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An Efficient and Low-Cost Indigenous Material for Removal of Hexavalent Chromium from Industrial Effluents

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Abstract. An indigenous biosorbent originated from orange peel was scrutinized the remediation of hexavalent chromium (Cr^{+6}) from industrial effluents. The analytical influences of different biosorption parameters such as biosorbent dosage, contact time, Cr^{+6} concentration, pH and temperature were also studied. The physical modeling study revealed that the biosorption of Cr^{+6} on orange peel biosorbent (OPB) followed the rate of kinetic pseudo second order with a multilayer biosorption. Meanwhile, the estimated mean sorption energy (E) indicated the chemisorption surface mechanism for the biosorption of Cr^{+6} on the surface of OPB. The thermodynamic changes of Gibbs free energy, enthalpy and entropy showed a spontaneous and exothermic biosorption of Cr^{+6} onto the OPB. The studied material of OPB showed an efficient removal of Cr^{+6} from collected industrial effluents with % biosorption Cr^{+6} up to 94%. The experimental adsorption capacity of Cr^{+6} on OPB is 0.222 mmol/g with negligible interference. The proposed OPB is found to be an economical biosorbent for the efficient removal of Cr^{+6} ions and successfully applied on different industrial effluents with biosorption > 94%.

Keywords: orange peel biosorbent, hexavalent chromium, industrial effluents, kinetics and thermodynamics study

Introduction

The increased rate of industrialization and urbanization is one of the global issues. The wastewater of residential areas and industrial effluents are the principal sources of organic and inorganic toxicants contamination in nearby water bodies (Baig *et al*., 2014; 2013; 2012a; Matos *et al*., 2009; Zhou *et al*., 2008; Narin *et al*., 2008; Iwegbue *et al*., 2007; Karadede *et al*., 2004). Amongst the inorganic toxicant, chromium (Cr) is a primary industrial contaminant. It may exist in both trivalent (Cr^{+3}) and hexavalent (Cr^{+6}) forms of Cr in aqueous systems (Pehlivan and Cetin, 2009). Cr^{+3} is recognized as an essential form of Cr at trace levels and has very significant functions in the biological structures including protein, lipid and glucose metabolism, maintaining insulin sensitivity as well as the reduction of triglycerides and cholesterol (Narin *et al*., 2008; Krishna *et al*., 2004). Whereas, Cr^{+3} is known to be extremely toxic for humans, flora and fauna. Various physiological consequences such as gastrointestinal ulcers, lungs and dermal cancers, kidney and liver damage, dermatitis, asthma, brain tumors, diarrhea, nausea and permanent head damage, as well as the reduction in plant growth, were also reported in the literature (Ahmed *et al*., 2013; Teixeira *et al*., 2013; He *et al*., 2004). The elevated levels of Cr^{+6} are claimed in industrial wastewater (Nag *et al*., 2017). Thus, international agencies have been established a discharge limit of 2.0 mg/L for Cr^{+6} into inland surface water (Nag *et al*., 2017).

For the remediation of Cr^{+6} from industrial effluents/ wastewater, the physico-chemical methods for the separation by ion-exchange mechanism, oxidation, precipitation, reverse osmosis and so on (Qureshi *et al*., 2009; Pehlivan and Cetin, 2009; Rojas *et al*., 2005). Traditional basis removal of Cr^{+6} ion was carried out by the reduction of the Cr^{+6} at highly acidic pH of the wastewater using a suitable reducing agent. After that, the Cr^{+3} precipitated as an oxide/hydroxide as the pH increased (Maitlo, 2020; Maitlo *et al*., 2018; López-Téllez *et al*., 2011). However, this technology is cost-effective and a large volume of sludge disposal could pose an environmental risk. Adsorption methods, as a substitute are a promising technology (Cabatingan *et al*., 2001; Bailey *et al*., 1999). The key factors that should be important for the development of efficient remediation may include its cost effectiveness and certainly available materials for the treatment process.

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However, different type of adsorbents like brown coal, humic acids, chitosan, peat and hazelnut shell are adopted for the efficient remediation of Cr^{+6} (Gode and Pehlivan, 2006; Lee *et al*., 2005; Cimino *et al*., 2000). Several cheapest bio-sorbents like treated sawdust (Baral *et al*., 2006), Opuntia (Barrera *et al*., 2006), *Tamarindus indica* (Agarwal *et al*., 2006), wheat bran (Dupont and Guillon, 2003), agricultural waste (Garg *et al*., 2007), eucalyptus bark (Sarin and Pant, 2006), micro-organisms (Kiran *et al*., 2007; Deepa *et al*., 2006) and several waste products were effectively used for the removal of Cr^{+6} (Park *et al*., 2007; Liu *et al*., 2006; Verma *et al*., 2006; Saeed *et al*., 2005). All these waste materials provided effective percentages removal of Cr^{+6} at low concentrations. Similarly, orange waste material provided good removal of several heavy metals (Li *et al*., 2008; Annadurai *et al*., 2003; Ajmal *et al*., 2000). However, orange peel has more advantageous for the removal of metals from contaminated water based on the presence of chlorophyll pigments, hemicellulose, cellulose, pectin substances and limonene (López-Téllez *et al*., 2011). Orange peel is an appealing choice because it can be purchased as waste in large amounts at a low cost or for free from juice industries and shops. The proposed study aimed to characterize the biosorbent followed by the optimization of the main affecting parameters (pH, amount of biosorbent, adsorbate contents, temperature and accumulation/contact time) for the biosorption experiment for the removal of Cr^{+6}. Moreover, its sensitive, selective application on real industrial effluents/wastewater for the decontamination of Cr^{+6} was studied in detail.

