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Chromium (VI) removal efficacy from aqueous solution by modified tea wastes-polyvinyl alcohol (TW-PVA) composite adsorbent

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ABSTRACT

Hexavalent chromium [Cr (VI)] from anthropogenic sources leads to toxicity in aquatic system and hence require efforts to remove it from the aqueous phase. Among many techniques, adsorption is used for Cr (VI) removal from aqueous phase. In the present investigation, tea waste-polyvinyl alcohol (TW-PVA) composite was synthesized to eliminate Cr (VI) from aqueous solution. Batch experiments showed operating conditions (dose, initial concentration, duration, pH and temperature) play significant role in Cr (VI) removal efficiency. However, TW-PVA composite (removal 94.22%) was found better in Cr (VI) removal efficiency compared with raw tea wastes (removal 81.99%). The maximum Cr (VI) removal (96%) was attained at 0.25 g TW-PVA composite dose and adsorption capacity decreased with the increase of dosages. Moreover, removal of Cr (VI) by TW-PVA composite decreased by elevated pH and the maximum removal efficiency of chromium (VI) was 94.91% at pH 2. Furthermore, the removal efficiency dropped as initial Cr concentration was increased. The highest Cr (VI) sorption was found to be 4.711 mg/g at 20°C and the adsorption capacity decreased with increasing temperature at a constant pH. The adsorption process reached at equilibrium within the first 50 min. It also well fitted with both Freundlich and Langmuir isotherm models and the overall kinetic data can be satisfactorily explained by pseudo-second-order rate expression which together attributes the chemisorption mechanism. The FTIR analysis revealed that carboxylate anion, sulfonyl chloride, and sulfonate groups were mainly involved in binding process of Cr (VI) onto the TW-PVA composite.

Keywords: Removal of chromium (VI); Modified natural adsorbent; Tea wastes-polyvinyl alcohol (TW-PVA) composite; Adsorption; Kinetic models and adsorption isotherms

1. Introduction

Chromium compounds have been reported to cause extensive industrial as well as environmental pollution problems because of their large-scale uses in industrial sectors, such as leather tanning, water cooling, metal finishing, wood preservation and textile dyes [1–3]. The transitional metal chromium has a number of oxidation states ranging from –2 to +6 but only trivalent [Cr (III)] and hexavalent [Cr (VI)] states are stable in natural environments. Cr (VI) is exceptionally soluble and bioavailable which results

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enhanced active transport of Cr (VI) through the biological membranes and thus responsible for various toxic, mutagenic and carcinogenic effects on living systems [4,5]. On the contrary, Cr (III) is less soluble and considered to be 1,000 times less toxic than Cr (VI) [6]. In Bangladesh, the tannery industries are mainly responsible for both aquatic and terrestrial Cr (VI) contamination. At present there are totally 250 tanneries in Bangladesh [7] and 95% of them are established in Hazaribagh, a heavily populated suburban area of capital Dhaka city. This particular area is popularly known for its tannery industry and has been listed as the fifth most polluted places of the world [8].

Ninety percentages of tanneries in Bangladesh are involved in chrome tanning process which results in discharge of liquid effluents and solid wastes that contain 180 mg/L of total chromium and other trace elements such as Cd, Pd, Zn, Cu and Mn with a mean concentration of 1.94, 23.66, 5.34, 1.88 and 9.71 mg/L, respectively [9–11]. Thus, the treatment of chromium containing tannery effluents and soil is a matter of great concern for Bangladesh. The removal/remediation of toxic metal ions such as Cr (VI) from the contaminated environments includes ion exchange [12], precipitation [13,14], ultrafiltration [13], reverse osmosis and electro-dialysis [15,16], adsorption [17], biological operations [18], coagulation/flocculation [19] and cementation [20]. However, almost all these methods have many drawbacks which include insufficient metal removal, huge capital and operational investments, necessities of expensive and sophisticated equipment, intensive reagents and energy needs and production of harmful secondary sludge [21].

On the contrary, adsorption is considered as one of the most popular technique for the removal of heavy metals from the wastewater because of its ability to eliminate chemical sludge production, complexities of operational tasks and its very high removal efficiency [22–26]. Activated carbons are considered as one the most efficient contender for the removal of heavy metals owing to have some special characteristics that significantly increase the use of activated carbons for the removal of environmental contaminants including heavy metals from drinking water supplies and wastewater [23,27,28]. Many scientific investigations have exploited diverse types of activated carbons to uptake Cr (VI) by adsorption such as coconut shell activated carbon [29], wood and dust coal activated carbons [30], hazelnut activated carbon [31], sawdust and used-tyre activated carbon [32], etc. Nano-sized super adsorbing materials known as hydrogels/nano-hydrogels have made the adsorption of heavy metals from aqueous medium more interesting. Nano-hydrogels have very small size and three-dimensional structures which can be used in various applications such as drug delivery, water purification, adsorption, electrode making, etc. Several authors researched on heavy metals and dyes removal by hydrogels/nano-hydrogels [33,34], different biopolymers [35,36] and multifunctional nano-composite [37].

Lignocellulose agricultural wastes have earned great scientific attention for wastewater treatment because of their abundance, renewable characteristics and easy accessibility throughout the world especially in the developing countries. Moreover, these compounds are biodegradable, thermally recyclable and have substantial stiffness and significant mechanical characteristics. These biomaterials hold various functional groups on their surfaces which provide strong affinity to bind heavy metal ions in wastewater [38].

Many agricultural residues/wastes had been used directly as biosorbents for the adsorption of trace metals from wastewater system which included soybean hull [39], olive cake [40], wheat straw [41], maize cob [42], rice husk [43], barley straw [44], bagasse pith [45], coconut husk [46], cocoa shells [47], tea leaves [48], orange peel and banana peel [49], peanut shell [50], etc. It has been concluded from recent investigations that tea wastes have great potential of removing heavy metals from wastewater in a cost effective and environmentally sustainable manner [51]. Bangladesh is a huge producer and consumer of tea where almost 50,000 tons of tea are produced yearly and 80% of which are consumed locally and eventually discarded into the natural environment as wastes [52]. The insoluble cell walls of tea are basically composed of cellulose, hemicelluloses, lignin, condensed tannins and structural proteins. An estimation by Cay et al. [53] showed that one third of the total dry matter in tea leaves have immense potential to remove metals from solutions as it contains functional groups primarily carboxylate, aromatic carboxylate, phenolic hydroxyl, and oxyl groups. Polyvinyl alcohol (PVA) is an environmental friendly, water soluble and synthetic polymer which is composed of numerous hydroxide groups and has been used in biomedical solicitations because of its biocompatible and nontoxic nature [54]. Moreover, PVA is a biodegradable polymer which has reported to provide good mechanical strength, chemical stability, and easy separation when it forms composite bead with tea wastes. Furthermore, cross-linking PVA beads has been widely used to develop bioadsorbents, which has better mechanical strength and regeneration capacities compared with cellulose beads [55–58].

Economical preparation procedures of macroporus PVA has been developed by Bai et al. [59]. Several researchers investigated the removal of Cr (VI) from wastewater by bioadsorbents made from tea-leaves wastes [60–62]. The low mechanical strength and powder shape or deficiency of desorption data make these sorbents unsuitable for practical use in real wastewater systems [63]. Removal of Pb^{+2}, Hg^{+2}, and Cu^{+2} using tea waste (TW) encapsulated by PVA (PVA/TW) were investigated by Zhang et al. [63]. In the present study, tea wastes-poly vinyl alcohol (TW-PVA) composite beads were used as modified natural biosorbent for the removal of Cr (VI) from aqueous medium. In order to characterize the key biomass functional groups responsible for the biosorption process, FT-IR spectrometric analysis was performed on raw tea wastes and tea wastes-PVA composites. Moreover, different process parameters were optimized to improve the biosorption process and the adsorption isotherms and kinetic models have also been designed from the equilibrium data to measure the ability of the biosorbent to remove Cr (VI) from aqueous solution.

2. Materials and methods

2.1. Reagents and chemicals

All the reagents and chemicals used in the present study were of analytical grade (AR). $K_2Cr_2O_7$ (CAS No. 7778-50-9), poly vinyl alcohol (PVA) (C_2H_4Ox) (CAS NO. 9002-89-5), sodium alginate ($C_6H_7O_8Na$) (CAS NO. 9005-38-3), calcium carbonate ($CaCO_3$) (CAS NO. 471-34-1), boric acid (CAS NO. 10043-35-3), HCl (CAS NO. 7647-01-0), KBr (FT-IR grade, ≥99% trace metals basis, CAS NO. 7758-02-3) and 1,5-diphenylcarbazide (CAS NO. 140-22-7) were purchased from Sigma-Aldrich, Germany.

2.2. Collection and preparation of tea-leaves wastes

The tea-leaves wastes collected from local tea stalls were washed thoroughly with tap water three times and boiled at 80°C in order to remove the colored compounds. The tea wastes were then dried at 50°C in an oven for 24 h which were then crumpled and sieved with vibratory sieves. The particle size of the grounded tea wastes powder was less than 1 mm.

