59			
25	5.23 × 10 ⁻⁴	485.88	0.9999	0.15	0.67	1.93	0.00	0.10
35	4.24 × 10 ⁻⁴	621.24	0.9999	0.42	1.03	3.41	0.01	0.02
45	4.29 × 10 ⁻⁴	670.67	0.9999	0.24	0.69	2.98	0.00	0.02
Elovich model								
C ₀	α (mg/g.min)	β (mg/g)	R ²	χ ²	Δq (%)	RMSE	ARE(%)	HYBRID
15	180.08	1.78 × 10 ⁻²	0.9526	7.76	5.93	11.38	0.35	0.60
25	335.29	1.12 × 10 ²	0.9912	10.26	5.68	16.34	0.32	0.53
35	460.63	8.91 × 10 ⁻³	0.9937	15.14	5.85	22.74	0.34	0.56
45	608.33	8.57 × 10 ⁻³	0.9946	15.76	5.77	24.29	0.33	0.51
Ritchie model								
C ₀	K _R (min ⁻¹)	q _e (mg/g)	R ²	χ ²	Δq (%)	RMSE	ARE(%)	HYBRID
15	2.38 × 10 ⁻¹	299.31	0.9978	0.46	1.59	2.44	0.03	0.01
25	2.55 × 10 ⁻¹	485.82	0.9999	0.14	0.64	1.96	0.00	0.04
35	2.63 × 10 ⁻¹	621.26	0.9999	0.42	1.03	3.41	0.01	0.02
45	2.88 × 10 ⁻¹	670.64	0.9999	0.24	0.69	2.98	0.00	0.02

Table 2
Results of kinetic parameters and statistical indices of different models for crystal violet dye adsorption by Keratin/DCNC adsorbent.

Pseudo-first order model								
C ₀	k ₁ (min ⁻¹)	q _{el} (mg/g)	R ²	χ ²	Δq (%)	RMSE	ARE (%)	HYBRID
15	1.86 × 10 ¹	275.06	0.9667	6.45	5.56	9.92	0.31	0.28
25	1.97 × 10 ¹	444.34	0.9897	12.32	5.87	17.85	0.35	0.20
35	2.02 × 10 ⁻¹	594.18	0.9932	18.24	6.03	25.77	0.36	0.14
45	2.20 × 10 ⁻¹	729.58	0.9947	23.32	6.14	32.00	0.38	0.08
Pseudo-second order model								
C ₀	k ₂ (g/mg.min)	q _{e2} (mg/g)	R ²	χ ²	Δq (%)	RMSE	ARE(%)	HYBRID
15	7.57 × 10 ⁻⁴	308.24	0.9980	0.32	1.09	2.45	0.01	0.02
25	5.04 × 10 ⁻⁴	495.60	0.9997	0.34	0.95	3.05	0.01	0.02
35	3.88 × 10 ⁻⁴	661.58	0.9999	0.15	0.55	2.29	0.00	0.04
45	3.52 × 10 ⁻⁴	806.76	0.9999	0.45	0.98	3.83	0.01	0.04
Elovich model								
C ₀	α (mg/g.min)	β (mg/g)	R ²	χ ²	Δq(%)	RMSE	ARE(%)	HYBRID
15	186.68	1.74 × 10 ²	0.9371	10.48	7.05	13.65	0.50	0.80
25	343.62	1.11 × 10 ⁻²	0.9865	14.72	6.53	20.49	0.43	0.67
35	484.70	8.41 × 10 ³	0.9935	17.03	6.22	25.09	0.39	0.61
45	748.68	7.21 × 10 ⁻³	0.9952	20.04	5.85	30.48	0.34	0.55
Ritchie model								
C ₀	K _R (min ⁻¹)	q (mg/g)	R ²	χ ²	Δq(%)	RMSE ARE(%)		HYBRID
15	2.33 × 10 ⁻¹	308.23	0.9980	0.32	1.09	2.45	0.01	0.02
25	2.50 × 10 ⁻¹	495.61	0.9997	0.34	0.95	3.05	0.01	0.01
35	2.57 × 10 ⁻¹	661.61	0.9999	0.15	0.55	2.29	0.00	0.03
45	2.85 × 10 ⁻¹	806.46	0.9999	0.45	0.97	3.87	0.01	0.04

following relation:

$$q_e = \frac{q_{\max} K_T C_e}{[1 + (K_T C_e)^n]^{1/n}}$$

Toth model

(29)

where K_T (L mg⁻¹) represents the Toth isotherm constant and n represents the Toth isotherm exponent.