Material and Method

Sampling and pre-treatment. The orange fruits as kinnow (a hybrid of two citrus cultivars as 'King' *Citrus nobilis* × 'Willow Leaf' *Citrus* × deliciosa) collected from the Tower market Hyderabad Sindh, Pakistan. The peels of the orange fruit were separated from the pulp and washed thoroughly with deionized water and dried for about one week at ambient temperature. Then the peels were pulverized and dried at 343 K in an electric oven for 2.0 h. The dried peel was ground to prepared orange peel biomass (OPB) and sieved in an electrical sieve sizer to obtain particle size > 100 µm. The resulted OPB was kept in a vacuum desicator.

Random samples of industrial effluents were collected from different industries of Hyderabad and Jamshoro from various places. The industries are classified into four categories based on their nature as food industry (FI), chemical industry (CI), textile and fabrics industry (TFI) and plastic industry (PI). Selected two to three industries for each category and collected three samples from each industry (n = 30). Industrial effluent samples collected in 1 L polyethylene plastic bottles. Then, each of the samples was tested against four quality parameters like biochemical oxygen demand (BOD), total dissolved solids (TDS), pH, electric conductivity (EC) before and after biosorption by OPB along with Cr^{+6} (AOAC, 1996).

Chemicals and reagents. Deionized water acquired from water purifier ELGA (Bucks, UK) was utilized for the experiment studies. The analytical grade reagents including HNO_3, H_2O_2, NaOH and HCl were purchased from Merck (Darmstadt, Germany). 52 mmol/L solution of Cr (stock solution) was made by dissolution 0.28 g of potassium dichromate ($K_2Cr_2O_7$) Sigma-Aldrich (Louis, USA) in 1.5% HNO_3 for making a solution of volume of 1.0 L. The pH adjusted with the addition of appropriate amount of 0.1 mol/L HCl/ NaOH solutions. The pH of solution was measured by pH meter.

Apparatus and instrumentation. The pH meter of Thermo Fisher Scientific (Massachusetts, USA) and centrifuge machine (Mechanika Phecyzyjna, Poland) were used for the pH measurement and centrifugation, respectively. Shaking experiments were done by an electric flask shaker Gallenkamp (London, England) while, grinding were performed by agate ball mixer mill Retsch GmbH and Co. (Haan, Germany). Atomic absorption spectrometer (AAS) Hitachi (Tokyo, Japan) assembled with a deuterium lamp, Cr hallow cathode lamp, flame burner and graphite furnace were used for the quantitative studies (Baig *et al*., 2014). The measuring conditions of flame and graphite furnace AAS for the determination of Cr^{+6} and total Cr were followed as reported elsewhere (Akhtar *et al*., 2017; Rajesh *et al*., 2008). The biosorption activity of biosorbent was determined by scanning electron microscope (SEM) JEOL Electronics Company (Tokyo, Japan) and furrier transform infra-red (FTIR) spectrometer Thermo Fisher Scientific (Fitchburg, WI, USA).

Batch biosorption procedure. The concentration of adsorbate (Cr^{+6}), OPB dose, pH, contact time and temperature were studied in the ranged from 0.0026-0.026 mmol/L, 0.05-0.50 g/L and 2.0-9.0, 5.0-600 min, and 298-363 $\overset{\circ}{K}$, respectively. The contents of Cr^{+6} in initial and final solutions were determined using a solid phase extraction (SPE) procedure followed by FAAS as reported elsewhere (Baig *et al*., 2012a; Rajesh *et al*., 2008).

Estimation of adsorption capacity. The adsorption capacity (q_e, mg/g) of OPB was calculated by using the equation:

$$q_e = \frac{C_i - C_e}{m} \times V \quad \text{.. (1)}$$

In the above equation, C_i and C_e are stand for the initial and final concentrations of the adsorbate (mg/L), respectively.

where:

m = the mass (dry basis) of OPB used as a biosorbent and V = abbreviated for the volume of the solution (L).

Analytical characterization procedure. Point of zero charge (pzc) of OPB was studied followed by introducing 0.10 g of OPB to 20.0 mL of 0.1M NaCl in 50 mL analytical grade beakers. The pH of resulted solutions adjusted by 0.1 M HNO_3 and 0.1 M NaOH in the pH range of 3-10. Then, the solutions mixed at 100 rpm for 24 h upto obtain the required equilibrium. The pH of each solution measured by pH meter. The change in pH (ΔpH) calculated by the difference in initial or original pH and the final pH of each solution and plotted between initial pH and the ΔpH. The point where the ΔpH is zero considered as *pzc* of OPB(Mahmood *et al*., 2011). Particles size of OPB measured by Laser scattering particle size distribution analyzer equipped with a diode laser. For FTIR spectroscopic study, the OPB sample pellets were made by pressing the mixture of the powder of OPB and potassium bromide (1:3; w/w) in a die (13-mm) under the force of 6 tonnes for about 5 min. The prepared pellets of OPB before and after loading of Cr^{+6} were analyzed by FTIR in the range of 4000 to 400 cm^{-1}. The dried OPB unloaded and loaded with Cr^{+6} coated with graphite mounted on the stubs using double-sided conductive tapes for the analyses of SEM. The coated samples were analyzed by SEM at different accelerating voltage and magnification.