2.3. Preparation of stock solution of Cr (VI)

Stock solution of Cr (VI) was prepared by standard procedures [64]. The stock solution containing 1,000 mg/L of Cr (VI) was prepared by dissolving 1.41 mg of $K_2Cr_2O_7$ in 500 mL of deionized water. This stock solution was used for analysis and further investigations.

2.4. Preparation of working solution of Cr (VI)

The working solution was prepared by diluting (serial dilution) the stock solution in accurate proportion to different initial concentration. 250, 200, 100, 50, and 10 mg/L working solutions were prepared for these experiments by using the following formula.

$$V_1 \times S_1 = V_2 \times S_2 \quad (1)$$

Here V_1 = required volume of stock solution; S_1 = concentration of stock solution; V_2 = intended volume; S_2 = required concentration.

In order to prepare 100 mL of 10, 20, 50, 100, 200 and 250 mg/L working solutions, 1, 5, 10, 20 and 25 mL of stock solutions were added, respectively, in solutions with desired pH (2–9) with deionized water to achieve desired concentrations. All the chemicals and reagents used in this study were of analytical grade.

2.5. Preparation of tea wastes-poly vinyl alcohol (TW-PVA) composite

The tea-wastes-poly vinyl alcohol composite was prepared by the slightly modified procedures described by Zhang et al. [63]. For the preparation of TW-PVA composite beads, quantitative PVA (8% w/w), $C_6H_7O_8Na$ (1% w/w) and $CaCO_3$ (0.3% w/w) were dissolved in deionized water in a water bath for 1 h. Sodium alginate, a polysaccharide-based biosorbent, highly viscous and is often used as an emulsifier and a gelling agent. Gels form when a calcium salt is added to a solution of sodium alginate in water. The gel forms by chemical reaction, the calcium displaces the sodium from the alginate, holds the long alginate molecules together and a gel is the result. In the process of adsorption, the heavy metal ions appear to exchange with calcium ions to form a metal alginate [65]. The PVA solution (8% w/w) mixed with TW powders as a ratio of 1:1. The resulting mixture extruded into a gently stirred saturated 3% boric acid solution by an injector and immersed for 24 h to form beads. 10 mL HCl solution was added into 500 mL water loaded with cleaned beads. The PVA/TW beads became porous after the reaction of HCl with $CaCO_3$. The porous beads were washed with deionized water to remove residual reagents. The beads were then oven dried and cooled in a desiccator. Fig. 1 shows the tea wastes powders and TW-PVA composite beads.

2.6. Characterization of functional groups present in the biosorbents

A Fourier transform infrared spectrophotometer (FTIR) (Model: IR Prestige–21, Shimadzu, Japan) was used to

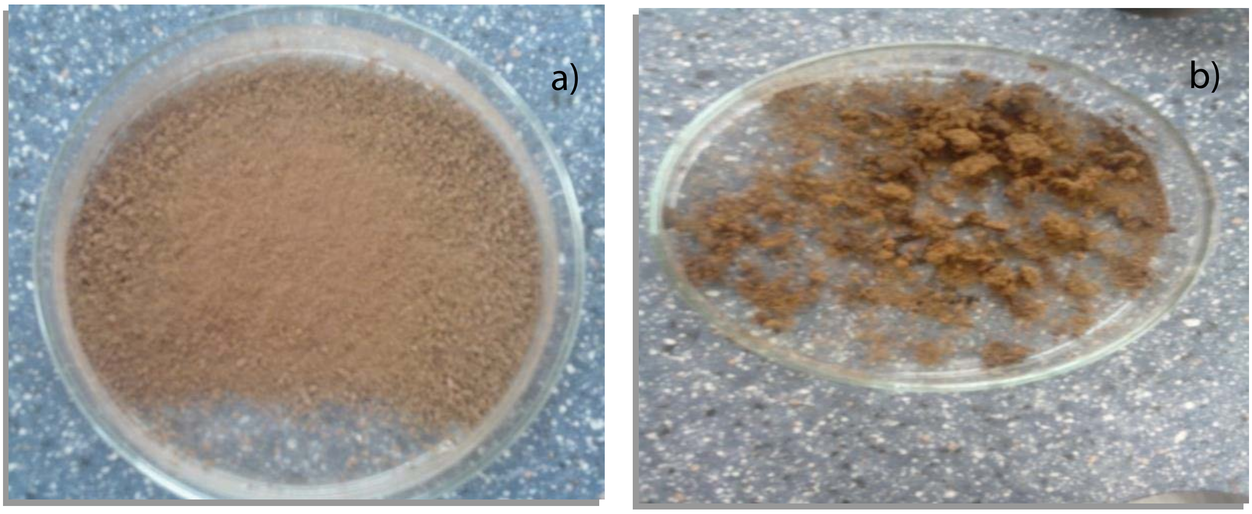

Fig. 1. (a) Raw tea wastes powders and (b) TW-PVA composite beads.

investigate the changes in vibrational frequencies of functional groups of the adsorbents due to Cr (VI) adsorption. The samples were dried appropriately in an oven. Then each fresh and Cr (VI)-loaded adsorbent was mixed separately with spectroscopic graded KBr and pellets were prepared at a pressure of about 1 MPa. The pellets were 10 mm in thickness. Then the adsorbents were scanned in the spectral range of 5,000–240 cm^{-1}.

2.7. Batch adsorption experiments

Adsorption experiments were carried out using batch equilibrium technique [66–68] in aqueous solutions at pH 2–9 and at desired temperatures (20°C–50°C). In general, a known amount of TW-PVA beads with 100 mL aqueous solution of Cr (VI) of the desired concentration (10, 50, 100, 200 and 250 mg/L) was taken and shaken in a rotary shaker with 250 rpm for a specific time period. The pH of the solution was carefully checked with a pH meter (Model HM-25R, DKK-TOA Corporation, Japan) and adjusted with NaOH or HCl solution. Apart from some specific situations, the adsorbent dosage was 1 g, the adsorbate dosage was 50 mg/L with pH of 2.0, the sample volume was 100 mL with shaking time of 120 min to reach complete equilibrium. At the time interval of 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 min, the supernatants were collected and centrifuged at 6,000 rpm for 10 min to eliminate the adsorbents from the collected supernatants. The supernatants were filtered using Whatman No. 41 (0.45 μm pore size) filter paper. The filtrated solution was then diluted to 10-fold with deionized water. The concentrations of Cr (VI) in the solution were then estimated colorimetrically with a UV-visible spectrophotometer (U-2910, HITACHI, USA) by 1,5-diphenylcarbazide method as described by Ilias et al. [7], using a standard curve of $K_2Cr_2O_7$.

2.8. Efficiency analysis

The removal percentages of chromium (VI) were calculated as follows:

$$\% \text{ removal of Cr } (\text{VI}) = \left(C_{\text{initial}} - C_{\text{final}}\right) \times \frac{100}{C_{\text{initial}}} \tag{2}$$

The amount of Cr (VI) adsorbed per unit mass of the adsorbents was calculated as follows:

$$q = \left(C_0 - C\right) \times \frac{V}{m} \tag{3}$$

Here q (mg/g) is the total adsorbed amount in time t (h); C_0 and C are the initial and equilibrium concentrations (mg/L) of metal ion in the solution; V is the volume of the solution and W is the weight (g) of the adsorbent.

2.9. Comparative study of Cr (VI) removal on TW and TW-PVA composite

A comparative study of Cr (VI) removal from the solution on TW and TW-PVA composite was conducted. It was performed by adding 1 g of both adsorbents into 250 mL glass stoppered conical flasks containing 100 mL of 50 mg/L Cr (VI) solution. The flasks were placed on a rotary shaker at 120 rpm for 120 min. The obtained supernatants were filtered and analyzed for remaining Cr (VI) concentration by 1,5-diphneylcarbazide (DPC) method as described in Section 2.10.

2.10. Influences of process parameters on Cr (VI) removal by TW-PVA composite

2.10.1. Effects of adsorbent doses

In order to investigate the effects of adsorbent doses on Cr (VI) removal by TW-PVA composite, 100 mL of 50 mg/L Cr (VI) solution with 0.25, 0.50, 0.75, 1.0 and 1.25 TW-PVA composites were placed in five individual 200 mL conical flasks into a shaker at room temperature and 120 rpm. After 120 min, supernatants were collected and filtered and residual Cr (VI) were analyzed by 1,5-diphenylcarbazide (DPC) method as described in Section 2.10.

2.10.2. Effects of initial Cr (VI) concentration

100 mL of 10, 50, 10, 200 and 250 mg/L initial concentrations in 250 mL individual Erlenmeyer flask with 1 g TW-PVA composite each were placed into a shaker. After 150 min supernatant was filtered and analyzed for residual Cr (VI).

2.10.3. Effects of contact time

100 mL of 50 mg/L Cr (VI) solution with 1 g TW-PVA composite in 250 mL conical flask was placed in a rotary shaker with a time interval of 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 min, and the supernatants were filtered for remaining Cr (VI) analysis.

2.10.4. Effects of pH

In order to investigate the effects of pH on Cr (VI) removal by TW-PVA composite, experiments were conducted in different pH, ranged from 2 to 9 at an initial Cr (VI) concentration of 50 mg/L with time interval of 150 min. The pH was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution.

