Adsorption of Cr(III) from aqueous solution on NaOH-treated scraped coconut waste

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Highlights

- Scraped coconut waste (SCW) contains -OH, -NH and -COO functional groups according to FTIR spectroscopy.
- High removal efficiency for Cr(III) was achieved by NaOH modified scraped coconut waste (NSCW).
- Sorption obeys the Langmuir adsorption isotherm, indicating that monolayer formation is predominant.
- Transfer of Cr(III) adsorbate species toward the NSCW adsorbent is not solely controlled by intra-particle diffusion.

RESEARCH ARTICLE

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Abstract: Scraped coconut waste left after coconut milk processing, is a low-cost, readily available natural substance in tropical countries, such as Sri Lanka. This study is based on the removal of Cr(III) ions using NaOH-treated scraped coconut waste (NSCW). Under optimized experimental conditions employed, treatment of the biosorbent with aqueous 0.10 mol L⁻¹ NaOH solution provides much enhanced Cr(III) removal of 92.9%. As compared to the 53.6% removal in the absence of any modification, it is an increase by 73.3%. The extent of biosorption of Cr(III) by NSCW depends on experimental conditions, such as mass of NSCW, initial solution pH, shaking time and settling time. Fourier transform infrared spectroscopy provides information on functional groups, such as O-H, C-H, C=O and C-O present in NSCW, which possesses a relatively high surface area of 10.8 (±1.1) m² g⁻¹. Adsorption equilibrium studies demonstrate that the Langmuir isotherm is more suitable than the Freundlich isotherm in explaining the interaction of Cr(III) with NSCW, leading to the adsorption capacity of 14.28 mg g⁻¹ for Cr(III) removal. Moreover, experiments conducted on kinetics provide the applicability of the pseudo first order model under low adsorbent dosage and ambient temperature conditions. Transfer of Cr(III) towards the NSCW surface is found to be controlled by intra-particle diffusion and boundary layer retarded diffusion, and the predominant mode depends on experimental conditions.

Keywords: Adsorption isotherms; kinetics; parameter optimization; scraped coconut waste.

INTRODUCTION

Adsorption of chemical species on reactive or porous surfaces has found numerous applications in various sectors. In textiles and paper industries, dyes and additives are deliberately made to adsorb on fibers without being much desorbed (Lim *et al.*, 2017). On the other hand, nutrients and essential metal ions are adsorbed, retained and released by soil for crops in agricultural systems (Badescua *et al.*, 2018). Toxic substances and environmental pollutants, including viruses, are effectively chemisorbed and transformed to nontoxic, or at least, to less toxic substances by the contents in the filter media of face masks (Khayan *et al.*, 2019). Heavy metal ions of variable oxidation states are made adsorbed on adsorbent beds to catalyze chemical reactions in many industrial processes (Weng *et al.*, 2008). Moreover, wastewater treatment systems use

the concept of adsorption to remove various contaminants, including heavy metal ions, their compounds, dyes and pesticides (Akunwa *et al.*, 2014; Priyantha *et al.*, 2018b; Khan and Ganai, 2020). Owing to inherent drawbacks of many of the above systems, alternative green and more economical approaches are being searched upon. The extent of adsorption of adsorbates, which is a measure of the effectiveness of the process, is usually investigated through adsorption isotherm measurements (Priyantha *et al.*, 2015a; Herath *et al.*, 2018). The rate of adsorption before the equilibrium is reached, on the other hand, is also important to optimize experimental parameters of the adsorbate/adsorbent system, which in turn would be useful in broadening or modernizing already existing industrial processes, or to design novel effluent treatment processes (Karia and Christian, 2006; Priyantha and Kotabewatta, 2019).