3.4.6. Redlich–Peterson isotherm model

The Redlich–Peterson isotherm is a hybrid three-parameter isotherm of both Freundlich and Langmuir isotherms, and is applicable in both heterogeneous and homogeneous processes, owing to its versatility [50]. This isotherm approaches to Freundlich relation once the concentrations of the adsorbates in the solution are high, as the exponent g tends to zero, and the low concentrations cause this model approaches the ideal Langmuir condition in which values of β are close to unity [51]. The nonlinear form of the Redlich–Peterson isotherm is described in Eq. (30) [38].

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^g}$$

Redlich – Peterson model

(30)

where K_{RP} (L/g) and a_{RP} (mg/L)^{-g} are the Redlich–Peterson isotherm constants, and g is Redlich–Peterson exponent that lies betwixt 0 and 1.

3.4.7. Khan isotherm model

Khan model is a generalized model of both Langmuir and Freundlich models, used for the adsorbate adsorption from pure solutions. This three-parameter isotherm model is designed for both multicomponent and single component and adsorption processes. In this model, at relatively high correlation coefficients, it can well determine the maximum adsorption values [52,53]. The nonlinear equation of the Khan model (Eq. (31)) is expressed as follows:

$$q_e = \frac{q_s b_K C_e}{(1 + b_K C_e)^{a_K}}$$

Khan model

(31)

Table 3Parameters and statistical indices of isotherms for Cd²⁺ adsorption onto Keratin/DCNC at three temperatures of 288, 298 and 318 Kelvin.

Langmuir isotherm model									
T (K)	Q_{max}^0 (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	χ^2	Δq (%)	RMSE	ARE (%)	HYBRID	
288	650.84	0.68	0.9990	0.03	0.13	5.53	0.03	0.13	
298	695.56	0.94	0.9990	0.04	0.42	6.19	0.04	0.42	
318	735.43	1.33	0.9992	0.02	0.28	5.77	0.02	0.28	
Freundlich isotherm model									
T(K)	K_F (mg ^{1-(1/n)} .L ^{1/n} /g)	n	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID	
288	288.84	4.55	0.8542	124.56	43.48	67.24	18.90	12.49	
298	339.24	5.02	0.8296	165.07	51.49	79.41	26.51	15.52	
318	375.64	5.16	0.8482	167.72	51.52	81.95	26.54	15.55	
Dubinin-Radushkevich isotherm model									
T(K)	q_e (mg/g)	β (kJ/mol)	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID	
288	575.56	0.43	0.7480	151.57	28.52	88.40	8.14	5.82	
298	618.03	0.59	0.7485	170.72	30.73	96.47	9.45	6.33	
318	658.03	0.85	0.7291	206.62	33.37	109.47	11.13	7.32	
Tempkin isotherm model									
T(K)	K_T (L/g)	B	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID	
288	11.62	106.72	0.9404	36.60	11.40	43.00	1.30	1.74	
298	18.28	108.71	0.9146	62.38	15.12	56.22	2.29	2.95	
318	28.89	109.60	0.9321	54.64	13.37	54.79	1.79	2.39	
Sips model									
T(K)	q_{max} (mg/g)	n	K_S (L/g)	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID
288	651.60	1.01	0.67	0.9991	0.78	1.75	5.40	0.03	0.19
298	688.59	0.94	0.98	0.9996	0.30	0.97	3.71	0.01	0.04
318	741.33	1.05	1.28	0.9997	0.19	0.62	3.48	0.00	0.06
Toth model									
T(K)	q_{max} (mg/g)	n	K_T (mg/L)	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID
288	653.35	1.02	0.69	0.9991	0.75	1.82	5.18	0.03	0.24
298	686.04	0.90	0.86	0.9996	0.26	0.80	3.74	0.01	0.02
318	743.91	1.08	1.44	0.9998	0.13	0.51	2.92	0.00	0.05
Redlich-Peterson model									
T(K)	K_{R-P} (L/g)	n_{R-P}	a	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID
288	446.57	0.99	0.70	0.999	0.73	1.78	5.19	0.03	0.24
298	627.23	1.01	0.86	0.9992	0.52	1.20	5.19	0.01	0.20
318	1029.48	0.99	1.47	0.9999	0.06	0.42	1.73	0.00	0.04
Khan model									
T(K)	q_s (mg/g)	a_K	b_K	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID
288	635.72	1.007	0.700	0.9991	0.73	1.76	5.21	0.03	0.23
298	734.95	0.98	0.864	0.9992	0.59	1.35	5.39	0.02	0.25
318	690.46	1.02	1.48	0.9999	0.06	0.51	1.74	0.00	0.071