Desorption procedure. The loaded Cr^{+6} on the surface of OPB were desorbed by using HCl and HNO_3 in the concentration range of 0.0-1.0 mol/L at 298 $\overset{o}{K}$ for about 30 min as reported in our previous study (Baig *et al*., 2010). The desorbed Cr^{+6} in solution separated from the biomass of OPB by filtration. The residual biomass of OPB washed and dried for further biosorption studies. The concentration of Cr^{+6} in the eluent solutions were measured by SPE microsample injection system (MIS) FAAS (Baig *et al*., 2012a; Rajesh *et al*., 2008).

Interference studies. The possible impact of co-existing ions in aqueous solution on the binding capacity of Cr^{+6} with OPB was studied in similar way as reported in our previous study (Baig *et al*., 2010). The common major ions and trace ions investigated in the range of 100-1000 and 10.0-50.0 mg/L, respectively (Baig *et al*., 2010).

Adsorption isothermal, kinetic and thermodynamic modeling. The kinetics study for the adsorption mechanism is an important tool. Lagergren explained rate of first order kinetics as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{........................ (2)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t \quad \text{.. (3)}$$

In the above equation, the abbreviated terms q_e and q_t are stand for the adsorbed concentration of Cr^{+6} (mg/g) at equilibrium condition and the time t (min), respectively.

where:

k_1 and k_2 denoted for the rate constant of first order (1/min) and second order (g/mol/min).

The biosorption of Cr^{+6} at the specific place of homogeneous sites of OBP was studied by the Langmuir isotherm model. The monolayer biosorption can be estimated by this model using following relation (Baig *et al*., 2012b).

$$C_e / q_e = 1/Qb + C_e/Q \quad \text{....................................... (4)}$$

Here in this equation, Q is used for the monolayer saturation biosorption capacity expressed in mol/g while, b characterized for the biosorption enthalpy (L/mol) at constant temperature. Similarly, quantitively measurement of multilayer adsorption explained by the Freundlich equation (Baig *et al*., 2012b) and the linear relation is given below:

$$\ln q_e = \ln C_m + 1/n \ln C_e \quad \text{.................................... (5)}$$

here C_m and n abbreviated for the Freundlich constants. Meanwhile, the current data at equilibrium studied by

D-R isotherm to estimate the biosorption experiment expressed physical/chemical process. The linear equation of the D-R isotherm is:

$$\ln q_e = \ln X_m - \beta\varepsilon^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The ε can be calculated as:

$$\varepsilon = RTn\ (1 + 1/C_e) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where:

Xm abbreviated to biosorption capacity in mol/g, β stand for coefficient of activity (mol^2/J^2) associated to average free energy for biosorption (kJ/mol) and ε denoted as Polanyi potential, the R in kJ/mol/K represented as the gas constant, whilst the absolute temperature is denoted by T (K). The constant Xm and β derived from intercept and slope of the plot of ln qe against ε^2.

The thermodynamic characteristics of Cr^{+6} biosorption on OPB, changes in enthalpy (ΔH○), entropy (ΔS○) and Gibbs free energy (ΔG○) were estimated from the relation given below:

$$\Delta G^\circ = -RT\ln K_c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where:

R abbreviated for the gas constant expressed as 8.314 kJ/mol/K, the temperature is denoted by T (K) and the coefficient of distribution $(K_c)C_a$.

Statistical studied. Basic statistics and regression calculations have been conducted to decorate the experimental data of current study. Unless otherwise indicated, the resulted data described as mean or mean and standard deviation (SD) at ±95% confidence intervals (Afridi *et al.*, 2011).

Results and Discussion

Surface characterization of OPB. The point of zero charge (pzc) described the zero/no charge on the surface of adsorbent at particular pH. Hence, the particle surface may have positive charge at pH lower than the pH of pzc and *vice versa* (Brahman *et al.*, 2016a). The pzc of proposed biosorbent measured at pH 4.0 (Fig. 1a). Thus, surface of OPB is positive. It is consisted to the reported study (Cardenas-Peña *et al.*, 2012). The distribution of particle size was observed in in range of 2.30 to 340 µm for OPB, whilst the maximum biosorption percentage comprises 60-130 µm particle size with a mean of 75.0 µm (Fig. 1b). It has been reported that the maximum adsorption can be obtained at smaller particle size of material because of small particles may have bulk surface areas with maximum available sites for proposed analytes with respect to the amount of biosorbent (Brahman *et al.*, 2016a). Moreover, it is depending on its texture, composition and porosity (Krishna and Swamy, 2012).

The characterization of molecules in the OPB was done by using FTIR spectroscopy based on the appearance of key functional groups (Brahman *et al.*, 2016b). The intense and broad FTIR peaks at 3446 and 3411/cm correspond to before and after Cr^{+6} loaded OPB

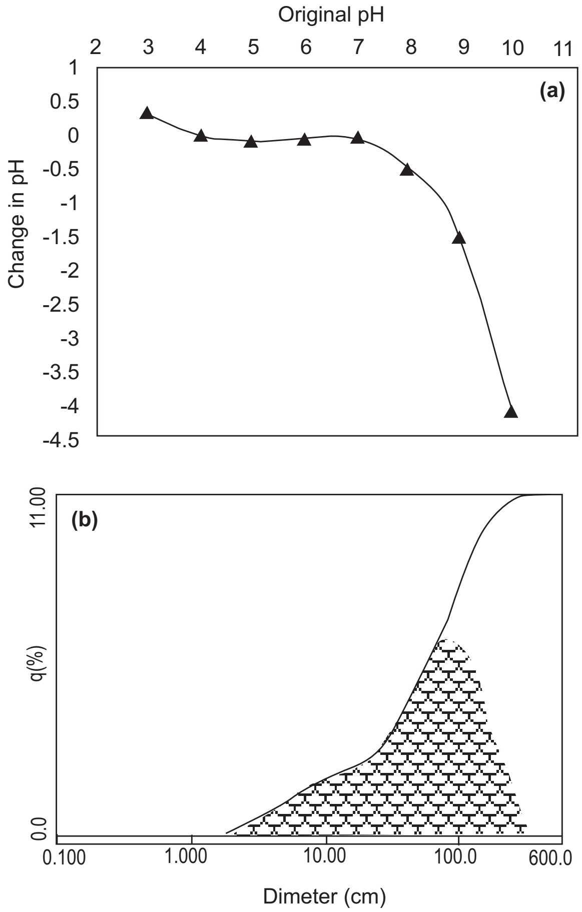

Fig.1. Graph showing (**a**) point of zero charge (pzc) (**b**) particle size distribution of the OPB.

