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Removal of chromium (VI) from aqueous solution using chemically modified orange *(citrus cinensis)* peel

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Abstract: *The removal of Cr (VI) from aqueous solutions onto chemically modified orange peel was studied at varying initial metal concentrations, adsorbent doses, pH and contact times. Batch experiments were carried out under optimized conditions to evaluate the adsorption capacity of the orange peel chemically modified with sodium hydroxide. The residual Cr (VI) concentrations after biosorption were analyzed by FAAS. The biosorbent was characterized by FT-IR spectroscopy and BET. The characterization of the orange peel biomass suggested the possible contribution of carboxyl and hydroxyl groups in Cr (VI) biosorption. Chemically modified orange peel exhibited more adsorption potential as compared to the raw orange peel. The biosorption efficiency of the orange peel was dependent on the pH of the Cr (VI) solution, with pH 2 being optimal. The removal rate of Cr (VI) ions increased with increase in contact time and remained constant after an equilibrium time of 180 min. The removal of Cr (VI) ions increased with increase in biosorbent concentration with the optimal adsorbent dosage at 4.0 mg/L. The increase in initial Cr (VI) ion concentration led to an increase in the percentage removal of Cr (VI). The adsorption data fitted well with the Freundlich isotherm model with* $R^2 = 0.987$ *for the raw orange peel and* $R^2 = 0.995$ *for the modified orange peel. The Freundlich constants* K_f *and n were 97.07 [mg/g (L/mg)*^{n}*] and 0.79 (g/L) for the raw orange peel and 139.0 [(mg/g)(L/mg)*^{n}*] and 0.815 (g/L) for modified orange peel respectively. The present study revealed that orange peel which is a low cost agricultural material could be used as an efficient sorbent for the removal of Cr(VI) from aqueous solutions and that chemical modification of the biosorbent using sodium hydroxide enhanced adsorption capacity.*

Keywords: *Adsorption isotherm, Biosorption, Chemical modification, Chromium (VI), Orange peel*

I. Introduction

The removal of heavy metals from industrial effluents is a field of research that has attracted increasing attention from the scientific community as the quest for green chemistry takes centre stage. Heavy metals in wastewaters are hazardous to the environment and therefore their removal before waste water discharge is apparent [1]. These substances are stable and persistent environmental contaminants since they are non-biodegradable [2]. Chromium is one of the toxic metals often found in effluents discharged from industries involved in paints, pigments, dyes, textiles, leather tanning, electroplating, metal finishing, nuclear power plants and chromate preparation [3]. Chromium can exist in several oxidation numbers but only chromium (III) and chromium (VI) are stable enough to occur in the environment. The hexavalent form is more toxic than the trivalent one [4].

Inhalation and retention of Cr (VI) containing material can cause damage to internal organs [5]. Skin contact of chromium (VI) compounds can lead to skin diseases [6]. The toxicological impact of chromium (VI) originates from its oxidizing ability as well as from the formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the cell [7].

Many physicochemical methods for heavy metal removal from aqueous solution have been developed. These methods include precipitation, resin chelation, electrochemical deposition, reverse osmosis, ion exchange, coagulation and solid-phase extraction [8]. These techniques however, have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge [9]. Cost effective alternative technologies to conventional methods are essential for the removal of heavy metals from industrial effluent. An innovative technique that is both efficient and economical is termed bioremediation or biosorption [10-12]. This has resulted in the easy and efficient removal of metals that could not be removed by other techniques. The major advantages of biosorption over other conventional treatment methods include low cost, high efficiency, minimization of chemical and biological sludge, and regeneration of biosorbent by desorption techniques and possibility of metal recovery [13]. In recent years, certain raw waste products from agricultural produce, like cocoa shell [14], rice husk, [15], olivestone [16], garlic peel [17], sawdust [18], Brazilian pine-fruit shell [19] banana peel [20], *Carica papaya* (pawpaw) seed [21], *Anabaena* and *Vetiveria* [22] and date tree leaves [23], have been tested for removal of metals from effluents. The utilization of these raw plant materials as biosorbents has been limited due to the leaching of organic compounds such as, cellulose lignin, pectin and lignocellulose into solution. Chemical modification on solid biomasses has been used as a remedy to improve their physical, chemical and biosorption capacity [24, 25].