where q_s (mg/g) represents the theoretical isotherm saturation capacities, b_K represents the Khan isotherm model constant and a_K represents the Khan isotherm model exponent.

Similar to kinetic equilibrium studies, the accurate fit of the experimentally computed data for various isothermal equations was conducted, recruiting non-linear model of regression and statistical indices, and the results can be observed visually in Fig. 4c and d as well as in Supplementary data (Figs. 6S–9S). The calculated data are also reported in Supplementary data (Tables 3 and 4). Based on the results obtained in this research and analysis of R^2 and statistical indices values, amongst the two-parameter isotherm models, Langmuir model displays that this model leads to a high fit for both Cd²⁺ ion and Crystal violet dye adsorption at various temperatures. Also, the experimental results approved that used three-parameter isotherm models provided good fit to the experimental results due to the higher regression coefficients along with the low values for the statistical parameters. Therefore, in addition to Langmuir model, such a high goodness-of-fit has obtained for all the studied three-parameter models, for the adsorption of both Cd²⁺ ion and Crystal violet dye. Notably, q_{max} amounts computed from the three-parameter equations are near to the amounts computed from Langmuir equation; Also, n exponents are close to one in all three-parameter isotherms. This result implies that the adsorption of Cd²⁺ and Crystal violet on Keratin/DCNC adsorbent is a mono-layer homogeneous coverage and the Langmuir isotherm is the best-fitted isotherm for describing this process [54]. The maximum adsorption capacities obtained by Langmuir model at 298 K are equivalent to 695.56 and 1166.67 mg/g for Cd²⁺ and Crystal violet, respectively. The new bio-adsorbent, Keratin/DCNC, displayed higher adsorption capacities than

the other adsorbents, including those fabricated from industrial waste (Table 5). These results affirm that wool keratin and bacterial cellulose could be recruited for fabrication of a valuable adsorbent with high adsorption capacities for retrieving of heavy metals ions and dyes from water medium.

3.5. Thermodynamic studies

Scrutinization of thermodynamic properties and parameters are and an eminent and indispensable step involved in adsorption process studies [66]. In particular, the thermodynamic behavior of a process is described by parameters like change in the standard Gibbs free energy (ΔG°), change in the standard enthalpy (ΔH°) and change in the entropy (ΔS°). Since the adsorption of Cd²⁺ ions and Crystal violet dye on Keratin/DCNC obeyed the Langmuir isotherm, the dimensionless thermodynamic equilibrium constants are numerically equivalent to the Langmuir equilibrium constants in L/mol ($K_{L,M}$), which can be employed as equilibrium constants value. Thermodynamic results of the current research were depicted and reported in Supplementary data (Figs. 10S and 11S; Tables 9S and 10S). As is obvious, the amounts of ΔG° at all temperatures are negative, indicating the spontaneity and feasibility of the adsorption processes. The more negative ΔG° amounts at higher temperatures exhibit that the removal process of Cd²⁺ and Crystal violet is more favorable, more spontaneous, and more feasible at the higher assessed temperatures. The adsorption process in this study is endothermic since the ΔH° amounts are positive. Also, the positive value of ΔS° might be justified by more randomly organizations of the Cd²⁺ ions and Crystal violet molecules at the solid/solution interfaces, and the liberating of hydration waters during the adsorption phenomena. Since