(Fig. 1) confirmed inter and intra molecular O-H stretching vibrations of polymeric compounds (Li *et al*., 2015). The peak at 2924/cm is representing the –CH stretching vibration of aliphatic acids. A stretching peak at 1741/cm attributing the –C=O of nonionic carboxy groups like –COOH and –$COOCH_3$ (Li *et al*., 2015). The FTIR peaks ranged from 1600 to 1000/cm may be corresponding peaks of lignin including a bending vibration peak at 1641/cm representing for the aromatic skeletal stretching bands. A peak at 1381/cm characteristics of phenolic hydroxyl functionality, while peak at 1246/cm indicated –C–N vibration. The peaks between 1100 to 1000/cm may be attributed to the primary –OH group in lignin as well as C–OH bending present in hemicellulose. Similarly, different stretching vibrational peaks appeared in between 1600 to 1000/cm representing the presence of cellulose, hemicellulose, pectin, lignin and protein (Martins *et al*., 2004) and consistence with the OPB powder composition reported elsewhere (Teixeira *et al*., 2020; Li *et al*., 2015). The after Cr^{+6} loaded OPB's FTIR spectra showed some shifting and deformation in the positions of peaks indicated the biosorption of Cr^{+6} (Fig. 2). A clear variance was noticed in the stretching vibration of –OH of cellulose and –NH_2 that was shifted to 3446 to 3410.8/cm after Cr^{+6} loading to OPB. Similarly, the peaks of –NH_2, C–N and–C–O shifted to higher frequencies in the region of 1300 to 1000/cm (Fig. 2).

The surface morphologies of unloaded and loaded OPB with Cr^{+6} were studied by SEM (Fig. 3a, b) at 10 kV accelerating voltage, 1,000 magnifications and 10 µm scan size. The dried samples were coating with graphite before analysis to increase the electron conductivity. The SEM micrograph specified that the surface of proposed OPB was irregular in nature with the cluster of mesoporous structure of surface (Fig. 3a) might be due to the presence of cellulose, hemicellulose, pectin, lignin and well as several minerals (Teixeira *et al*., 2020; Li *et al*., 2015). This could be responsible for high biosorption capacity due to large available surface area for biosorption. The change in morphology of OPB after Cr^{+6} loading might be due to the bio-sorption of Cr^{+6} on the surface of OPB (Fig. 3b).

Optimization of different parameters for the removal of Cr^{+6}. The influence of pH on biosorption of Cr^{+6} on OPB was also checked it is because of vital role of pH during the biosorption experiment (Memon *et al*., 2008). The change in the pH can create an excessive impact on the binding sites of sorbent surface and the analyte of interest in aqueous solution. The

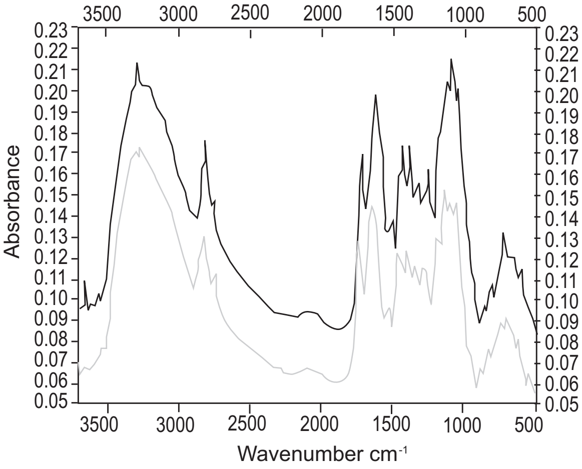

Fig. 2. FTIR spectra of unloaded OPB (black line) and Cr^{+6} loaded OPB (red line).

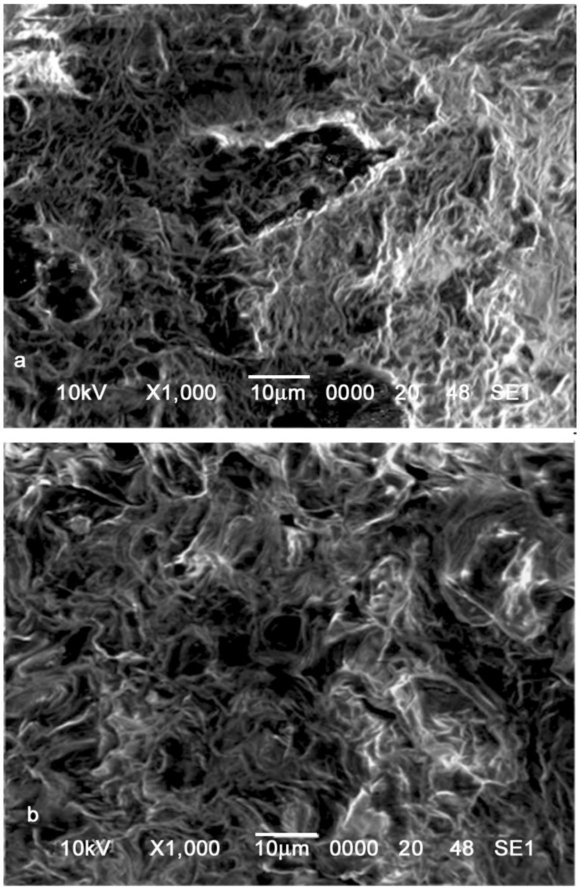

Fig. 3. SEM micrographs of (**a**) unloaded OPB and (**b**) Cr^{+6} loaded OPB.