Adsorption of heavy metal ions on orderly surfaces can satisfactorily be characterized using advanced surface analytical techniques, such as X-ray photoelectron spectroscopy, Auger electron spectroscopy and secondary ion mass spectrometry, in an attempt to predict possible modes of mass transfer (Saha and Orvig, 2010). However, when green adsorbents, such as plant-based biosorbents, are used, sorption of heavy metal ions on biomass would occur through several mechanisms, most commonly, ion exchange, chelation, complexation, oxidation and reduction (Wang and Chen, 2009; Barakat, 2011; Herath *et al.*, 2018). Further, in addition to surface diffusion on such heterogeneous adsorbents, diffusion through macropores, mesopores and micropores is also possible (Priyantha *et al.*, 2015b; Hubbe *et al.*, 2019). Another complication of mass transfer effect does arise when the surfaces of biosorbents are chemically modified thereby introducing more variables to be considered. On the other hand, chemical modification of adsorbents, especially biosorbents, is beneficial in order to improve the efficiency of industrial processes (Wang and Chen, 2009; Lim *et al.*, 2016; Ranasinghe *et al.*, 2018). When an adsorbent is chemically modified, it would thereafter behave as a new material resembling the properties of the modifying agent, allowing the flexibility for selection of a suitable modifier for the intended application, for instance, those possessing reactivities toward complexation,

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decomposition, hydrolysis, and protonation (Priyantha *et al.*, 2013; Priyantha *et al.*, 2015c; Tran *et al.*, 2017; Ranasinghe *et al.*, 2018). Consequently, removal of environmental pollutants by modified biosorbents would find applications in industrial effluent treatment, although such studies are yet to be much explored and developed. Moreover, mechanistic approaches of biosorption have not been paid adequate attention despite its importance to extend laboratory findings to large-scale operations.

This aspect is the focus of the present research on characterization of NaOH-modified scraped coconut waste (NSCW) as an effective biosorbent for a system containing aqueous Cr(III) species as the adsorbate. Removal of Cr(III) has been reported by some biosorbents, such as *Artocarpus nobilis* peel (Samaraweera *et al.*, 2020), orange peel (Tomul *et al.*, 2017) and saw dust (Ahmad, 2005), in their unmodified and modified forms. In this study, impact of NaOH treatment on biosorption ability of scraped coconut waste (SCW) was investigated through X-ray fluorescence spectrophotometry (XRF) and Fourier transform infrared (FTIR) spectroscopy. Moreover, models on adsorption isotherms, pseudo-order kinetics and intra-particle diffusion were also applied in order to obtain information at both macroscopic and microscopic scales. It should also be stressed that SCW, being a waste material, possesses many desirable properties, such as environmentally friendliness, a porous structure, and is readily available at no-cost. Its porosity which determines the adsorption capability can be further enhanced through surface modification employing selected chemical agents targeting the intended application.

MATERIALS AND METHODS

Materials and sample preparation

Standard solutions of Cr(III) were prepared using $\text{CrCl}_3 \cdot 8\text{H}_2\text{O}$ purchased from VWR Scientific (UK). Scraped coconut waste (SCW) samples were randomly collected from houses in the Kandy District, Sri Lanka. As SCW was not homogeneous, a bulk sample of SCW was collected and mixed well to make it more homogeneous. This manually homogenized mixture was dried at 105 °C for a period of 3.0 h. After natural cooling, dried SCW samples were treated using 0.10 mg L⁻¹ NaOH, prepared using analytical grade NaOH purchased from Sigma-Aldrich (Germany); The ratio of the mass of SCW (g) and the volume of the modifying agent (mL) was taken as 1:10. Thereafter, NaOH-treated scraped coconut waste (NSCW) was thoroughly rinsed with tap water several times until the supernatant reached the pH of tap water. NSCW samples were again oven dried at 105 °C for a period of 3.0 h. Powdered SCW/NSCW particles of diameter, $d < 1.0$ mm were used for FTIR and XRF spectroscopic analyses. Distilled water was used to prepare stock solutions, subsequent dilutions and in all experiments.

Instrumentation

SCW samples were dried using drying oven (Model DHG-9140A). The total concentration of chromium in all solutions was determined using Spectro-Electronic M Series atomic absorption spectrophotometer (AAS) based on a freshly

constructed calibration curve. When concentrations were above the linear dynamic range (LDR), necessary dilutions were carried out to bring the concentrations within the LDR. FTIR spectra of dried samples of SCW and NSCW were recorded on BRUKER, TENSOR II, Model 545 FTIR spectrophotometer. Dried samples of NSCW before and after treatment with Cr(III) solutions were subject to XRF analysis using XRF analyzer (Fischerscope Model-DF500FG-456). Absorbance measurements of methylene blue solutions were recorded on UV-Visible spectrophotometer (Shimadzu UV 1800 series)

Optimization of parameters for preparation of NSCW

Samples of NSCW of known masses were individually added to 50.00 cm³ of Cr(III) solutions placed in small jars. Each sample was shaken for a pre-determined period of time and allowed to settle for a pre-determined period of time. Thereafter, each suspension was filtered, and the filtrate was used for AAS measurements. The percentage removal was determined using Equation (1).