Table 4

Parameters and statistical indices of Isotherms for crystal violet dye adsorption onto Keratin/DCNC at three temperatures of 288, 298 and 318 Kelvin.

Langmuir isotherm model									
T (K)	Q_{max}^0 (mg/g)	K_L (L/mg)	R^2	χ^2	Δq (%)	RMSE	ARE (%)	HYBRID	
288	1159.50	0.42	0.9978	2.37	1.60	13.75	0.026	0.10	
298	1166.67	0.48	0.9979	2.51	1.77	13.50	0.031	0.15	
318	1177.62	0.57	0.9977	3.14	2.11	14.45	0.045	0.10	
Freundlich isotherm model									
T(K)	$K_F(mg^{1-(1/n)}.L^{1/n}/g)$	n	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID	
288	484.49	4.56	0.9038	141.66	20.10	90.55	4.039	4.47	
298	506.47	4.71	0.8982	149.97	20.57	94.52	4.23	4.63	
318	533.25	4.91	0.8906	169.00	22.28	100.44	4.96	5.15	
Dubinin-Radushkevich isotherm model									
T(K)	q_e (mg/g)	β (kJ/mol)	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID	
288	1059.95	0.72	0.8661	216.18	18.56	111.15	3.45	0.32	
298	1036.28	0.69	0.8026	246.56	20.95	131.60	4.39	3.92	
318	1059.95	0.72	0.8661	216.18	18.56	111.15	3.45	0.32	
Tempkin isotherm model									
T(K)	K_T (L/g)	B	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID	
288	7.96	191.69	0.9615	48.16	8.59	57.30	0.74	1.02	
298	9.75	188.46	0.9578	52.56	8.93	60.87	0.80	1.08	
318	12.44	184.74	0.9498	69.14	11.05	68.03	1.22	1.55	
Sips model									
T(K)	q_{max} (mg/g)	n	K_S (L/g)	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID
288	1181.30	1.08	0.40	0.999	1.14	1.17	9.17	0.01	0.07
298	1192.48	1.10	0.45	0.9996	0.59	0.98	6.00	0.01	0.06
318	1184.84	1.03	0.56	0.9982	2.96	2.30	12.97	0.05	0.19
Toth model									
T(K)	q_{max} (mg/g)	n	K_T (mg/L)	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID
288	1189.30	1.13	0.48	0.9992	0.94	1.06	8.26	0.01	0.07
298	1200.74	1.16	0.56	0.9997	0.4	0.81	4.93	0.01	0.05
318	1190.78	1.07	0.6	0.9984	2.75	2.32	11.98	0.05	0.21
Redlich-Peterson isotherm model									
T(K)	K_{R-P} (L/g)	n_{R-P}	a	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID
288	531.59	0.97	0.51	0.9995	0.50	0.78	5.99	0.01	0.05
298	616.77	0.97	0.59	0.9998	0.23	0.54	4.02	0.003	0.02
318	706.39	0.98	0.64	0.9989	2.15	2.22	9.69	0.05	0.23
Khan isotherm model									
T(K)	q_s (mg/g)	a_K	b_K	R^2	χ^2	Δq (%)	RMSE	ARE(%)	HYBRID
288	1040.39	1.03	0.501	0.9996	0.44	0.72	5.61	0.005	0.044
298	1043.1	1.03	0.579	0.9998	0.24	0.53	4.25	0.003	0.005
318	1093.6	1.02	0.639	0.9991	2.02	2.17	9.26	0.047	0.227

Table 5Comparison of sorption capacities of Keratin/DCNC with the previously employed adsorbents for Cd²⁺ and Crystal violet dye removal.