effect of pH for the binding of Cr^{+6} on the surface of OPB was studied in between pH 1 to 9 at fixed concentration of Cr^{+6} (0.013 mmol/L), contact time (20 min), biosorbent dosage (0.01 g/L) and temperature (298 $\overset{o}{K}$) as shown in Fig. 4a. The % biosorption was found to be > 90% in pH range from 2 to 4. This is because of the surface charge of OPB is positively charged at lower pH ($pH \leq 4$) than the pH at pzc (4.0). The Cr^{+6} species in aqueous solution may be altered with respect to the change in the pH. The different forms of Cr^{+6} such as $Cr_2O_7^{2-}$, $HCrO_4^-$ and Cr_3O10^{2-} are existed in water at pH range 2 to 6. The experimental data of current study indicated that the surface of OPB was positively charged at lower pH (2-6), which might be responsible for the quantitative removal of Cr^{+6} from waste water or industrial effluent (Nakkeeran *et al.*, 2016; Singh *et al.*, 2005). Similarly, the OPB surface might be occupied with negatively charge OH^- with respect to the increment in pH of solution, cause decrease in the % removal of Cr^{+6} ions from aqueous media (Nakkeeran *et al.*, 2016; Singh *et al.*, 2005). However, the Cr^{+6} is more stable at pH 2.0. Thus, pH of 2.0 was considered as optimal pH for the quantitative removal of Cr^{+6} for the rest of optimization study.

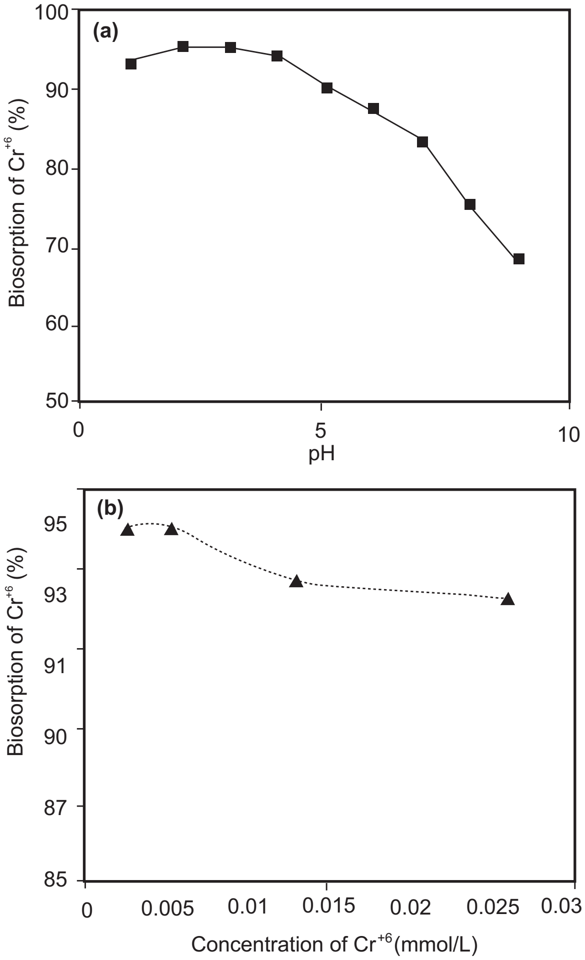

Fig. 4. Effect of (**a**) pH and (**b**) concentration of Cr^{+6} (mg/L) for biosorption of Cr^{+6} by OPB at adsorbent dosage 0.01 g/L and temperature 298 $\overset{o}{K}$.

The effect of Cr^{+6} concentration for the quantitative biosorption has been study in range of 0.0026-0.026 mmol/L at constant values for other parameters (Fig. 4b). The results indicated that the % biosorption of Cr^{+6} was constant upto 0.013 mmol/L. Afterward, the gradual decrease in % biosorption has been noticed (Fig. 4b). Such conditions may be happened due to the less availability of active sites within the biosorbent for Cr^{+6}. Therefore, 0.013 mmol/L concentration of Cr^{+6} was chosen as quantitative concentration for further experiments. The influence of biosorbent (OPB) dosage on the % biosrption of Cr^{+6} were studied in the range of 0.05-0.5 g/L at Cr^{+6} concentration 0.013 mmol/L, contact time 20 min, temperature 298 $\overset{o}{K}$ and pH 2.0 (Fig. 5a). When the OPB dosage increased from 0.05 to 0.10 g/L (Fig. 5a), the gradual increase in the biosorption was noticed (50.0-95.5%). However, there was not any remarkable increase in % biosorption with the increase of OPB dosage. It is because of the availability of multiple binding sites on the surface of OPB for Cr^{+6} in the solution. Thus, 0.10 g/L OPB dosage has been selected for quantitative removal of Cr^{+6}.