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

where C_i is initial concentration of Cr(III) in solution before treatment and C_f is final concentration of Cr(III) in the filtrate after treatment. Percentage removal of untreated SCW samples, treated as the control, was also investigated in a similar manner. All experiments were carried out in triplicate, and average values were reported.

Optimization of concentration of NaOH solution

The concentration of NaOH solution was optimized using many concentrations ranging from 0.01 mol L⁻¹ - 0.50 mol L⁻¹ followed by a constant shaking time of 1.0 h and a settling time of 24.0 h. The optimum concentration of NaOH was determined based on the percentage removal values calculated using Equation (1). The NaOH solution of the optimized concentration was used to prepare NSCW samples for subsequent experiments.

Optimization of shaking time

Effect of shaking time was determined using NSCW samples with different shaking times from 10 min to 120 min followed by a constant settling time of 24.0 h. The optimum shaking time was determined based on the percentage removal values calculated using Equation (1). The optimized shaking time was thereafter used to prepare NSCW samples for adsorption experiments.

Optimization of solution parameters of Cr(III) – NSCW interactions

Optimization of dosage of NSCW

Dried NSCW sample masses ranging from 0.100 g to 1.000 g were separately mixed with 50.00 mL of 10.00 mg L⁻¹ Cr(III), and each suspension was thoroughly shaken at a speed of 150 rpm for 1.0 h, followed by a constant settling time of 1.0 h. The pH of initial Cr(III) solutions was kept at its natural value of 3.5. The suspension was filtered, and the

filtrate was used for AAS measurements. The percentage removal of Cr(III) was calculated using Equation (1), and the optimum dosage of NSCW was determined.

Optimization of initial solution pH

Experiments for optimization of initial solution pH were conducted using the pre-determined optimum dosage of NSCW, followed by a constant shaking time of 1.0 h and a constant settling time of 1.0 h. For this purpose, effect of initial solution pH, ranging from 2.00 to 10.00, on the removal of Cr(III) was studied. Solutions of different pH values were prepared using 0.10 mol L⁻¹ HNO₃ and/or 0.10 mol L⁻¹ NaOH. The percentage removal of Cr(III) at each pH was calculated using Equation (1), and the optimum pH was determined. Further, both the initial pH and the pH of each solution after treatment of Cr(III) solutions with NSCW were also recorded.

Optimization of stirring time and settling time

In order to optimize shaking time, 50.00 cm³ aliquots of 10.00 mg L⁻¹ Cr(III) solution at the optimized pH of 5.0 were stirred at a speed of 150 rpm with NSCW samples of optimized mass for different shaking times up to 60 min followed by a constant settling time of 1.0 h. After optimizing shaking time, similar experiments were carried out to optimize settling time using the pre-determined optimum dosage, pH and stirring time. Settling time was varied from 0 min to 60 min to determine the optimum value.

Determination of the extent of removal of Cr(III) under optimized conditions

The extent of removal of Cr(III) by NSCW was determined, in triplicate, with the aid of Equation (1) employing the parameters optimized, and the average value was reported. For comparison, the extent of removal of Cr(III) by SCW was determined under the same experimental parameters.

Methylene blue adsorption

Using 1000 mg L⁻¹ methylene blue (MB) stock solution, a concentration series of MB solutions was prepared. Each solution was treated with 0.50 g of NSCW for 2.0 h and settled for 24.0 h. Using standard solutions of MB, the mass of MB adsorbed on NSCW was calculated based on absorbance measurements recorded at 662.5 nm, the λ_{max} of methylene blue in aqueous medium. Using the above data, the surface area of NSCW was determined. All experiments were carried-out in triplicate, and the average value was reported.