The application of orange peel as a biosorbent material presents strong potential due to its main components of cellulose, pectin, hemicellulose and lignin which contain functional groups as possible binding sites for metals [26], [27]. Orange peel is an attractive and economic alternative for the removal of metal ions from waste water. The aim of this work was to study the adsorption capacity of orange peel that was chemically modified with sodium hydroxide for removing Cr (VI) ions from aqueous solutions. The effects of contact time, initial metal ion concentration, pH and biosorbent dosage on the biosorption efficiency were also investigated. The equilibrium data was tested on adsorption-type isotherms.

II. Materials and methods

2.1 Chemicals and instruments

All the chemicals used in this study were of analytical grade. $K_2Cr_2O_7$, HNO_3 and NaOH were supplied by Skylabs. Instruments used were Flame Atomic Absorption Spectrometer (FAAS) (Spectra AA 50B Varian), Fourier Transform Infra-red Spectrophotometer (FT-IR) (Digilab Merlin 2000 model Samitar) and Brunauer Emmett Teller (BET) (Micromeritis ASAP 2020).

2.2 Preparation of biosorbents

2.2.1 Preparation of raw orange peel

The biowaste material used for the study was obtained from a local market. The orange peels were washed with distilled water, dried in an oven at 80ºC to constant mass and crushed into smaller particles of approximate size ≤ 200 µm. The resulting powder was washed with distilled water several times, oven dried at 80ºC to constant mass and then put in air tight bottles and stored in a desiccator for further use in FT-IR analysis, batch experiments and chemical modification.

2.2.2 Chemical modification of orange peel

The crushed orange peel was treated with NaOH to improve the efficiency of metal uptake. In this study 100 g of dried orange peel biomass was treated with 1 L of (0.1M) NaOH for 48 h with shaking at 120 rpm. After repeated decantation and filtration, the modified biomass was washed with distilled water until the pH value of solutions was neutral. The modified orange peel was then oven dried at 80°C to constant mass, put in air tight bottles and stored in a desiccator for further use in batch experiments and FT-IR analysis.

2.3 Characterization of biosorbent

FT-IR spectroscopy was used to identify the functional groups in the orange peel biosorbent. FT-IR spectra of the biosorbent before and after biosorption of Cr (VI) were recorded in the range 4000-400 cm^{-1} using a Digilab Merlin 2000 model FT-IR spectrometer with KBr discs (Sigma).

2.4 Preparation of Cr (VI) stock solution

Stock solution (1000 mg/L) of Cr (VI) was prepared by dissolving $K_2Cr_2O_7$ in deionized water. For biosorption experiments, Cr (VI) solutions (100 mg/L) were prepared from the stock solution by dilution. Calibration standards 5, 10, 20, 50 and 100 mg/L were prepared and used for calibrating the FAAS. The pH of the solution was adjusted using either 0.1 M HNO_3 or 0.1 M NaOH solutions.

2.5 Batch equilibrium studies

50 mL of Cr (VI) solution (100 mg/L) at the uncontrolled pH was taken in a 250 mL conical flask with a fixed dosage (2 g/L) of sorbent. The mixture was agitated on a shaker at a speed of 120 rpm at room temperature for a time which was sufficient for the chromium uptake process to reach equilibrium. Batch adsorption studies were performed at room temperature at different pH (1, 2, 3, 4, 6, and 8), sorbent dose (0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 3.0, 4,0 and 5.0 g), initial Cr (VI) concentration (2, 5, 10, 20, 50 and 100 mg/L) and contact time (30 min, 1 h, 2 h, 3 h and 4 h) to obtain the equilibrium data. All experiments were performed in replicates with reproducibility within at most 5% error and the results average was reported.