Adsorbent	Adsorption capacity (mg/g)	Ref.
Cadmium ion		
Keratin/DCNC	695.56	Present study
Magnetized activated carbons (MAC)	73.3	[55]
spherical porous adsorbent (SPA)	278.77	[56]
chitosan modification of kiwi branch biochar (CHKB)	126.58	[57]
modified sugarcane bagasse (MSB)	33.2	[58]
(IOM-ESCF)	76.3	[10]
Fe-Mn oxide-modified biochar (BC-FM)	120.77	[59]
Crystal violet		
Keratin/DCNC	1166.67	Present study
Sugarcane bagasse-bentonite/sodium alginate (SCB-Ben/SA)	839.9	[60]
Coconut husk powder (CHP)	454.54	[61]
gCuO	200	[62]
cCuO	142.86	
MoS ₂ @bentonite magnetic nanocomposite (M-MoS ₂ @bentoniteNC)	384.61	[63]
Lignin copper ferrite (LCF)	34.12	[64]
Fe ₃ O ₄ -graphene-biochar composite (GBC-Fe ₃ O ₄)	436.68	[65]

the ΔH° magnitude are equal to 25.158 and 10.973 kJ/mol for Cd²⁺ and Crystal violet, respectively, the sorption of Cd²⁺ and Crystal violet onto Keratin/DCNC are physical sorption type and adsorption processes may also proceed via electrostatic interaction. In addition, the more negative values of ΔH° for cadmium ions might be due to the adsorption of this ion via ion-exchange and chelating ion-exchange forces.

3.6. Recyclability studies

Generally, recyclability and good reusability are desirable for an ideal adsorbent. Evaluation of this capability was done by desorption and washing the adsorbent during 5 consecutive cycles. In Fig. 5, a schematic display has been reported for visual observation of recyclability of the Keratin/DCNC biocomposite. From the results reported in Fig. 6, one can grasp that removal performance of Cd²⁺ and Crystal violet by Keratin/DCNC adsorbent slightly declined after five recycles, so that in the fifth cycle, the removal efficiency was more than 92%, vouchsafing that Keratin/DCNC adsorbent can be reemployed at least five times, exhibiting satisfactory recyclability.

4. Conclusion

Bested by the high cost of industrial products, scientists thrive to fabricate useful products out of abandoned waste materials. Therefore, beeswax recycling wastewater was exploited as culture medium for synthesizing cellulose which was utilized for fabrication of a