The contact time impact on the quantitative biosorption of Cr^{+6} studied in between 5.0-60 min at optimum levels of remaining parameters (Fig. 5b). The rate of biosorption of Cr^{+6} was very fast at the early stage (Fig. 5b). It was noticed that about greater than 80% removal of Cr^{+6} were observed in 5.0-10 min. Afterward, it became slower near the equilibrium time of 20 min, afterward, there was no significant impact on the % biosorption of Cr^{+6}. Therefore, 20 min contact time has been chosen for quantitative % biosorption at equilibrium condition. Similarly, the effect of temperature for the quantitative % biosorption of Cr^{+6} has been carried out in the range of 298-363 $\overset{o}{K}$ at optimum levels of remaining parameters. It has been observed that with increase in the temperature the % biosorption will have gradual decreased in % biosorption of Cr^{+6} by OPB. Thus, the proposed OPB is most suitable biosorbent for efficient removal of Cr^{+6} from contaminated aqueous solution at normal temperature (298-318 $\overset{o}{K}$).

Equilibrium study of Cr^{+6} biosorption. The proposed biosorption of Cr^{+6} on the OPB was studied at equilibrium followed by the isotherm models *i.e.*, Langmuir, Freundlich and Dubinin-Radushkevich models. The basic concept of Langmuir theory is to explain the sorption mechanism that is happened at definite homogeneous sites of the proposed sorbent (Kundu and Gupta, 2006). A graph of Ce/qe *vs* Ce plotted to estimate bisorption capacity (Q) and Langmuir constant (b) based on the slope of 1/Q and intercept of 1/Qb of the linear calibration curve with quantitative linearity ($R^2 > 98.0$) for the biosorption of Cr^{+6} on OPB (Table 1). The values of Q and b found to be 0.298-0.308 mmol/g and 4.70-6.30×10^{-2} L/mol at 298 $\overset{o}{K}$, respectively. The high value of b indicated the strong bonding of Cr^{+6} within OPB at 298 $\overset{o}{K}$. The valuable attributes of Langmuir isotherm may be calculated as dimensionless constant (RL) of separation factor. It can be estimated as (Brahman *et al*., 2016b).

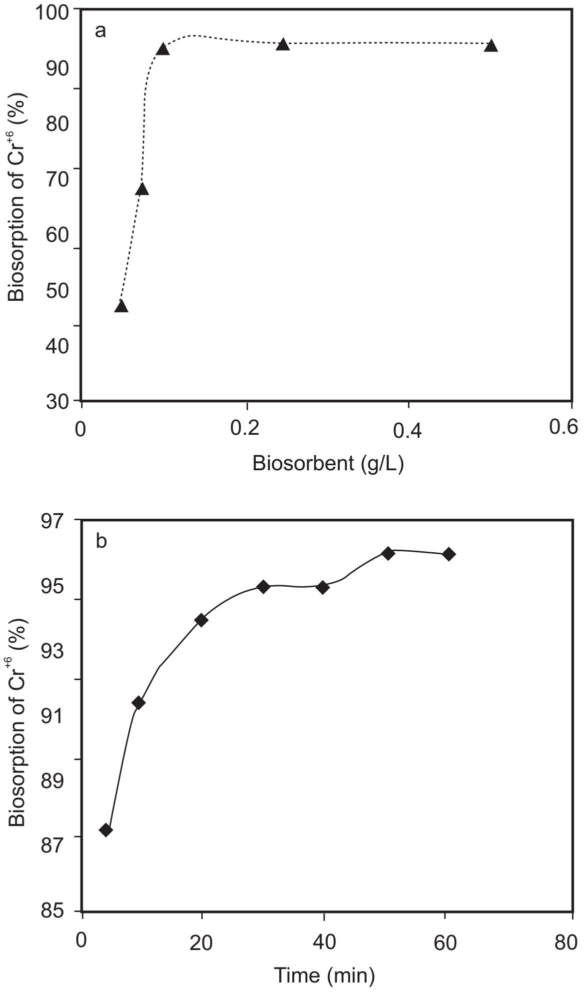

Fig. 5. Effect of (**a**) biosorbent dosage (g/L) and (**b**) contact time (min) for the removal of Cr^{+6} by OPB at Cr^{+6} concentration 0.25 mg/L, contact time 20 min, temperature 298 $\overset{o}{K}$ and pH 2.

$$R_L = \frac{1}{1 + bC_i} \text{ .... } (10)$$

where:

b represented the Langmuir constant; C_i stand for the initial Cr^{+6} concentration in solution. The estimated positive values of R_L at different concentrations (0-1) predicted the favorability of Cr^{+6} biosorption on OPB at 298 $\overset{o}{K}$.

The estimation of Freundlich biosorption capacity Cm and its constants 1/n was done based on the intercept (c) and slope (m) of lnqe *vs*. lnCe linear graph, respectively. The value of 1/n in between 0-1 indicated that the Cr^{+6} biosorption on OPB found to be favourable at equilibrium (Table 1). The value of co-efficient of determination ($R^2 > 0.99$) indicated the applicability of multilayer formation of Cr^{+6} on OPB at the equilibrium condition. The resulted data at the equilibrium condition were used to measure the biosorption behaviour (physical or chemical) based on the estimation of D-R isotherm. It can be predicted the possible biosorption mechanism. Estimation of free energy of transfer (E) for Cr^{+6} biosorption on OPB is done through the slope (β) value of the linear D–R plot by using the relation of $E = 1/\sqrt{-2\beta}$. The value of E was laying in between 8.60-9.00 kJ/mol indicated that biosorption may be followed the mechanism of chemisorption, because E > 8.0 kJ/mol (Brahman *et al*., 2016b; Baig *et al*., 2010). The studied isotherm models indicated the applicability of Cr^{+6} biosorption showed both monolayer and multilayer biosorption with favourable heterogeneous distribution on the active sites of OPB.