Studies on adsorption isotherms

Solutions of Cr(III) of initial concentration varying from 10 mg L⁻¹ to 2000 mg L⁻¹ were shaken with NSCW under optimized conditions of shaking time, settling time and pH. Each solution was then allowed to reach adsorption equilibrium, and thereafter, the concentration of the chromium in the supernatant solution was measured after diluting each sample to relevant concentration ranges. For each initial concentration, the same experimental procedure

was performed in triplicate. The extent of adsorption was calculated as mass of Cr(III) adsorbed on 1.00 g of NSCW (mg g⁻¹). A graph of the extent of adsorption versus initial Cr(III) concentration was plotted to identify the isotherm type. Adsorption data with equilibrium concentration of Cr(III) in solution were also analyzed to investigate the validity of the Langmuir and Freundlich isotherms, and to determine isotherm constants of the models. Using the appropriate model, adsorption capacity of NSCW for Cr(III) was determined.

Studies on adsorption kinetics

For studies on adsorption kinetics of Cr(III) with NSCW, 0.200 g of NSCW was treated with 950 mL of 10.00 mg L⁻¹ Cr(III) solution, and it was stirred slowly with a magnetic stirrer. While the solution was being stirred, 5.00 mL aliquots of the supernatant solution were withdrawn at regular intervals for a period of 120 min. The concentration of chromium in each sample withdrawn was determined by AAS, and the extent of adsorption was calculated. Several experiments of kinetics were done by changing adsorbent dosage, solution pH and solution temperature. By applying suitable models for the data obtained in the above experiments, the order of the reaction was investigated. The same data obtained prior to establishment of adsorption equilibrium were used for investigation of the validity of intra-particle diffusion models.

RESULTS AND DISCUSSION

FTIR spectroscopic analysis

The FTIR spectrum of untreated SCW shows a strong broad band at 3290 cm⁻¹ which is attributed to O-H stretching and N-H stretching (Figure 1). The band at 1742 cm⁻¹ indicates the presence of C=O groups in esters. The bands at 2922 cm⁻¹ and 2853 cm⁻¹ show the existence of C-H stretching (Khalid *et al.*, 2014). The only significant shift in spectral band positions observed after treatment of SCW with NaOH solution is the O-H/N-H stretching band, which changed from 3290 cm⁻¹ to 3356 cm⁻¹.

Figure 1: FTIR spectrum of (a) untreated SCW and (b) NaOH-treated SCW.

Changes in spectral features at other locations in the spectrum are not much visible probably due to the fact that the surface changes that occurred as a result of Cr(III) adsorption are not sensitive enough to produce specific spectral features in the FTIR spectrum of the bulk sample. The above change is probably due to the reaction of functional groups present in the SCW following NaOH treatment, and it can therefore be attributed to base hydrolysis of ester groups and reaction of carboxylic acids forming respective carboxylate anions, thereby enhancing the possibility of attraction between positively charged Cr(III) species with negatively charged reactive moieties formed in NSCW through Coulombic forces and/or complexation, which would not take place to a significant extent without NaOH treatment.

XRF analysis

XRF spectrum in Figure 2(a) shows that NSCW contains S and Ca among the detectable elements. It is not possible to obtain much information regarding all component elements of the SCW due to the limited range of elements which can be identified by XRF. However, the XRF spectrum in Figure 2(b) provides strong evidence for the presence of Cr. Therefore, it is confirmed that Cr has been adsorbed by NSCW upon its treatment with Cr(III) solution. It should also be stated that Ca is a major constituent in cell wall, and the elements such as C, H, N, O and S can be present due

to the cellulose and hemicellulose structure of the SCW although many elements present are not detectable in the XRF spectra.

Determination of surface area of NSCW

Specific surface area is an important factor of porous surfaces, and it affects the surface charge, surface site density and reactions that would occur on the surface (Yukselen and Kaya, 2008). This parameter can effectively be determined using the adsorption of MB, a cationic dye, on the NSCW surface. The point of completion of adsorption, where the amount of MB adsorbed becomes a constant, can be used to determine the specific surface area (S_s), with the assumption that adsorption occurs in a 1:1 stoichiometric ratio, according to Equation (2).

$$S_s = \frac{m_{MB} \times A_v \times A_{MB}}{m_s M} \quad (2)$$

where S_s is the surface area of NSCW ($\text{m}^2 \text{g}^{-1}$), m_{MB} is the mass of MB adsorbed at the point of complete cation replacement (g), A_v is the Avogadro constant, A_{MB} is the area covered by a MB molecule ($1.30 \times 10^{-20} \text{ m}^2$), m_s is the mass of the NSCW sample, and M is the molar mass of MB ($319.87 \text{ g mol}^{-1}$) (Priyantha *et al.*, 2018a). Equation (2) is derived with the assumption that MB molecules lie flat on the NSCW surface resulting in chemisorption forming a

Figure 2: XRF spectrum of NSCW (a) Before treatment with Cr(III) and (b) After treatment with Cr(III).