After attainment of equilibrium, the samples were filtered through Whatman No. 1 filter paper and the residual Cr (VI) concentration in the filtrate was estimated using the FAAS. The amount of metal ion adsorbed per gram of biomass and the sorption efficiency (%) were calculated according to the following expressions;

$$Q_e = \frac{(C_o + C_e)V}{M} \qquad (1)$$

$$Sorption\ efficiency = \frac{(C_o - C_o)}{C_o} \times 100 \qquad (2)$$

Where, Q_e is the amount of Cr (VI) biosorbed per gram of biomass, mg/g, C_o and C_e are the initial and equilibrium concentrations of Cr (VI) (mg/L) respectively, V is the volume of solution (L), and M is the mass of biosorbent (g).

The experimental data tested for conformity to Langmuir and Freundlich isotherm models from their linearized equations. The R^2 (regression coefficient square value) and isotherm constants values were deduced from the models.

III. Results and discussion

3.1 Characterization of the biosorbent

3.1.1 FT-IR analysis of biosorbent

Infrared techniques have been used for identification of functional groups in biomaterials. In order to determine which functional groups were responsible for metal uptake, FT-IR spectra of the biosorbent before and after Cr (VI) bonding were recorded in the range of 4000-400cm^{-1}. The FT-IR spectrum of raw orange as shown in Fig. 1 exhibits a broad peak at 3420 cm^{-1}, which is characteristic of the O-H stretching vibrations of cellulose, pectin, hemicellulose, and lignin components. Free hydroxyl groups and bonded OH bands of carboxyl group were observed as the OH stretching vibrations occurred within a broad range of frequencies [28]. The band at 2920 cm^{-1} is attributed to C-H stretching vibration of methyl, methylene and methoxy groups. The peak observed at 1744 cm^{-1} is the stretching vibration due to non-ionic carboxyl groups (-COOH, -$COOCH_3$), and may be due to carboxylic acids or their esters. The peaks at 1760 and 1620 cm^{-1} may be due to asymmetric and symmetric stretching vibrations of the carbonyl groups in ionic carboxylic groups respectively. The peaks between 1400 and 1200 cm^{-1} may be as a result of symmetric stretching of -COO$^-$ of pectin. Peaks at 1060 cm^{-1} may be due to stretching vibration of C–OH of alcohols and carboxylic acids [29].