2.11. Determination of Cr (VI)

The concentration of hexavalent chromium Cr (VI) was estimated colorimetrically with a UV-visible spectrophotometer (U-2910, HITACHI, USA) by following the 1,5-diphenylcarbazide (DPC) method as described by Ilias et al. [7]. The supernatant was collected from each flask into small vial by using micro pipette and filtrated. The filtered supernatant (3 mL) was transferred in the test tubes where 375 μL of DPC (diphenylcarbazide) reagent was added followed by gentle mixing and kept at room temperature for 20 min in order to develop the red-violet color of DPC-Cr (VI) complex. The concentration of Cr (VI) in the samples was then estimated by the using the $K_2Cr_2O_7$ standard curve.

2.12. Statistical analysis

Each experiment was performed at least three times, and mean ± standard deviation (SD) was used for data interpretation. All statistical analysis was performed by using Graphpad Prism (Version 7) Software Inc. CA, USA and Microsoft Excel 2007 (version Office Xp). The correlation coefficient (R^2) values of the linear form of Langmuir isotherm, Freundlich isotherm and pseudo-second-order kinetic model were determined by using statistical functions of Microsoft Excel 2007.

3. Results and discussion

3.1. Fourier transform infrared analysis

A detailed Fourier transform infrared (FTIR) spectra study of raw adsorbents and Cr (VI)-loaded adsorbents was carried out to identify the different functional groups which were responsible for the adsorption process. The spectra were measured within the range of 500–4,000 cm^{-1} wave number and were plotted using the same scale on the transmittance axis. The spectra shown in Fig. 2 and Table 1 display a number of absorption peaks corresponding to different functional groups indicating its complex nature with affinity towards chromium species.

As depicted in Fig. 2 and Table 1, comparing TW-PVA composite with tea waste, there were remarkable changes in peak wave numbers. Surface O–H stretching, aliphatic C–H stretching, unsaturated group such as alkene, amide C–O stretching, amide C–NO_2 stretching, alkane group stretching all were found to have shifting of wave numbers. Based on the attribution of peaks, it can be noted that TW-PVA composite contains a number of functional groups, for example –OH, –NH_2, –COOH etc. Figs. 2 and 3 represent the shift in the wave number of the dominant peaks associated with the fresh TW-PVA composite and Cr (VI)-loaded TW-PVA composite in the FT-IR plots. These shifts in the wavelength demonstrated that there occurs metal binding process on the surface of the adsorbent [69,70].

Significant changes were observed for the characteristic peaks at 1,150 cm^{-1} which shifted to 1,162.6 cm^{-1}and were corresponding to sulfonyl chlorides stretching and peak number shifted from 1,244.14 to 1,276.93 cm^{-1} indicates –SO_3 stretching. Aliphatic ketones might be responsible for Cr (VI) adsorption as wave number shifted from 1,734.08 to 1,725.40 cm^{-1}. Amide C–O stretching was found to be responsible one for adsorption at wave number with shifting from 1,556.62 to 1,549.87 cm^{-1}. A remarkable wave number shift from 1,318.40 to 1,384.95 cm^{-1} was observed, which suggests that carboxylate anion was a predominant contributor for Cr (VI) adsorption. So it is evident that carboxylate anion, sulfonyl

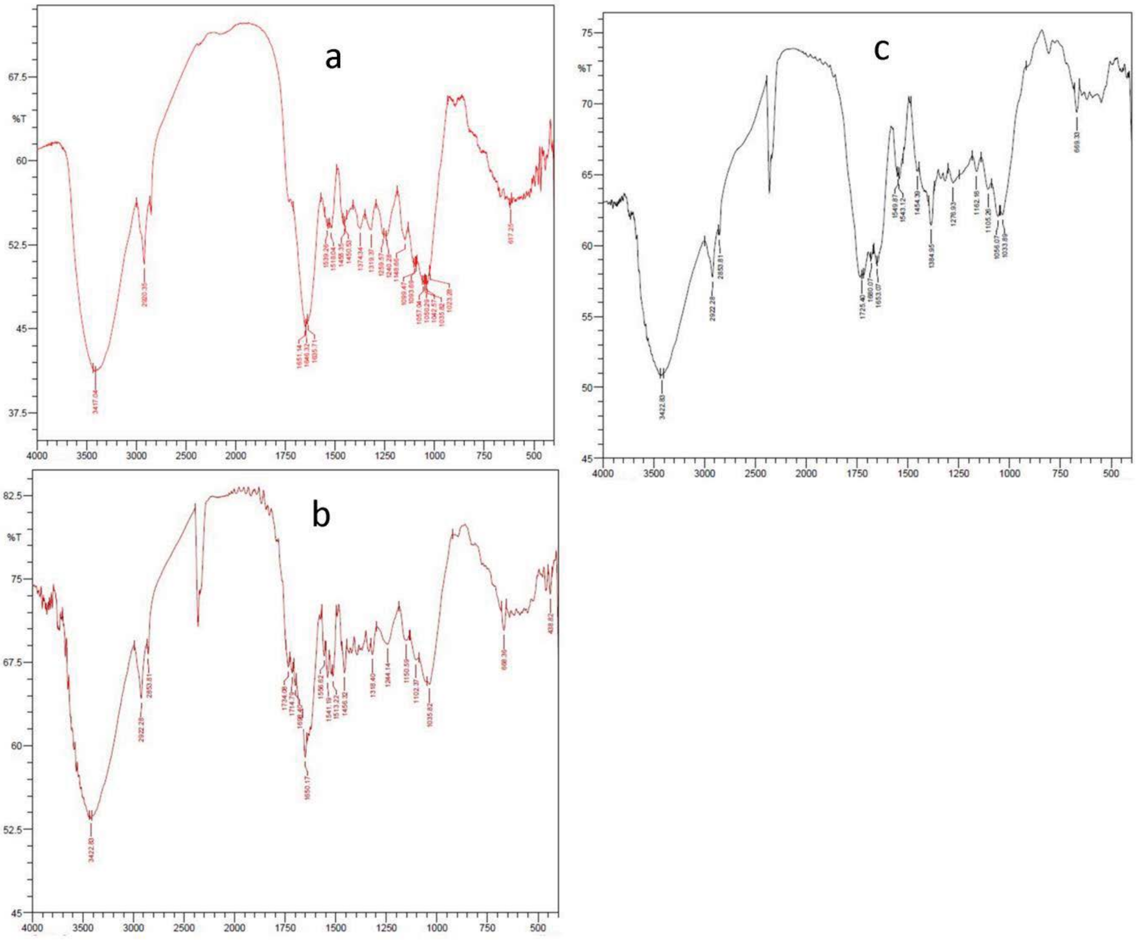

Fig. 2. FT-IR spectrum of raw tea waste (a), TW-PVA composite (b), Cr (VI) loaded on TW-PVA composite (c).

Table 1
Wave number (cm^{-1}) for the dominant peak from FTIR for Cr (VI) sorption

Functional groups	Tea waste	TW-PVA composite	Cr (VI) loaded on
Surface O–H stretching	3,440.19	3,422.83	3,422.83
Aliphatic C–H stretching	2,920.35	2,922.28	2,922.28
Aldehyde C–H stretching	–	2,853.81	2,853.81
Aliphatic acid (C=O stretching)	–	1,734.08	1,725.40
Unsaturated group like alkene	1,651.14	1,650.17	1,653.07
Amide C–O stretching	1,539	1,556.62	1,549.87
Amide C–NO_2 stretching	1,539.26	1,541.19	1,543.12
Alkane group stretching	1,455.35	1,456.32	1,454.39
Carboxylate anion (C=O stretching)	–	1,318.40	1,384.95
–SO_3 stretching	1,259.57	1,244.14	1,276.93
Sulfonyl chlorides stretching	1,148	1,150.59	1,162.16
Si–O stretching	–	1,102.37	1,105.26
Sulfonic acid S=O stretching	1,035	1,035.82	1,033.89
Sulfonate (S–O stretching)	617.2	668.3	669.3

chloride, and –SO_3 groups played major role in binding of Cr (VI) on the TW-PVA composite. It was also observed that there was minor or no shift for the other bands (aldehyde C–H stretching, Si–O stretching, sulfonic acid S=O stretching, sulfonate S–O stretching, surface O–H stretching, aromatic nitro, C–NO_2 stretching, aliphatic C–H stretching, aldehyde C–H stretching) which indicate that these groups were not involved in the adsorption process.

3.2. Comparative study of Cr (VI) removal on tea waste and TW-PVA composite

The removal rate of Cr (VI) by tea wastes and TW-PVA composite was calculated at different time intervals (30, 60, 90 and 120 min). Fig. 3 shows removal efficiency of Cr (VI) by TW-PVA composite is higher when it is compared with tea waste. At 30 min, the removal efficiency of tea waste was only about 60.68% compared with 79.6% by TW-PVA composite as an adsorbent and after 120 min, the removal was 94.22% by TW-PVA composite compared with 81.99% by tea wastes which suggest that TW-PVA composite had the potential of being used as an efficient adsorbent than that of using tea waste itself. The comparison of adsorption efficiency of TW-PVA composite with other natural modified and synthesized adsorbents has been illustrated in Table 2. TW-PVA used in the present investigation has significantly higher removal efficiency (96%) of Cr (VI) compared with other natural and synthetic adsorbents such as tea waste, coconut husk, chitosan-alumina composite, boiled and formaldehyde treated rice husk, cereal by-products, coconut shell charcoal and coconut shell, etc.