Table 1: Specific surface area reported by different natural adsorbents.

Adsorbent	Specific surface area/ $\text{m}^2 \text{g}^{-1}$	Reference
Rice husk heated at 100 °C	110.1	Priyantha <i>et al.</i> , 2018a
Orange peel	20.6 - 23.5	Annadurai <i>et al.</i> , 2002
Banana peel	20.6 - 23.5	Annadurai <i>et al.</i> , 2002
Almond shells	10.5	Ardejani <i>et al.</i> , 2005
Raw peach shell	0.985	Markovic <i>et al.</i> , 2015
NSCW	10.8	This study

Figure 3: Extent of removal of 10.0 mg L⁻¹ Cr(III) by (a) SCW treated with different NaOH concentrations (b) NSCW for different process shaking times (0.50 g of NSCW, 1.0 h settling time).

monolayer. The specific surface area of NSCW determined using the saturation point of MB is 10.8 (± 1.1) $\text{m}^2 \text{g}^{-1}$, which is comparable to many biosorbents (Table 1).

Optimization of parameters that affect the removal of Cr(III) by NSCW

Optimization of process parameters

Concentration of NaOH and shaking time used for the modification of SCW affect the removal of Cr(III) because surface modification depends on the above parameters.

Optimization of NaOH concentration: Figure 3(a) shows the percentage adsorption of Cr(III) for SCW treated with different concentrations of NaOH. The results in the figure indicate that 0.10 mol L⁻¹ NaOH shows the highest percentage removal which becomes a relatively constant for higher concentrations. Therefore, the optimum concentration of NaOH for modification of the adsorbent was taken as 0.10 mol L⁻¹.

Optimization of process shaking time: Dried samples of NSCW formed by treatment of SCW with the optimized NaOH concentration when subjected to different process shaking times lead to the extent of removal of Cr(III) as shown in Figure 3(b). There is no any significant difference in the values; however, it was decided to use 60 min shaking time to assure sufficient interaction between NSCW and the adsorbent.

Optimization of solution parameters

Optimization of adsorbent dosage: In order to optimize the

dosage, other parameters, namely, shaking time, settling time, initial pH, and initial Cr(III) concentration, were kept constant. Figure 4(a) indicates the extent of removal of Cr(III) from 10.0 mg L⁻¹ solution by NSCW for different dosages. Accordingly, the extent of removal of Cr(III) increases considerably with increasing the dosage. As the optimum (minimum) dosage for the most efficient removal of Cr(III), a mass of 0.70 g was selected beyond which the extent of removal becomes constant regardless of the adsorbent dosage.

Optimization of shaking time: When conducting experiments to optimize the shaking time, other parameters, such as settling time, initial pH, initial metal ion concentration and temperature, were kept constant in addition to the optimized dosage of adsorbent (0.70 g). As clearly evident in Figure 4(b), the extent of removal increases considerably during the initial 90 min period of shaking, beyond which it becomes constant. Therefore, the optimum shaking time for removal of Cr(III) was taken as 90 min.

Optimization of settling time: It is clear from the results of Figure 4(c) that the extent of removal remains almost the same during the entire settling time period of 120 min at the optimum dosage and optimum shaking time conditions. However, a settling time of 30 min was taken as the optimum settling time in subsequent adsorption experiments of Cr(III) to assure the establishment of equilibrium.

Optimization of pH: The pH of a solution is an important parameter which affects adsorption

characteristics of Cr(III) because precipitation begins when the medium is sufficiently basic, thus limiting solution studies. As the precipitation of Cr(III) begins at pH = 6.0, optimization studies had to be limited to pH = 7.0. Further, it is observed that the extent of Cr(III) removal becomes constant beyond pH = 4, and hence, the ambient pH of Cr(III) solutions, which is 5.0, is considered to be the most suitable for adsorption experiments [Figure 4(d)].