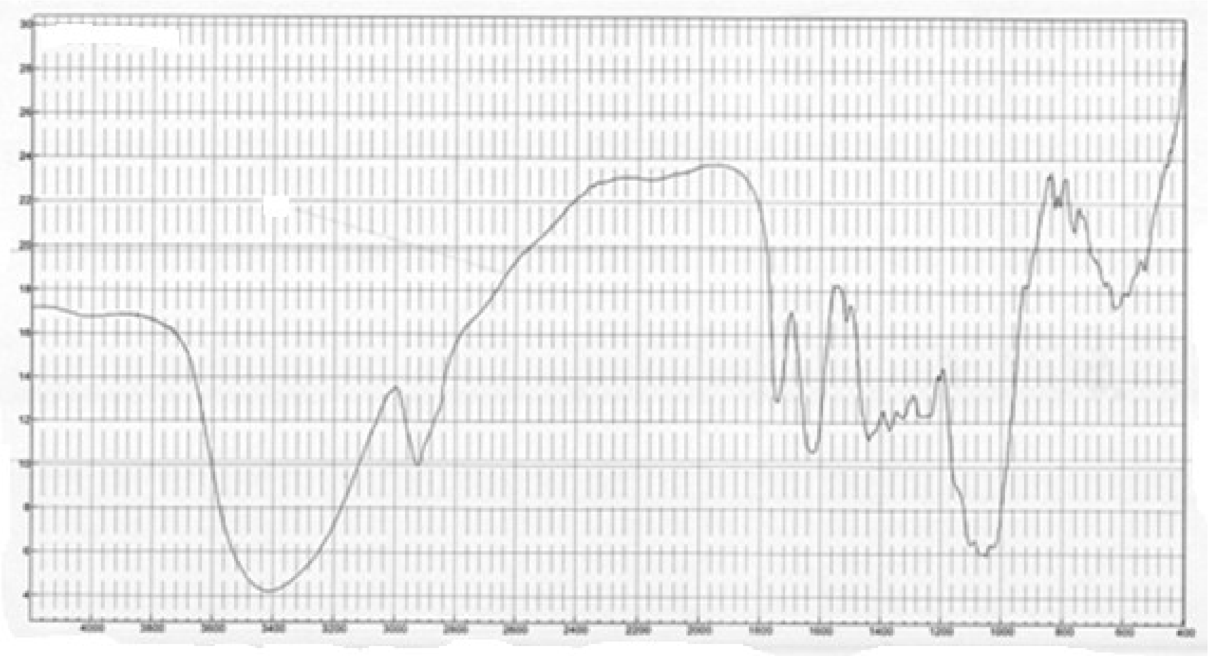

Fig 1. FT-IR spectrum of raw orange peel.

The FT-IR spectrum of orange peel modified with NaOH in Fig. 2 shows the weakening intensity of the peak at 1740 cm^{-1} indicating that the methyl esters were hydrolyzed with NaOH and the ester group was converted to the carboxylate ion [30].

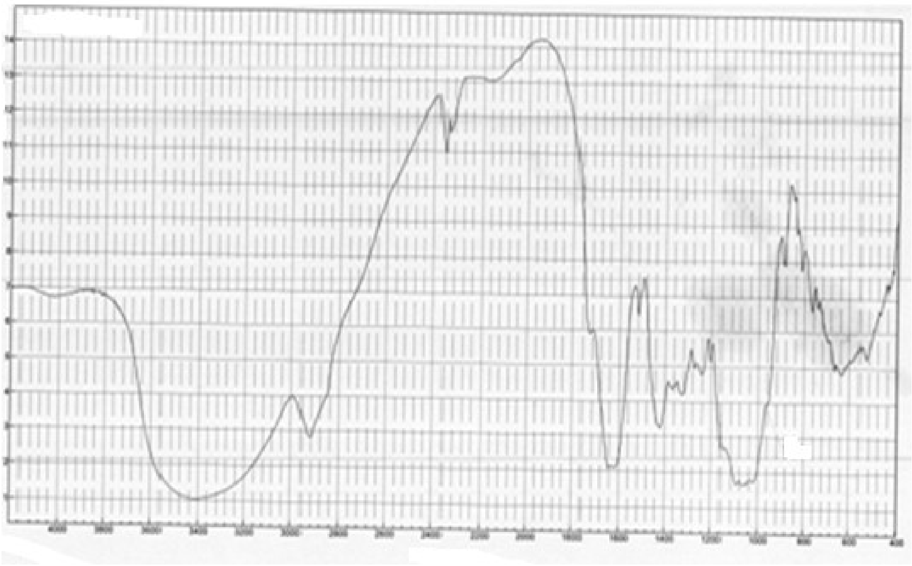

Fig. 2. FT-IR spectrum of chemically modified orange peel.

The FT-IR spectra after Cr (VI) sorption is shown in Fig. 3. Comparing the spectra before and after sorption of Cr (VI), differences in the position of the absorbance peaks appeared. The asymmetrical stretching vibration at 3420 cm^{-1} after the biosorption of Cr (VI) is significantly distorted suggesting that chemical interactions occur between the metal ions and the hydroxyl groups on the biosorbent surface. Notable changes in hydroxyl groups' peak were observed and thus further confirming their involvement in the sorption process. Slight shifting was observed on the asymmetric and symmetric C=O band (1760 cm^{-1} to 1640 cm^{-1} and 1620 cm^{-1} to 1380 cm^{-1}, respectively). The peak at 1060cm^{-1} (C-OH stretching of alcohols) disappeared while the peak at 1744 cm^{-1} shifted to 1640 cm^{-1} as the OH was involved in binding of Cr (VI). These results indicate that carboxyl and hydroxyl groups are involved in Cr (VI) bonding to the orange waste.