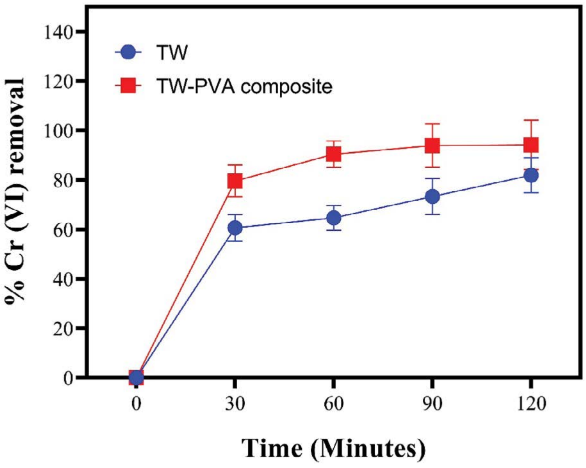

Fig. 3. Comparison of chromium (VI) removal efficiency on tea waste and TW-PVA composite (pH 2, dosage: 1 g, initial concentration: 50 mg/L). Values are mean numbers ± standard deviations derived from three independent experiments.

3.3. Influence of different operating conditions on Cr (VI) removal by TW-PVA composite

The influences of different operating conditions such as dosage, pH, temperature, initial Cr (VI) concentration, contact time on Cr (VI) removal by TW-PVA composite have been shown in Figs. 3 and 4.

3.3.1. Effects of dosage

The dose dependence of Cr (VI) adsorption was examined by varying the amount of adsorbents (0.25, 0.50, 0.75, 1 and 1.25 g) for a time interval of 120 min. Fig. 4a illustrates that the removal efficiency of the adsorbent generally improved with increasing dose. The maximum Cr (VI) removal efficiency is about 96.00% at the dose of 1.25 g where it was about 87.98% at 0.25 g of dose. This can be explained with the fact that with increase in the adsorbent dose, more binding sites will be free for the complexation of Cr (VI) and there will be an increase in the rate of adsorption. An increase in the percentage adsorption with adsorbent dose may be the fact of increasing in the adsorbent's surface area and availability of more adsorption sites [78].

Table 2
Comparison of adsorption efficiency of TW-PVA composite with other natural modified and synthesized adsorbents

Name of the adsorbents	Adsorption efficiency of Cr (VI)	References
Tea Waste	92%	Hanit et al. [71]
Tea waste and coconut husk	86% and 82%, respectively.	Pragesh et al. [72]
Chitosan-alumina composite	90.17%	Kabiraz et al. [73]
Boiled and formaldehyde treated rice husk	71.0% and 76.5%, respectively.	Manjeet et al. [74]
Cereal by-products	90.60%	Arris et al. [75]
Coconut shell charcoal	86%	Babel and Kurniawan [76]
Coconut shell	83%	Nilisha and Yogesh [77]
TW-PVA	96%	Present Study

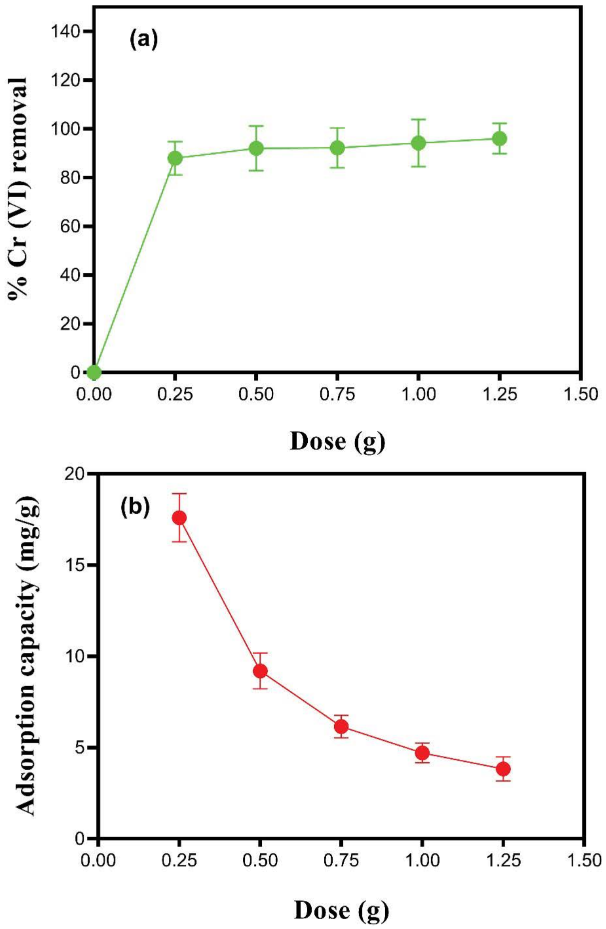

Fig. 4. (a): Effect of adsorbent dosages on Cr (VI) removal efficiency (pH: 2, contact time: 120 min, initial concentration: 50 mg/L), (b): Effect of dosages on adsorption capacity for Cr (VI) on TW-PVA composite (pH: 2, contact time: 120 min, initial concentration: 50 mg/L). Values are mean numbers ± standard deviations derived from three independent experiments.

In Fig. 4b the adsorption capacity shows a decreasing trend with increasing dosage. The adsorption capacity of TW-PVA composite decreased from 17.60 to 3.84 mg/g with the increase of dose from 0.25 to 1.25 g at an initial concentration of 50 mg/L. This decrease may be due to several factors such as at high adsorbent dosage, the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in low metal uptake; and at high adsorbent dose interference between binding sites also results in low uptake [79].

3.3.2. *Effects of pH*

pH affects both the surface charge of an adsorbent and the speciation of metal ions [80]. The effect of pH in the range 2.0–9.0 on the removing of Cr (VI) using TW-PVA was investigated and is illustrated in Fig. 5 which revealed that the maximum removal efficiency of chromium was 94.91% at pH 2 and hence it was taken as the optimal pH value for further adsorption experiments. With increasing pH, the removal rate of Cr (VI) dramatically decreased pointed out that acidic environment play an important role in reducing the rate of Cr (VI) and its interaction with TW-PVA composite. Cr (VI) exists in the form of oxyanions such as $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} in an acidic medium and lowering of pH is attributed to the strong attraction between these oxyanions of Cr (VI) and positively charged surface of the bio-adsorbent, therefore, the uptake increases with the decrease of pH of the solution [81]. When pH is less than 1 then chromic acid (H_2CrO_4) may occur [80]. From acidic pH 1 to the neutral pH 7, the hydrogen chromate ion ($HCrO_4^-$) exists, whereas, above the neutral pH, only chromate ions (CrO_4^{2-}) exist in the solution.

At a lower pH, the adsorption effect is high because predominant Cr (VI) species mainly occur in monovalent $HCrO_4^-$ form, which is then gradually transformed to divalent CrO_4^{2-} and $Cr_2O_7^{2-}$ as pH increases. The adsorption free energy of $HCrO_4^-$ is lower than that of CrO_4^{2-} and $Cr_2O_7^{2-}$; and consequently, $HCrO_4^-$ is more easily adsorbed than CrO_4^{2-} and $Cr_2O_7^{2-}$ at the same concentration. As the pH increases, the composites surface becomes increasingly deprotonated so that the amount of positive surface charges is significantly decreased, leading to a reduction in the adsorption capacity of Cr (VI). Thus, at a lower pH, the adsorption quantities of Cr (VI) are larger than that of at higher pH [82,83].

3.3.3. *Effects of initial metal concentration*

The effect of initial Cr (VI) concentration on removal efficiency is depicted in Fig. 5. It is evident that the Cr (VI) removal percentage has decreased with increase in Cr (VI) concentration. From the experimental results, the maximum