The kinetic study can be assisted to explain the possible mechanism under the favourable rate of reaction for the proposed biosorption experiment (Baig *et al*., 2010). To test the equilibrium experimental data the kinetics of pseudo-first and second-order models were studied as reported earlier (Baig *et al*., 2010). The calculated k_1 and qe values based on the slope and intercept of ln(qe-qt) against time plot (Table 1). Its regression coefficient ($R^2 = 0.957$) at studied temperatures was not supported to the proposed biosorption study. However, the pseudo first order qe value was significantly lower than the experimental qe indicated the unfavourable condition of pseudo first order rate of reaction for biosorption of Cr^{+6} on OPB (Baig *et al*., 2010). On other hand, the pseudo second order kinetic model was found to be probable to predict kinetic behaviour of biosorption (Baig *et al*., 2010). The q_e and k_2 of this model were measured based on the intercept and slope of regression analysis of t/qt against t (Table 1). The qe of pseudo second order and experiment were in agreements to each other with reasonable linearity ($R^2 > 0.96$). This showed that the biosorption on the surface of OPB may be chemisorption.

The ΔH°, ΔS°, and ΔG° values were estimated followed by equations 10 and 11 (Table 1). The calculated values of ΔH° and ΔS° were obtained from slope, and intercept of the linear graph of ln Kc against 1/T (graph of van't Hoff). It is reported that the ΔG° is indicated the degree of freedom for the biosorption experiment (Baig *et al*., ~~2010). The calculated Gibbs free energy (ΔG°) negative~~ values elaborated that OPB may follow the spontaneous biosorption (Table 1). Moreover, the spontaneity of biosorption of Cr^{+6} on OPB is directly proportional to the temperature (Table 1). The value of ΔH° (-2.73 kJ/mol) indicated the exothermic biosorption process followed by chemisorption of Cr^{+6} on OPB. It is because the enthalpy or heat of biosorption < 20.9 kJ/mol (Deng *et al*., 2007; Singh *et al*., 2005). Meanwhile, the positive value of ΔS° suggested the favorability of biosorption mechanism (Table 1).

Desorption and regeneration of Cr^{+6}. Desorption of biosorbed Cr^{+6} on OPB was performed by using different levels of eluents (HCl, HNO_3 and NaOH). The resulted data indicated that the > 93% of Cr^{+6} leaching was observed by using 1.0 M HCl, while 91.4 and 89.5% desorption of Cr^{+6} were noticed with the application of 1.0 M HNO_3 and NaOH, respectively. Thus, 10 mL solution of 1.0 M HCl was found to be optimal level for the maximum desorption of Cr^{+6} from proposed biosorbent. The biosorption capacity of Cr^{+6} on OPB was remained same (RSD < 2%) after 30 experiments. Thus, the proposed biosorbent OPB was adequate for multiple experiments. The selectivity of the proposed biosorption of Cr^{+6} was also study. The resulted data of binding capacity experiments were of common ions and trace ions revealed that the relative error was less than ±5% in each case.

Comparison of Cr^{+6} removal with literature. The ~~adsorption capacity of current study has been compared~~ with the reported adsorbents for the removal of Cr^{+6} (Table 2). However, all the selected reported adsorbents showed the formation of monolayer adsorption and the reported values for the experimental data in some cases are comparable (Omer *et al*., 2019; Aigbe *et al*., 2018; Preethi *et al*., 2017; Nag *et al*., 2017; Nag *et al*., 2016; Araghi *et al*., 2015; Gupta and Majumder, 2014; Gupta *et al*., 2013; Bhattacharya *et al*., 2008; Pehlivan and Altun, 2008; Sarin and Pant, 2006; Vennilamani *et al*., 2005; Kobya, 2004; Dakiky *et al*., 2002). The adsorption

Table 1. Results of characteristic parameters of isotherm, kinetic and thermodynamic for Cr^{+6} biosorption by OPB

Langmiur isotherm	Q (mmol/g)	b (L/mol)	R^2	R_L
	0.303±0.01	5.50×10^{-2} ±0.88	0.987	0.04-0.124
Freundlich isotherm	C_m (mmol/g)	n		R^2
	1.120±0.22	0.810±0.25		0.991
D-R isotherm	X_m (mmol/g)	E (kJ/mol)		R^2
	12.2±0.15	8.77±0.18		0.992
	q_e, Exp. (μmol/g)		220±2.50	
pseudo first order	k_1 (1/min)	q_e (μmol/g)		R^2
	9.60×10^{-2}	10.2		0.957
pseudo second order	k_2 (g/μmol. min)	q_e (μmol/g)		R^2
	1.70×10^{-2}	132		0.964
Change in free energy (-ΔG in kJ/mol)	298 $\overset{\circ}{K}$	318 $\overset{\circ}{K}$		333 $\overset{\circ}{K}$
	7.46	6.08		4.75
Change in enthalpy (ΔH° in kJ/mol)	-2.73	--		--
Change in entropy (ΔS° in kJ/mol)	0.056	--		--

capacities of the reported adsorbents were lower than the proposed biosorbent except hazel nutshell activated carbon (Table 2). Synthetic materials like aluminium-lanthanum mixed oxyhydroxide (ALMOH), polypyrrole magnetic nanocomposite and mesoporous silica embedded with magnetite nanoparticles have comparable adsorption capacities for Cr^{+6} (Aigbe *et al*., 2018; Preethi *et al*., 2017; Araghi *et al*., 2015), whereas tetraethylenepentamine functionalized alginate beads showed lower adsorption capacities for Cr^{+6} as compared to the proposed material (Omer *et al*., 2019).