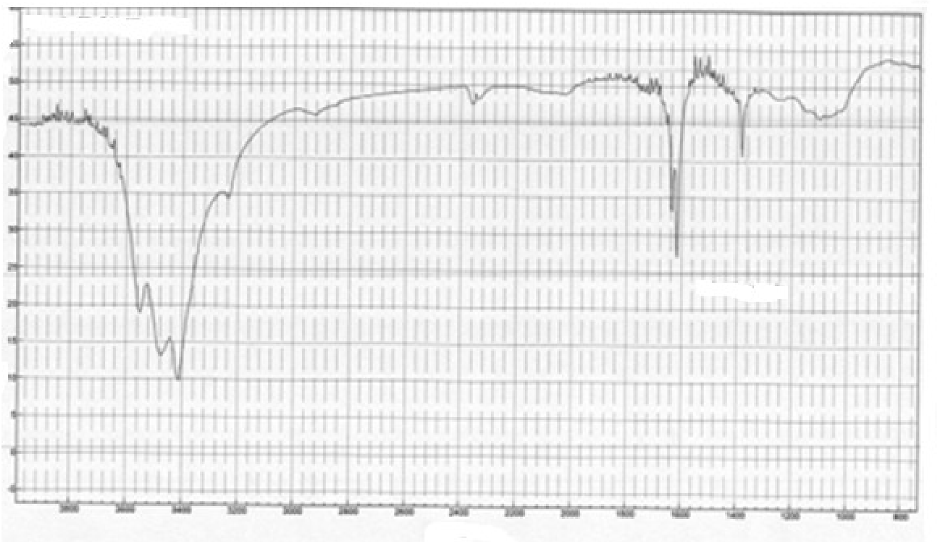

Fig. 3. FT-IR spectrum of raw orange peel after Cr (VI) sorption.

3.1.2 Surface area analysis

Table 1 gives a summary of some of the physical properties of the orange peel which were determined by BET. The N_2 adsorption gave the specific surface area (S_{BET}) of 0.8311 m^2/g and the value is close to other values reported in literature for orange peels [30].

Table 1. Physical properties of orange peel

Property	Magnitude
Surface area (m^2g^{-1})	0.8311
Total pore volume (cm^3g^{-1})	0.000246
Pore diameter (Å)	23.699

3.2 Batch biosorption experiments

3.2.1 Effect of pH on Cr (VI) uptake

The pH of the solution affects the protonation of the functional groups on the biomass as well as the metal chemistry. Fig. 4 shows the removal of Cr (VI) at varying pH range applying an initial constant Cr (VI) concentration of 100 mg/L, biosorbent concentration of 2 g/L and contact time of 180 min. As illustrated in Fig. 4, the maximum adsorption of Cr (VI) ions was observed at pH 2.0 for both biosorbents and significantly decreased by increasing the pH values up to 8.0. This observation may be attributed to the fact that by decreasing pH, hydroxyl groups in lignocellulosic wastes, tend to diffuse into the solution, so, it would be more probable for $Cr_2O_7^{2-}$ ions to be adsorbed on available adsorption sites. At lower pH, the biosorbent is positively charged due to protonation resulting in electrostatic attraction with the dichromate [31]. A sharp decrease in adsorption above pH 2 may be due to occupation of the adsorption sites by anionic species like $HCrO_4^-$, $Cr_2O_7^{2-}$ or CrO_4^{2-} which retards the approach of such ions further toward the sorbent surface [32, 33].