Determination of the extent of removal of Cr(III) under optimized conditions

More importantly, the extent of removal of Cr(III) by NSCW under the optimized conditions is determined to be 92.9%, which is a significant enhancement of 73.3% when compared to the removal with untreated biosorbent, SCW, which shows 53.6% removal. Even though NSCW shows a better removal of Cr(III) than that of many other biosorbents, its life-time is less when in contact with water. Moreover, the composition of SCW would vary with the variety of coconut and the geographical origin.

Isotherm studies of NSCW

Sorption data are important in various industrial processes which include adsorption as one of the steps which involve adsorbate-adsorbent systems. Such systems are characterized by analyzing sorption data according to adsorption isotherms. Common isotherm models used in this regard are Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Redlich-Peterson. Among these, the mostly fitted models for natural sorbents are Langmuir and Freundlich models.

The Langmuir model is the best known and the most widely applied sorption isotherm which assumes homogeneous, monolayer adsorption. The Langmuir isotherm is based on the main assumption that adsorption can only occur at a fixed number of localized sites which are identical and equivalent (Azizian, 2004). This adsorption isotherm is defined as,

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_e is the mass of adsorbate adsorbed from solution at equilibrium (mg kg^{-1}), q_{max} is the adsorption capacity (mg g^{-1}), K_L is Langmuir constant (L mg^{-1}), and C_e is concentration of adsorbate in solution at equilibrium (mg L^{-1}). The linearized form of this model can be given as,

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (4)$$

The Freundlich isotherm is often used to describe the adsorption on solid surfaces. It describes physical adsorption from liquids; assuming multilayer adsorption, with non-uniform distribution over a heterogeneous surface. The empirically derived Freundlich isotherm is given in Equation (5),

$$q_e = K_f C_e^{1/n} \quad (5)$$

where K_f is the Freundlich adsorption constant (mg kg^{-1}) and n is a dimensionless constant. The linear form of this equation is given as,

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

Figure 4: (a) Extent of removal of Cr(III) from 10.0 mg L^{-1} solutions by NSCW for different dosages (1.0 h shaking time, 1.0 h settling time) (b) For different shaking times (0.70 g of NSCW, 1.0 h settling time) (c) For different settling times (0.70 g of NSCW, 1.0 h shaking time) (d) For different pH values (0.70 g of NSCW, 1.0 h shaking time, 30 min settling time).

Table 2: Adsorption capacity (q_{max}) values reported by different natural adsorbents.

Adsorbent	q_{max} / mg g ⁻¹	Reference
Rice husk	0.77	Priyantha <i>et al.</i> , 2015a
Saw dust	5.52	Li <i>et al.</i> , 2007
Palm flower	6.24	Elangovan <i>et al.</i> , 2008
<i>Pinus sylvestris</i> bark	8.69	Alves <i>et al.</i> , 1993
Vineyard pruning waste	12.45	Karaoğlu <i>et al.</i> , 2010
NSCW	14.30	This study

The linear regression coefficients (R^2) of adsorption data of Cr(III) on NSCW, when applied to linearized forms of the Langmuir and the Freundlich isotherms, are determined as 0.9128 and 0.8189, respectively, indicating that Cr(III)-NSCW system can be better described by the Langmuir adsorption isotherm. The parameters, q_{max} and K_L based on this model are 14.30 mg g⁻¹ and 1.02×10^{-2} L mg⁻¹. More importantly, NSCW shows a higher q_{max} value when compared to other biosorbents, demonstrating its very strong affinity towards Cr(III) (Table 2).

Modelling of adsorption kinetics

Reaction kinetics and equilibrium studies are very important to have a complete understanding about the underlying mechanism of a sorption process. Kinetics of a single step reaction is straight forward; however, adsorbate-adsorbent reactions take place in a two-phase system – solid phase and liquid phase. Such reactions would occur through multi-steps leading to complex kinetics. During investigation of adsorption kinetics, another problem faced is that the concentration of the solid phase cannot be conveniently changed unlike in the liquid phase. One approach to this issue is to investigate the kinetics during the initial stages of the adsorption reaction with a small mass of the adsorbent, so that, it can be assumed that the change in the concentration of the adsorbate is not significant. Under these circumstances, kinetics of the adsorption process can be assumed to be pseudo order with respect to the adsorbate.