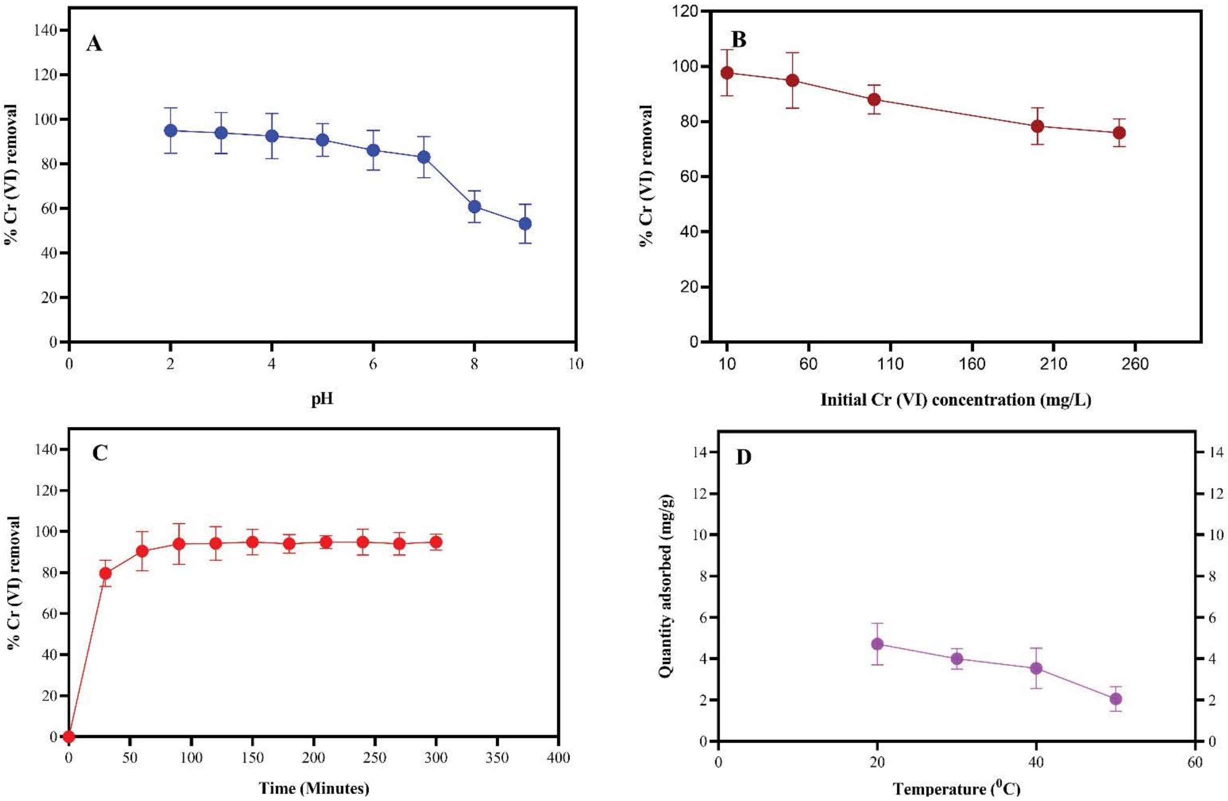

Fig. 5. Effects of (A) pH on Cr (VI) removal efficiency (contact time: 150 min, dosage: 1 g, initial concentration: 50 mg/L), (B) initial concentration on Cr (VI) removal efficiency (pH: 2, dosage: 1 g, contact time: 150 min), (C) contact time on Cr (VI) removal efficiency (pH: 2, dosage: 1 g, initial concentration: 50 mg/L) and (D) temperature on Cr (VI) removal efficiency (pH: 2, dosage: 1 g, contact time: 150 min) by TW-PVA composite. Values are mean numbers ± standard deviations derived from three independent experiments.

Cr (VI) percentage removal is noticed at a concentration of 10 mg/L by TW-PVA composite and the maximum value obtained is 97.66% that has been decreased to 75.95% at a concentration of 250 mg/L. It may be due to an increase in the number of Cr (VI) ions for the fixed amount of adsorbent doses meaning there was no more adsorption sites on the adsorption surface of the material. At the lowest concentration of Cr (VI), the maximum chromium removal occurs due to higher cell density attained than higher concentrations of Cr (VI) [84].

3.3.4. Effects of contact time

It is evident from the results that the percentage removal increases with increasing contact time. Fig. 5 shows that the Cr biosorption has occurred in two steps: an initial fast step which lasts for 30 min followed by the slower second phase which has continued until the equilibrium reached within 150 min. Lower adsorption rate in the latter stage may be due to the difficulty faced by Cr ions to occupy the remaining vacant surface sites because of forces between the solute molecules of the solid and bulk phase [85,86]. Qaiser et al. [87] explained that in the starting phase, large number of vacant sites may be present, which led to fast adsorption, but afterward, it slows down as the vacant sites may be exhausted. This was due to repulsion between the solute molecules and bulk phase.

3.3.5. Effects of temperature

The effects of temperature on Cr (VI) removal by TW-PVA composite are demonstrated in Fig. 5. Temperature is considered to be a critical parameter in the adsorption of Cr (VI) by biosorbents [88]. In order to investigate the effects of temperature on the removal of Cr (VI) ions by both TW-PVA composite were studied at different temperatures (20°C, 30°C, 40°C and 50°C). The maximum Cr (VI) sorption occurred at 20°C which decreased continuously by increasing temperature at constant values of pH: 2, adsorbent dose: 1 g/L, contact time: 120 min, initial Cr (VI) concentration: 50 mg/L and shaking speed: 200 rpm suggesting that the adsorption process was exothermic in nature [89]. These results also indicate that no permanent chemical bonds may not form during the adsorption process [90]. According to the adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface have a tendency to desorb from the surface at higher temperatures [91]. These results are in accordance with the earlier reported works [92–94].

3.4. Adsorption isotherms

Investigation of equilibrium data is significant for developing an equation that can be used for design purposes. Classical adsorption models, such as the Langmuir and Freundlich models, have been widely used to explain the equilibrium established between adsorbed metal ions on the biomass and metal ions remaining in solution at a constant temperature. The Langmuir adsorption isotherm [95] defines the surface as homogeneous considering that all the adsorption sites have equal adsorbate affinity and that adsorption at one site does not affect adsorption at an adjacent site. It provides information on uptake capabilities and reflects the usual equilibrium process behavior. The Freundlich model [96] describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity and can only be applied in the low to intermediate concentration range. The experimental data were analyzed by Langmuir and Freundlich isotherm models which are mathematically expressed in Eqs. (4) and (5), respectively. The results are plotted in Figs. 6 and 7 and Table 3.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{4}$$

Here q_e is the metal concentration adsorbed on solid (biomass), C_e is the metal residual concentration in solution, $q_{\max}$ is the maximum specific uptake corresponding to site saturation, and b is the ratio of adsorption/desorption rates. The high value of correlation coefficient would indicate the good agreement between the parameters. Linear form of Freundlich equation is

$$\log q_e = \log K_f + \log C_e \tag{5}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of adsorbate (mg/dm^3) and K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

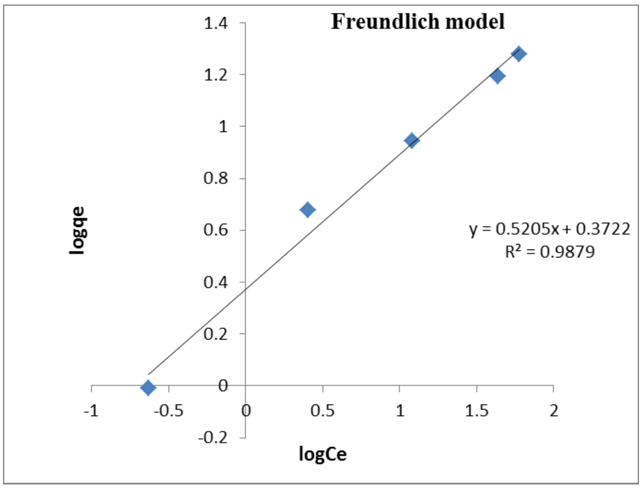

Fig. 7. Freundlich isotherm for Cr (VI) adsorption onto TW-PVA composite.

Table 3
Langmuir and Freundlich isotherm constants for the adsorption of Cr (VI)

Langmuir isotherm			Freundlich isotherm		
R^2 Correlation-coefficient	$Q_{\max}$ Maximum sorption capacity(mg/g)	b adsorption/desorption on energy	n Intensity of adsorption	K_f Adsorption capacity(mg/g)	R^2 Correlation-coefficient
0.964	20.83	0.129	1.92	2.36	0.987

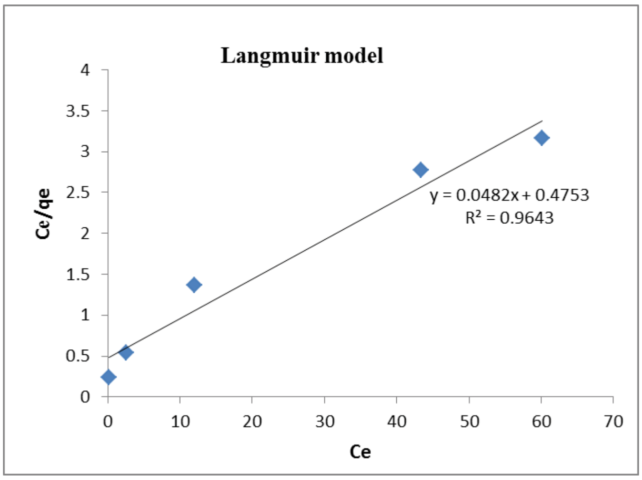

Fig. 6. Langmuir isotherm for Cr (VI) adsorption onto TW-PVA composite.

The results given in Table 3 suggest that the Langmuir isotherm fits quite well with the experimental data; the results revealed that the maximum monolayer adsorption capacity was obtained with a $Q_{\max}$ value of 20.83 mg/g from the Langmuir model. The R^2 value is an important parameter for selecting the best isotherm model. The higher R^2 value suggests that the model describes the adsorption data more effectively [97]. It is well known that the Langmuir equation is intended for a homogeneous surface and a good fit of this equation reflects monolayer adsorption. This implies that the adsorption of Cr (VI) on the TW-PVA composite is confined to one layer adsorption which further indicates the homogeneity of the adsorbent surface.