Uptake of Cr (VI) increased markedly with decreasing pH. At pH 2 and 8 corresponding uptake yield values were found to be 37.2% and 17.4 % for raw orange peel, 38.6% and 18.6 % for chemically modified orange peel respectively. The decrease in adsorption at high pH values may be due to the competitiveness of the oxyanion of chromium and OH^- ions in the bulk. These results suggest that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biosorbent [34-37].

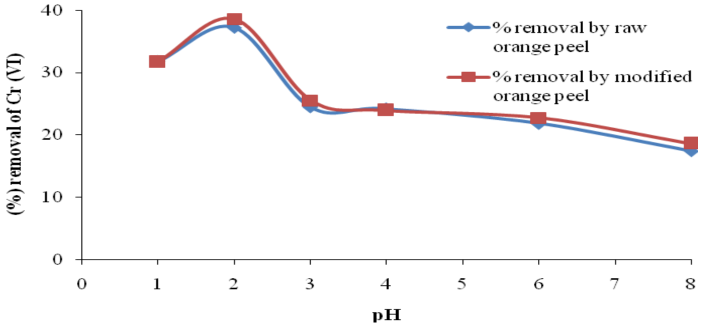

Fig. 4. Effect of pH on the biosorption of Cr (VI).

3.2.2 Effect of contact time on Cr (VI) uptake

The time required for the biosorption of Cr (VI) on 2 g/L raw and chemically modified orange peels to equilibrate was studied. Fig. 5 illustrates the effect of contact time on adsorption efficiency of Cr (VI). The initial concentration was kept constant at 100 mg/L and pH was set at 2.0. The experimental data indicate that Cr (VI) ion adsorption increased with increasing contact time. This is due to prolonged contact between the sorbent surface and the chromium ion. Fig. 5 shows that adsorption capacity sharply increased with increase in time and attains equilibrium in 180 min for both adsorbents (29.8% for modified orange peel and 29.6% percentage uptake for raw orange peel respectively). The rate of adsorption is higher within the first 20 min due to large available surface area of the biosorbent and a high concentration gradient. After the active sites of the adsorbent gets exhausted, when equilibrium is attained, the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the biosorbent particles [38].

Lower adsorption rate in the latter stage (after 180 min) was due to the difficulty encountered by Cr ions in occupying the remaining vacant surface sites because of forces between the solute molecules of the solid and bulk phase [39]. This may also be due to intraparticle diffusion process dominating over adsorption [40]. The results also indicate that chemically modified orange peel showed better sorption capacities than the raw orange peel.

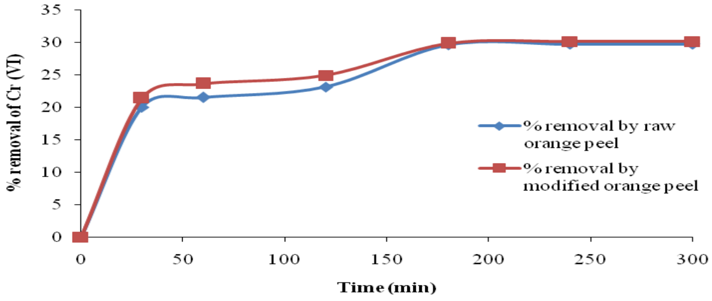

Fig. 5. Effect of contact time on the biosorption of Cr (VI).

3.2.3 Effect of biosorbent dosage on Cr (VI) uptake

The effect of biosorbent dosage on the removal of chromium (VI) at room temperature was investigated by varying the amount of sorbent from 0.2 to 5 g/L and agitated at 120 rpm for 180 min using initial Cr (VI) ion concentration of 100 mg/L and at pH value of 2.0. The results indicate that the percent removal of chromium (VI) increased with the increase in the amount of adsorbent and the removal efficiency for chemically modified orange peel was better than that of the raw orange peel as illustrated in Fig. 6.