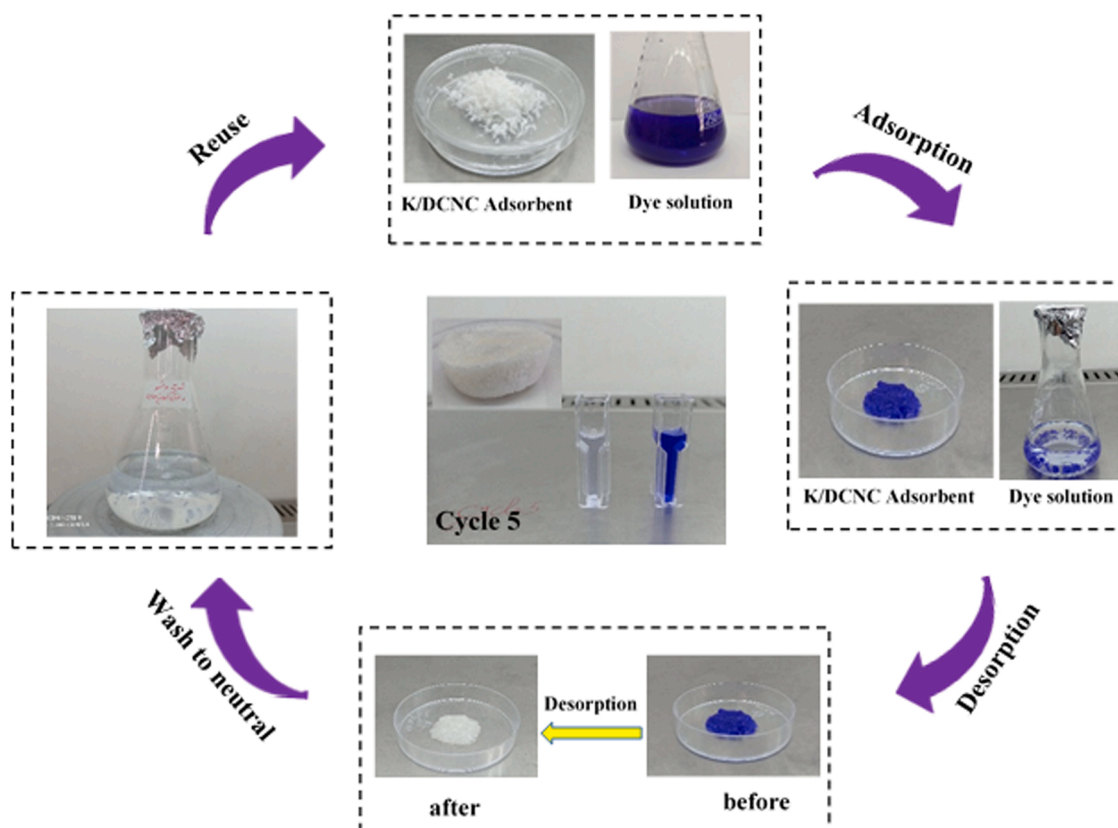


Fig. 5. Regeneration and reuse of Keratin/DCNC adsorbent in crystal violet adsorption experiments.

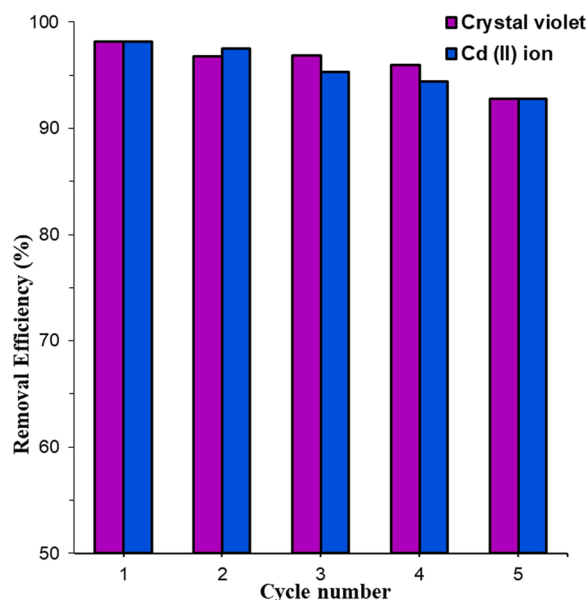


Fig. 6. Recyclability and reuse study of Keratin/DCNC adsorbent.

biocomposite with keratin extracted from wool which is another natural waste abandoned in the nature. The removal of Cd^{+2} and Crystal violet from water media by Keratin/DCNC bioadsorbent was triumphally studied, and the results revealed the high effectiveness of the adsorption process. Kinetics and isotherms studies vouchsafed that the pseudo-second-order and Langmuir models were fitted with experimental data, respectively. The maximum adsorption capacity was found to be 695.56 and 1166.67 mg/g for Cd^{+2} and crystal violet, respectively. The thermodynamic results vouchsafed the favorability, spontaneity and endothermic nature of the processes. These features, along with excellent recyclability, confirmed the high-efficiency of Keratin/DCNC bioadsorbent for treatment of waters and wastewaters.

CRediT authorship contribution statement

Ozra Peiravi Rivash: Investigation, Data curation, Writing – original draft, Writing – review & editing. **Mansour Mashreghi:** Supervision, Writing – original draft. **Omirsarik Baigenzhenov:** Writing – original draft. **Ahmad Hosseini-Bandegharai:** Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2022.130355](https://doi.org/10.1016/j.colsurfa.2022.130355).

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