Intensity of adsorption (n) value is 1.92 which is in good agreement with Wang et al. [98], who mathematically assessed values of n for a number of mass transfer operations of the system and described that the values of n between 1 and 10 would present beneficial adsorption. It is indicated that the applicability of a heterogeneous coverage of the Cr (VI) on the surface of adsorbent. The Freundlich equation is suitable for homogeneous and heterogeneous surfaces, indicating a multi-layer adsorption [99]. Adsorption takes place at both homogeneous and heterogeneous sites and not confined to one layer adsorption. This kind of results indicates the complexity of the structure and composition of adsorbent.

3.5. Kinetic studies

Adsorption kinetics study is considered one of the most effective tool for understanding the underlying mechanisms involved in the adsorption process of metal ions from the aqueous solution [100]. Various theoretical models provide significant insights into the mechanisms by which the adsorbate accumulates on the surface of the adsorbent such as Lagergren pseudo-first order model, pseudo-second order model, Elovich equation, intra-particle diffusion model, etc. [101]. In order to study the mechanism of sorption and potential rate determining step, the experimental data were simulated by the pseudo-second-order kinetic model [52,102,103] and represented by the following linear equation:

$$\frac{t}{q_t} = \frac{1}{kq_e} + \frac{t}{q_e} \tag{6}$$

Here, k is the overall rate constants of pseudo-second-order adsorption (g/mg/min), and q_e is the equilibrium adsorption capacity. Linear regression data for pseudo-second order kinetics are given in Table 4. The values of k and q_e can be determined experimentally by plotting t/q_t vs. t (Fig. 8). The linear plots of t/q_t vs. t, the correlation coefficient of the pseudo-second-order kinetic model has found 1, which indicates that the pseudo-second-order kinetic model provides satisfactory correlation for the adsorption of Cr (VI) ions onto the adsorbent. The experimental data agree well with the pseudo-second-order equation (correlation coefficient R^2 was observed to be close to 1 or equal to 1), which suggests that the process controlling the rate may be a chemical sorption involving valency forces through sharing or exchange of electrons between biosorbent and sorbate [60,100].

Table 4
Linear regression data for pseudo-second-order kinetics model

Correlation coefficient (R^2)	K (g/mg/min)
0.999	2.57

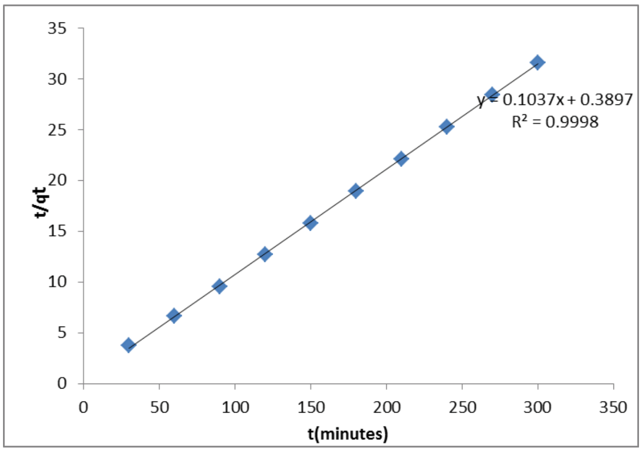

Fig. 8. Pseudo-second-order kinetic model.

4. Conclusions

In the present study, the potentiality of tea waste-polyvinyl alcohol (TW-PVA) composite for the removal of chromium (VI) has been confirmed. Chemical reduction and sorption are the potential mechanisms to remove chromium (VI) by TW-PVA composite. Thus, the findings demonstrated the potentiality of TW-PVA composite as an alternative adsorbent for the removal of Cr (VI) from wastewater. However, further investigation, that is, scanning electron microscopy analysis of TW-PVA composite is recommended to confirm the morphology of composite and exact pore size distribution. In addition, most of the previous experiments including the present one illustrated second order kinetic model hence other kinetic models have to be studied to describe the Cr (VI) removal process more accurately and precisely.

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References

[1] M. Megharaj, S. Avudainayagam, R. Naidu, Toxicity of hexavalent chromium and its reduction by bacteria isolated from soil contaminated with tannery waste, Curr. Microbiol., 47 (2003) 51–54.

[2] R. Bartlett, B.R. James, Mobility and bioavailability of chromium in soils, Adv. Environ Sci. Technol., 20 (1988) 267–304.

[3] R.M. Stern, Chromium Compounds: Production and Occupational Exposure, In: S. Langard, Ed., Biological and Environmental Aspects of Chromium, Elsevier, Amsterdam, 1982, pp. 5–47.

[4] M.K. Chaturvedi, Studies on chromate removal by chromium resistant *Bacillus sp.* isolated from tannery effluent, J. Environ. Protect., 2 (2011) 76–82.

[5] V.K. Singh, K.P. Singh, D. Mohan, Status of heavy metals in water and bed sediments of river Gomti–A tributary of Ganga River, India, Environ. Monit. Assess., 105 (2005) 43–67.

[6] G. Lofroth, B.N. Ames, Mutagenicity of inorganic compounds in *Salmonella typhimurium:* arsenic, chromium and selenium, Mutat. Res., 53 (1978) 59–65.

[7] M. Ilias, I.M. Rafiqullah, B.C. Debnath, K.S. Mannan, M. Mozammel Hoq, Isolation and characterization of chromium (VI)-reducing bacteria from tannery effluents, Ind. J. Microbiol., 51 (2011) 76–81.

[8] A. Bernhardt, N. Gysi, The World's Worst 2013: The Top Ten Toxic Threats; Clean Up, Progress and Ongoing Challenges, New York, Zurich, 2013, 17 p.

[9] K.M. Shams, G. Tichy, M. Sager, T. Peer, A. Bashar, M. Jozic, Soil contamination from tannery wastes with emphasis on the fate and distribution of tri- and hexavalent chromium, Water Air Soil Pollut., 199 (2009) 123–137.

[10] M.M. Kabir, A.N.M. Fakhruddin, M.A.Z. Chowdhury, Z. Fardous, R. Islam, Characterization of tannery effluents of Hazaribagh area, Dhaka, Bangladesh, Pollution, 3 (2017) 395–406.

[11] M.M. Kabir, A.N.M. Fakhruddin, M.A.Z. Chowdhury, M.K. Pramanik, Z. Fardous, Isolation and characterization of chromium (VI)-reducing bacteria from tannery effluents and solid wastes, World J. Microbiol. Biotechnol., 34 (2018) 126.

[12] D.D. Maksin, A.B. Nastasovic, A.D. Milutinovic-Nikoloc, L.T. Surucic, Z.P. Sandic, R.V. Hercigonja, A.E. Onjia, Equilibrium and kinetics study on hexavalent chromium adsorption onto diethylene triamine grafted glycidyl methacrylate based copolymers, J. Hazard. Mater., 209–210 (2012) 99–110.

[13] A. Esmaeili, A. Mesdaghi Nia, R. Vazirinejad, Chromium (III) removal and recovery from tannery wastewater by precipitation process, Am. J. Appl. Sci., 10 (2005) 1471–1473.

[14] F. Fu, Q. Wang, Removal of heavy metal ions from wastewater: a review, J. Environ. Manage., 92 (2011) 407–418.

[15] J.H. Harker, J.R. Backhurst, J.F. Richardson, Coulson and Richardson's Chemical Engineering, 5th ed., Butterworth-Heinemann, 2002.

[16] J. Peric, M. Trgo, V. Medvidovic, Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms, Water Res., 38 (2004) 1893–1899.

[17] S. Rengaraj, K. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, J. Hazard. Mater., 87 (2007) 273–287.

[18] L.K. Wang, D.B. Dahm, R.E. Baier, Treatment of tannery effluents by surface adsorption, J. Appl. Chem. Biotechnol., 25 (1975) 475–490.

[19] A. Kapoor, T. Viraraghavan, D.R. Cullimore, Removal of heavy metals using the fungus *Aspergillus niger*, Bioresour. Technol., 70 (1999) 95–104.

[20] Z. Song, C.J. Williams, R.G.J. Edyvean, Treatment of tannery wastewater by chemical coagulation, Desalination, 164 (2004) 249–259.

[21] A. Filibeli, N. Buyukkamaci, H. Senol, Solidification of tannery wastes, Resour. Conserv. Recyl., 29 (2000) 251–261.

[22] A. Hora, K. Vidya Shetty, Inhibitory and stimulating effect of single and multi-metal ions on hexavalent chromium reduction by *Acinetobacter sp*. Cr-B2, World J. Microbiol. Biotechnol., 30 (2014) 3211–3219.

[23] Z.A. AL-Othman, R. Ali, Mu. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies, Chem. Eng. J., 184 (2012) 238– 247.

[24] P. Dhiman, Mu. Naushad, K.M Batoo, A. Kumar, G. Sharma, A.A. Ghfar, G. Kumar, M. Singh, Nano $Fe_xZn_{1-x}O$ as a tuneable and efficient photocatalyst for solar powered degradation of Bisphenol A from water, J. Clean. Prod., 164 (2017) 1542–1556.