The highest uptake was obtained at biosorbent concentration of 4 g/L for both biosorbents at 41.4% and 39.9% uptake for modified and raw orange peels respectively. The removal of metal ions increased with the increase in biosorbent concentration and equilibrium was attained after 4 g/L of adsorbent dosage for the chromium (VI) ions. This is due to availability of more biosorbent sites as well as enhanced surface area [41]. The decrease in the rate of Cr (VI) uptake at adsorbent dose greater that 2 mg/L may be due to competition of the Cr (VI) ion for the sites available [42]. Similar results are also reported by researchers for a variety of batch experiments on sorption [29, 36, 43-45].

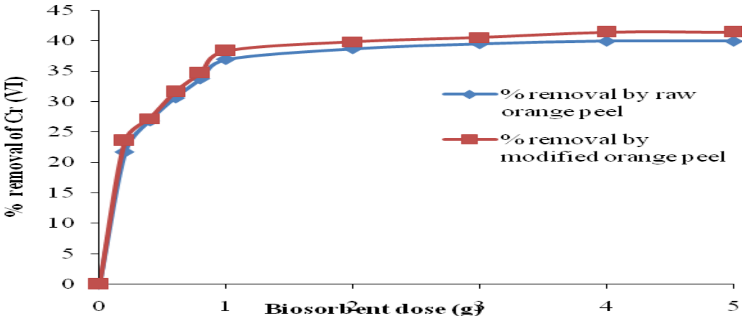

Fig. 6. Effect of biosorbent dosage on the biosorption of Cr (VI).

3.2.4 Effect of initial metal concentration on Cr (VI) uptake

Effect of initial Cr (VI) ion concentration on its removal was carried out at optimized adsorbent dose (4g/L), contact time (180 min) and pH (2.0) at room temperature by varying the metal ion concentration from 2-100 mg/L. At lower Cr (VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is smaller and subsequently the fractional adsorption process becomes independent of the initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration. The percentage of Cr (VI) ions uptake for both biosorbents increased with the initial metal concentrations as expected and remained nearly constant after equilibrium time as shown in Fig. 7. It also showed that the adsorption was rapid in the initial stages upto 50 mg/L and gradually decreased with progress of adsorption. Similar results were obtained by [46]. This can be attributed to the saturation of sorption sites on adsorbents. The initial concentration provides a significant driving force to overcome all mass transfer resistance of metals ion between aqueous and solid phases. Hence, a higher initial concentration of Cr (VI) increased the rate of biosorption [33].

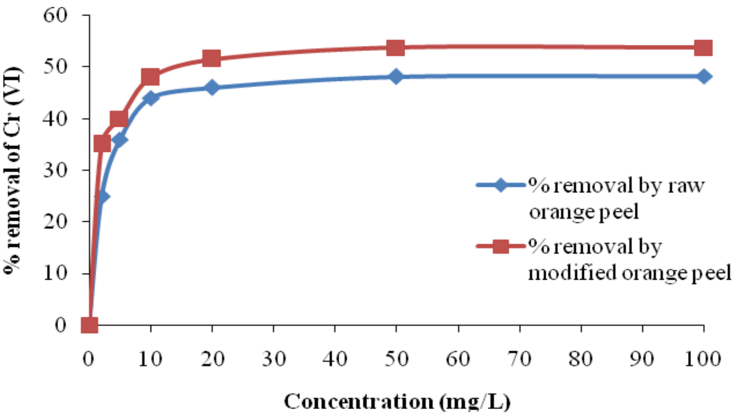

Fig. 7. Effect of initial metal concentration on the biosorption of Cr (VI).

3.3 Adsorption isotherms

The equilibrium biosorption of Cr (IV) ions was modeled using the adsorption-type isotherm. The Freundlich isotherm model produce a better fit than the Langmiur one and is therefore used to describe the biosorption equilibrium of the biomass. The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules. This can be linearized as;

$$Log\,Q_e = log\,K_f + \frac{1}{n} log\,C_e \qquad (3)$$

Where Q_e is the amount of chromium (VI) adsorbed by orange peel biomass (mg/g) C_e is equilibrium adsorbate concentration in mg/L, K_f is the adsorbent capacity measure and n is the adsorption intensity.