Application on industrial effluents. The proposed biosorbent OPB was applied on real industrial effluent samples of different industries of Jamshoro and Hyderabad for the removal of Cr^{+6}. The proposed biosorbent is the most attractive because of its easy availability as waste of juice industries and/or shops of fresh juices in the local markets. Most of the collected industrial effluent samples have $Cr^{+6} > 10.0$ mg/L (Table 3). The resulted data indicated that the proposed OPB was efficiently removed Cr^{+6} from all studied samples up to 94% at pH 2 (Table 3). Similarly, the pH, TDS, EC and BOD values in all industries before biosorption ranged from 7.60-8.50, 2360-3394 mg/L, 1.11-3.72 mS/cm, and 173 to 281 mg/L respectively (Table 3). Th pH of industrial effluents were within the WHO permissible limit for industrial effluents (pH = 6.50-8.50). Whereas, TDS, EC and BOD of industrial effluents before biosorption were above the permissible limits of WHO in industrial effluents (TDS = 2000 mg/L; EC = 1.00 mS/cm; BOD = 80 mg/L) (WHO, 2011). However, the resulted data listed in Table 3 indicated that pH, TDS, EC and BOD of studied industrial effluents were lowered by 5.00-11.0, 38.0-53.0, 28.0-70.0 and 94.0-97.0% respectively after biosorption by OPB (Table 3). Thus, it is the best alternative for the efficient removal of Cr^{+6} from the effluent of different industries.

Table 2. Comparison of adsorption capacities (mg/g) of the adsorbents for the removal of Cr^{+6}

Adsorbents	Adsorption capacity (mg/g)	References
Clarified sludge; Rice husk ash; Activated alumina; Fuller's earth; Fly ash; Saw dust; Neem bark	26.3; 25.6; 25.6;23.6; 23.9; 20.7; 19.6	(Bhattacharya *et al*., 2008)
Almond; Cactus; Coal; Olive cake; Pine needles almond; Saw dust; Wool	10.6; 7.08; 6.80; 33.4; 21.5; 15.8; 41.1	(Dakiky *et al*., 2002)
Ficus carica bark	19.7	(Gupta *et al*., 2013)
Bagasse	25.1	(Gupta and Majumder, 2014)
Hazel nutshell activated carbon	170	(Kobya, 2004)
Rubber leaf	23.0	(Nag *et al*., 2016)
Eucalyptus bark	45.0	(Sarin and Pant, 2006)
Jackfruit leaves; Mango leaf; Onion peel; Garlic peel; Bamboo leaves; Treated rubber leaves; Coconut shell	32.3; 35.7; 19.9; 9.22; 10.8; 29.8; 8.73	(Nag *et al*., 2017)
Almond shell; Hazelnut shell; Wallnut shell	3.40; 8.28; 8.01	(Pehlivan and Altun, 2008)
Sago waste activated carbon	5.78	(Vennilamini *et al*., 2005)
Aluminium–lanthanum mixed oxyhydroxide (ALMOH)	49.8	(Preethi *et al*., 2017)
Polypyrrole magnetic nanocomposite	49.7	(Aigbe *et al*., 2018)
Tetraethylenepentamine functionalized alginate beads	30.0	(Omer *et al*., 2019)
Mesoporous silica embedded with magnetite nanoparticles	50.5	(Araghi *et al*., 2015)
Orange peel	48.0	Current study

Table 3. The physico-chemical parameters and concentration of Cr^{+6} in industrial effluent samples before and after biosorption on OBP

Parameters	FI (n = 30)		PI (n = 30)		CI (n = 30)		TFI (n = 30)	
	Before	After	Before	After	Before	After	Before	After
	biosorption							
Cr^{+6} (mg/L)	29.5±6.50	1.76±0.37	19.5±0.50	1.22±0.03	16.0±7.00	1.10±0.420	32.0±16.0	1.90±1.02
pH	7.90±0.30	7.20±0.12	7.70±0.10	7.10±0.10	8.30±0.20	7.80±0.23	8.20±0.20	7.70±0.10
TDS (mg/L)	2403±43.5	1450±10.0	3365±20.0	1890±7.20	3370±24.0	1710±4.80	2951±12.4	1380±3.60
EC (mS/cm)	1.33±0.22	0.90±0.10	3.30±0.30	1.30±0.12	3.30±0.42	1.25±0.18	2.83±0.75	1.00±0.36
BOD (mg/L)	275±6.14	12.0±4.20	175.0±1.51	5.80±0.44	265±3.10	11.1±0.85	180±2.00	6.20±0.93

Conclusion

The OPB is an economical, sensitive, selective and reusable biosorbent for Cr^{+6} from contaminated aqueous solutions. The proposed study indicated that the Cr^{+6} biosorption capacity of biosorbent material was 0.222 mmol/g from its aqueous solutions under the optimal conditions. The proposed biosorption study described that the biosorption of Cr^{+6} on OPB obeying the multi-layer formation based on the chemisorption. Moreover, the proposed biosorbent followed the pseudo-second-order kinetic for the removal of Cr^{+6}. The proposed OPB is followed by the endothermic and spontaneous mechanism. The proposed study concluded that OPB is an efficient and effective choice to remove Cr^{+6} from contaminated aqueous solution might be because of its good adsorption capacity, easy availability and eco-friendly nature. Meanwhile, the 1.0 mol/L HCl is the best eluent for efficient desorption of Cr^{+6} from OPB.

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