[25] A. Kumar, Mu. Naushad, A. Rana, Inammuddin, Preeti, G. Sharma, A.A. Ayman,, F.J. Stadler, M. R. Khan, ZnSe-WO_3 nano-hetero-assembly stacked on Gum Ghatti for photodegradative removal of Bisphenol A: symbiose of adsorption and photocatalysis, Int. J. Biol. Macromol.., 104 (2017) 1172–1184.

[26] A. Kumara, A. Kumara, G. Sharmaa, Mu. Naushad, R.C. Vesesc, A.A. Ghfarb, F.J. Stadlerd, M.R. Khan, Solar-driven photodegradation of 17-β-estradiol and Ciprofloxacin from waste water and CO_2 conversion using sustainable Coal-char/polymeric-g- C_3N_4/RGO metal free nano-hybrids, New J. Chem., 41 (2017) 10208–10224.

[27] G. Sharma, D. Pathania, Mu. Naushad, N.C. Kothiyal, Fabrication, characterization and antimicrobial activity of polyaniline Th (IV) tungstomolybdophosphate nanocomposite material: efficient removal of toxic metal ions from water, Chem. Eng. J., 184 (2012) 238– 247.

[28] Mu. Naushad, Surfactant assisted nano-composite cation exchanger: development, characterization and applications for the removal of toxic Pb^{2+} from aqueous medium, Chem. Eng. J., 235 (2014) 100–108.

[29] G.J. Alaerts, V. Jitjaturant, P. Kelderman, Use of coconut shell based activated carbon for chromium (VI) removal, Water Sci. Technol., 21 (1989) 1701–1704.

[30] C. Selomulya, V. Meeyoo, R. Amal, Mechanisms of Cr (VI) removal from water by various types of activated carbons, J. Chem. Technol. Biotechnol., 74 (1999) 111–122.

[31] M. Kobya, Adsorption kinetic and equilibrium studies of Cr (VI) by hazelnut shell activated carbon, Adsorpt. Sci. Technol., 22 (2004) 51–64.

[32] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust, Chem. Eng. J., 81 (2001) 95–105.

[33] X.U. Tao, X.Q. Liu, Peanut shell activated carbon: characterization, surface modification and adsorption of Pb^{2+} from aqueous solution, Chin. J. Chem. Eng., 16 (2008) 401–406.

[34] G. Sharmaa, Mu. Naushad, A. Kumara, S. Rana, S. Sharma, A. Bhatnagar, F.J. Stadlerd, A. Ayman, A. Ghfar, M.R. Khan, Efficient removal of coomassie brilliant blue R-250 dye using starch/poly(alginic acid-cl-acrylamide) nano-hydrogel, Process Saf. Environ., 109 (2017) 301–310.

[35] G. Sharma, Mu. Naushad, A.H. Al-Muhtaseb, A. Kumar, M.R. Khan, S. Kalia, S. ManjuBala, A. Sharma, Fabrication and characterization of chitosan-crosslinkedpoly (alginic acid) nanohydrogel for adsorptive removal of Cr (VI) metal ion from aqueous medium, Int. J. Biol. Macromol., 95 (2017) 484–493.

[36] G. Sharma, Mu. Naushad, D. Pathania, A. Mittal, G.E. El-desoky, Modification of *Hibiscus cannabinus* fiber by graft copolymerization: application for dye removal, Desal. Wat. Treat., 54 (2015) 3114–3121.

[37] D. Pathania, G. Sharma, Mu. Naushad, V. Priya, A biopolymer-based hybrid cation exchanger pectin cerium (IV) iodate: synthesis, characterization, and analytical applications, Desal. Wat. Treat., 57 (2016) 468–475.

[38] G. Sharma, Mu. Naushad, D. Pathania, A. Kumar, A multifunctional nanocomposite pectin thorium (IV) tungstomolybdate for heavy metal separation and photoremediation of malachite green, Desal. Wat. Treat., 57 (2016) 19443–19455.

[39] M.M. Rao, D. Ramana, K. Seshaiah, M. Wang, S. Chang, Removal of some metal ions by activated carbon prepared from *Phaseolus aureus* hulls, J. Hazard. Mater., 166 (2009) 1006–1013.

[40] J.A. Laszlo, F.R. Dintzis, Crop residues as ion exchange materials, treatment of soybean hull and sugar beet fiber (pulp) with epichlorohydrin to improve cation-exchange capacity and physical stability, J. Appl. Polym. Sci., 52 (1994) 531–538.

[41] S. Doyurum, A.C. Elik, Pb (II) and Cd (II) removal from aqueous solutions by olive cake, J. Hazard. Mater., 138 (2006) 22–28.

[42] A. Kumar, N.N. Rao, S.N. Kaul, Alkali treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal-preparation, characterization and application, Bioresour. Technol., 71 (2000) 133–142.

[43] A.A. Abia, J.C. Igwe, Sorption kinetics and intraparticulate diffusivities of Cd, Pb, and Zn ions on maize cob, Afr. J. Biotechnol., 4 (2005) 509–512.

[44] K.K. Wong, C.K. Lee, K.S. Low, M.J. Haron, Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions, Chemosphere, 50 (2003) 23–28.

[45] E. Pehlivan, T. Altun, S. Parlay, Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions, J. Hazard. Mater., 164 (2009) 982–986.

[46] K.A. Krishnan, T.S. Anirudhan, Removal of cadmium (II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar cane bagasse pith: kinetics and equilibrium studies, Water SA, 29 (2003) 147–156.

[47] N.A.A. Babarinde, Adsorption of zinc (II) and cadmium (II) by coconut husk and goat hair, J. Pure Appl. Sci., 5 (2002) 81–85.

[48] N. Meunier, J. Laroulandie, J.F. Blais, R.D. Tyagi, Cocoa shells for heavy metal removal from acidic solutions, Bioresour. Technol., 90 (2003) 255–263.

[49] T.W. Tee, R.M. Khan, Removal of lead, cadmium and zinc by waste tea leaves, Environ. Technol. Lett., 9 (1988) 1223–1232.

[50] G. Annadurai, R.S. Juang, D.L. Lee, Adsorption of heavy metals from water using banana and orange peels, Water Sci. Technol., 47 (2002) 185–190.

[51] Y. Zhang, L. Xiaoli, L. Yanfeng, Influence of solution chemistry on heavy metals removal by bioadsorbent tea waste modified by poly (vinyl alcohol), Desal. Wat. Treat., 53 (2015) 2134–2143.

[52] M.A. Islam, Statistics on Bangladesh Tea Industry, Project Development Unit, Bangladesh Tea Board, 2002, pp. 5–98.

[53] S. Cay A. Uyanik, A. Ozajik, Single and binary component adsorption of copper (II) and cadmium (II) from aqueous solutions using tea-industry waste, Sep. Purif. Technol., 38 (2004) 273–280.

[54] X. Bai Z. Ye, Y. Li, Preparation and characterization of a novel macroporous immobilized microorganism carrier, Biochem. Eng. J., 49 (2010) 264–270.

[55] E.S.A. Hegazy, K.M. El-Salmawy, A.A. El-Naggar, Recovery of heavy metals from aqueous solution by using radiation

crosslinked poly(vinyl alcohol), J. Appl. Polym. Sci., 94 (2004) 1649–1656.

[56] N.K. Mishra, Removal of chromium (VI) from aqueous solution using low cost adsorbent, J. Indian Chem. Soc., 80 (2003) 661–662.

[57] M.A. Hossain, M. Kumita, Y. Michigami, S. Mori, Kinetics of Cr (VI) adsorption on used black tea leaves, J. Chem. Eng. Jpn., 38 (2005) 402–408.

[58] E. Malkoc, Y. Nuhoglu, Fixed bed studies for the sorption of chromium (VI) onto tea factory waste, Chem. Eng. Sci., 61 (2006) 4363–4372

[59] X. Bai, Z.F. Ye. Y.Z. Qu, Y. F. Li, Z.Y. Wang, Immobilization of nanoscale Fe0 in and on PVA microspheres for nitrobenzene reduction, J. Hazard. Mater., 172 (2009) 1357–1364.

[60] United Nations Environmental Protection Agency (USEPA), Method 7196A: Chromium, hexavalent (Colorimetric), 1992. Available at: https://www.epa.gov/sites/production/files/2015-12/documents/7196a.pdf (Accessed on 06 February 2019).

[61] M.T. Sikder, Y. Mihara, M.S. Islam, T. Saito, S. Tanaka, M. Kurasaki, Preparation and characterization of chitosan–caboxymethyl-β-cyclodextrin entrapped nanozero-valent iron composite for Cu (II) and Cr (IV) removal from wastewater, Chem. Eng. J., 236 (2014) 378–387

[62] V.C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solutions onto RHA, J. Hazard. Mater., 134 (2006) 257–267

[63] Y. Zhang, Y.F. Li, X. Li, L. Yang, X. Bai, Z. Ye, Selective removal for Pb^{2+} in aqueous environment by using novel macroreticular PVA beads, J. Hazard. Mater., 181 (2010) 898–907.

[64] P. Pavasnt, R. Apiratikul, V. Sungkhum, Y.P. Suthiparin, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera,* Bioresour. Technol., 97 (2006) 2321–2329.