Fig. 8 shows the Freundlich isotherm model of Cr (VI). In the Freundlich model a linear plot of log Q_e vs log C_e give a straight line for both biosorbents with R^2 = 0.987 and 0.995 for the raw and the chemically modified orange peels respectively. The R^2 values of the Freundlich model is greater than 0.95, indicating applicability of this model. The equilibrium data agreed well with the Freundlich isotherm than the Langmuir one and thus for this study only the former was reported. The values for K_f and n were found to be (97.07; 0.79) and (139; 0.82) for the raw and modified orange peels respectively. The adsorption capacity (K_f) of Cr (VI) on modified orange peel is 139 mg/g which is higher than that of raw orange peel (K_f = 97.07) thus indicating the efficiency of the sodium hydroxide modification process.

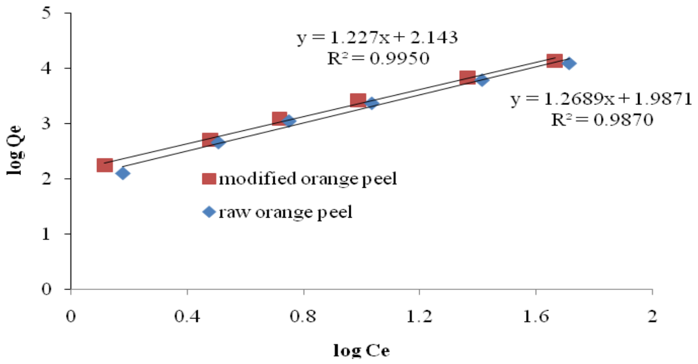

Fig. 8. Freundlich isotherm model for biosorption of Cr (VI).

A comparison of Freundlich parameters for the biosorption of Cr (VI) in the present research and in other studies where different biosorbents were used are shown in Table 2. It can be seen that the K_f and R^2 values for the current study are higher than those obtained in past studies (Table 2) and thus it is observed that modified orange peel is a better biosorbent for the removal of Cr (VI) ions from aqueous solution.

Table 2. Overview summary of Freundlich isotherm parameters on selected studies on Cr (VI) sorption by biosorbents.

Biosorbent	**R^2**	**n** (g/L)	**K_f** [mg/g (L/mg)^n]	**Reference**
Raw wheat husk	0.9171	2.237	4.5708	[41]
Raw maize bran	0.8910	4.470	0.313	[44]
Raw sugarcane bagasse	0.8909	2.08	2.9471	[41]
Raw pine needles	0.9843	3.74	21.22	[43]
Raw coconut husk	0.9627	0.788	0.02468	[44]
Oxalic acid treated tamarind fruit shell	0.9800	0.800	4.8700	[28]
NaOH-modified coconut husk	0.9595	1.088	0.10864	[44]
Raw orange peel	0.9870	0.79	97.07	(Present study)
NaOH-modified orange peel	0.9950	0.82	139.0	(Present study)

IV. Conclusion

The modification of orange peel with sodium hydroxide enhances the removal efficiency of Cr (VI) ions from aqueous solutions. Characterization of the biomass suggested the possible contribution of carboxyl and hydroxyl groups of the biomass in Cr (VI) biosorption. The removal of Cr (VI) from aqueous solutions is strongly depended on pH of the solution, adsorbent dosage, initial Cr (VI) concentration, and contact time. The maximum adsorption of Cr (VI) was obtained at pH 2.0, adsorbent dosage of 4.0 mg/L and a contact time of 180 min. The biosorption equilibrium data fitted well to the Freundlich isotherm. The adsorption capacities (K_f) were 97.07 and 139.0 mg/g for raw and chemically modified orange peels respectively. Orange peel is an easily available material from citrus processing industries and can therefore be applied for the removal of Cr (VI) in industrial effluent before it is discharged into water bodies.

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