[65] E. Klimiuk, M. Kuczajowska-Zadrożna, The effect of poly (vinyl alcohol) on cadmium adsorption and desorption from alginate adsorbents, Pol. J. Environ. Stud., 11 (2002) 375–384.

[66] B. Shah, U. Chudasama, Synthesis and characterization of a novel hybrid material titanium amino tris (methylenephosphonic acid) and its application as a cation exchanger, Ind. Eng. Chem. Res., 53 (2014) 17454–17467.

[67] B. Shah, U. Chudasama, Kinetics, thermodynamics and metal separation studies of transition (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and heavy metal ions (Cd^{2+}, Hg^{2+}, Pb^{2+}) using novel hybrid ion exchanger—zirconium amino tris methylene phosphonic acid, Sep. Sci. Technol., 54 (2019) 1560–1572.

[68] V.K. Garg, R. Gupta, R. Kumar, R.K. Gupta, Adsorption of chromium from aqueous solution on treated sawdust, Bioresour. Technol., 92 (2004) 79–81.

[69] S.K. Prabhakaran, K. Vijayaraghavan, R. Balasubramanian, Removal of Cr (VI) ions by spent tea and coffee dusts: reduction to Cr (III) and biosorption, Ind. Eng. Chem. Res., 48 (2009) 2113–2117.

[70] S.H. Hasan, K.K. Singh, O. Prakash, M. Talat, Y.S. Ho, Removal of Cr (VI) from aqueous solutions using agricultural waste 'maize bran', J. Hazard. Mater., 152 (2008) 356–365.

[71] K.T. Hanit, S.T. Sumint, K.P. Laxmi, Removal of chromium (VI) from synthetic waste water using tea waste as a low cost adsorbent, STM J. Water Pollut. Pur. Res., 2 (2015) 70–74.

[72] N.D. Pragesh, P. Nishtha, T. Hannah, Adsorption of Cr (VI) from aqueous solution on tea waste and coconut husk, Indian J. Chem. Technol., 19 (2012) 111–117.

[73] M.K. Kabiraz, I.A. Jahan, S.M. Masum, M.M. Islam, S.M. Hassan, B. Saha, H.N. Purvin, Effective removal of chromium (VI) ions from tannery effluent using chitosan-alumina composite, Int. Res. J. Pure Appl. Chem., 10 (2015) 1–12.

[74] B. Manjeet, G. Umesh, S. Diwan, V.K. Garg, Removal of Cr (VI) from aqueous solutions using pre-consumer processing agricultural waste: a case study of rice husk, J. Hazard. Mater., 162 (2009) 312–320.

[75] S. Arris, M.B. Lehocine M. Abdeslam-Hassen, Sorption study of chromium sorption from wastewater using cereal by-products, Int. J. Hydrogen Energy, 41 (2016) 10299–10310.

[76] S. Babel, T.A. Kurniawan, Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, Chemosphere, 54 (2004) 951–967.

[77] I. Nilisha, P. Yogesh, Management of hexavalent chromium (Cr6+) from industrial waste using low cost waste biomass, Procedia Soc. Behav. Sci., 133 (2014) 219–224.

[78] T. Srinath, T. Verma, P.W. Ramteke, S.K. Garg, Cr (VI) biosorption and bioaccumulation by chromate resistant bacteria, Chemosphere, 48 (2002) 427–435

[79] H. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of chromium (VI) from aqueous solution by cone biomass of *Pinus sylvestris,* Bioresour. Technol., 85 (2002) 155–158.

[80] N.R. Bishnoi, G.A. Garima, Biosorption of copper from aqueous solution using algal biomass, J. Sci. Ind. Res., 63 (2004) 813–816

[81] W. Liu, L. Yang, S. Xu, Y. Chen, B. Liu, Z. Li, C. Jiang, Efficient removal of hexavalent chromium from water by an adsorption–reduction mechanism with sandwiched nanocomposites, RSC Adv., 8 (2018) 15087–15093.

[82] J.H. Chen, K.C. Hsu, Y.M. Chang, Surface modification of hydrophobic resin with tricaprylmethylammonium chloride for the removal of trace hexavalent chromium, Ind. Eng. Chem. Res., 52 (2013) 11685–11694.

[83] K. Zhu, Y. Gao, X.L. Tian, C.L. Chen, Polyaniline-modified Mg/Al layered double hydroxide composites and their application in efficient removal of Cr (VI), ACS Sustain. Chem. Eng., 4 (2016) 4361–4369.

[84] Y.H. Li, B. Xia, Q.S. Zhao, F.Q. Liu, P. Zhang, Q.J. Du, D.C. Wang, D. Li, Z.H. Wang, Y.Z. Xia, Removal of copper ions from aqueous solution by calcium alginate immobilized kaolin, J. Environ. Sci., 23 (2011) 404–411.

[85] R. Treybal, Mass Transfer Operations, McGraw-Hill, New York, 1980.

[86] J.C. Igwe, A.A. Abia, Maize cob and husk as adsorbent for removal of Cd, Pb and Zn ions from waste water, Phys. Sci., 2 (2003) 283–294.

[87] S. Qaiser, A.R. Saleemi, M. Umar, Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: batch and column study, J. Hazard. Mater., 166 (2009) 998–1005

[88] T. Vidhyadevi, A. Murugesan, S.S. Kalaivani, M.P. Premkumar, V. Vinothkumar, L. Ravikumar, S. Sivanesan, Evaluation of equilibrium, kinetic, and thermodynamic parameters for adsorption of Cd^{2+} ion and methyl red dye onto amorphous poly (azomethinethioamide) resin, Desal Wat. Treat., 52 (2014) 3477–3488.

[89] S.S. Kalaivani, T. Vidhyadevi, A. Murugesan, K.V. Thiruvengadaravi, D. Anuradha, S. Sivanesan, L. Ravikumar, The use of new modified poly (acrylamide) chelating resin with pendent benzothiazole groups containing donor atoms in the removal of heavy metal ions from aqueous solutions, Water Res. Ind., 5 (2014) 21–35.

[90] Z. Aksu, Equilibrium and kinetic modelling of cadmium (II) biosorption by C. vulgaris in a batch system: effect of temperature, Sep. Purif. Technol., 21 (2001) 285–294.

[91] M.H. Jnr, A.I. Spiff, Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by *Caladium bicolor* (wild cocoyam) biomass, Electron. J. Biotechnol., 8 (2005) 162–169.

[92] Z. Aksu, T.A. Kutsal, A bio-separation process for removing Pb (II) ions from wastewater by using C. vulgaris, J. Chem. Technol. Biotechnol., 52 (1991) 108–118.

[93] M.X. Loukidou, A.I. Zouboulis, T.D. Karapantsios, K.A. Matis, 2004). Equilibrium and kinetic modeling of Cr (VI) biosorption by *Aeromonas cavicic*, Colloids Surf., A, 242 (2004) 93–104.

[94] A. Ozer, D. Ozer, Comparative study of the biosorption of Pb (II), Ni (II) and Cr (VI) ions onto S. cerevisiae: determination of biosorption heats, J. Hazard. Mater., 100 (2003) 219–229.

[95] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[96] H. Freundlich, W.J. Helle, Rubber die adsorption in Lusungen, J. Am. Chem. Soc., 61 (1939) 2–28.

[97] C.S. Zhu, L.P. Wang, W.B. Chen, Removal of Cu (II) from aqueous solution by agricultural by-product: peanut hull, J. Hazard. Mater., 168 (2009) 739–746.

[98] L.Y. Wang, L.Q. Yang, Y.F. Li, Y. Zhang, Ma, Z. Ye, Study on adsorption mechanism of Pb (II) and Cu (II) in aqueous solution using PS-EDTA resin, Chem. Eng. J., 163 (2010) 364–372.

[99] L. Wang, J. Zhang, R. Zhao, Y. Li, C. Li, C. Zhang, Adsorption of Pb (II) on activated carbon prepared from *Polygonum orientale* Linn: kinetics, isotherms, pH, and ionic strength studies, Bioresour. Technol., 101 (2010) 5808–5814.

[100] S.S. Gupta, K.G. Bhattacharyya, Kinetics of adsorption of metal ions on inorganic materials: a review, Adv. Colloid Interface Sci., 162 (2011) 39–58.

[101] H. Chen, G. Dai, G.L. Zhao, J. Zhong, A.G. Wu, H. Yan, Removal of copper (II) ions by a biosorbent—*Cinnamomum camphora* leaves powder, J. Hazard. Mater., 177 (2010) 228–236.

[102] V.K. Monika, K. Garg, Kadirvelu, Chromium (VI) removal from aqueous system using *Helianthus annuus* (sunflower) stem waste, J. Hazard. Mater., 162 (2009) 365–372.

[103] Mu. Naushad, T. Ahamad, G. Sharma, A.H. Al-Muhtaseb, A.B. Albadarin, M.M. Alam, Z.A. ALOthman, S.M. Alshehri, A.A. Ghfar, Synthesis and characterization of a new starch/SnO_2 nanocomposite for efficient adsorption of toxic Hg^{2+} metal ion, Chem. Eng. J., 300 (2016) 306–316.