A generalized equation for pseudo order kinetics can be given as.

$$\frac{d(q_t)}{dt} = k'(q_e - q_t)^n \quad (7)$$

where k' is the apparent rate constant, t is contact time, q_e and q_t are masses of adsorbate adsorbed per unit mass of adsorbent at equilibrium and at time t , respectively, n is the order of the reaction with respect to the adsorbent. By rearranging the above equation followed by integration, the linearized relationships pseudo first order kinetics and pseudo second order kinetics can be obtained.

Linearized equation pseudo first order kinetics:

$$\log(q_e - q_t) = -\frac{k_1}{2.303} t + \log q_e \quad (8)$$

Linearized equation pseudo second order kinetics:

$$\frac{t}{q_t} = \left(\frac{1}{q_e} \right) t + \left(\frac{1}{k_2 q_e^2} \right) \quad (9)$$

The pseudo first order equation describes adsorption in solid–liquid systems based on the sorption capacity of solids (Ho, 2004). The pseudo first order and the pseudo second order models are applied when changing the adsorbent dosage, the initial solution pH and the solution temperature, during the early stages up to 60 min reaction time, and resulted in the parameters and regression coefficients for adsorption kinetics given in Table 3. The conformity of the Cr(III)-NSCW system to pseudo order models depends on the experimental conditions according to the respective R^2 values given in the table. Nevertheless, the adsorption of Cr(III) on NSCW is a complicated process as detailed below.

At low adsorbent dosage values, the system follows the pseudo first order kinetics, and therefore, it is assumed that Cr(III) ion is not able to differentiate sorption sites on the NSCW surface. When the adsorbent dosage is increased, the adsorbate species would experience a high frequency of collision with adsorbent sites, thereby being able to differentiate sorption sites, leading to higher order kinetics. Having satisfied the pseudo second order kinetics is an indication that the adsorbate would be able to identify two distinct types of sorption sites during mass transfer from the solution phase to the solid adsorbent phase. Nevertheless, the validity of the pseudo order condition with respect to the adsorbate at higher adsorbent dosages is questionable as the rate of adsorption of adsorbate would be fast reaching equilibrium within a short period of time. Therefore, the results obtained at the adsorbent dosages of 1.0 g and 2.0 g would be more reliable. Accordingly, the average adsorption capacity of Cr(III) can be estimated to be 6413 mg kg⁻¹. Moreover, to avoid the complication stated above, effect of solution pH and temperature on adsorption kinetics was investigated with an adsorbent dosage of 2.0 g.

At low solution pH of 3.0, Cr(III) species is more soluble, and hence the mobility would be high. Therefore, the adsorbate species would not be able to differentiate sorption sites, leading to pseudo first order kinetics with a high regression coefficient value, $R^2 = 0.9683$. For the same reason, the adsorption capacity determined was low (Table 3). The situation at pH = 4 is not as desirable as at pH = 3.0 for adsorption kinetics due to solubility issues. Lower R^2 value of 0.9195 observed at pH = 4.0 can thus be explained. At pH = 5.0, which is close to the pH of 5.6 required for complete precipitation of Cr(OH)₃ from a 10.00 mg L⁻¹ solution, according to solubility product calculations, precipitation would start. This disrupts the

Table 3: Parameters of pseudo first order and pseudo second order models for adsorption of 10.00 mg L⁻¹ Cr(III) solution of volume 950.0 mL on NSCW. Change in adsorbent dosage: pH = 4.0, solution temperature = 28 °C; Change in pH: Adsorbent dosage = 2.0 g, solution temperature = 28 °C; Change in solution temperature: Adsorbent dosage = 2.0 g, pH = 4.0.

		Pseudo first order			Pseudo second order		
		$k_1/\text{mg kg}^{-1} \text{min}^{-1}$	$q_e/\text{mg kg}^{-1}$	R^2	$k_2/\text{mg}^{-1} \text{kg min}^{-1}$	$q_e/\text{mg kg}^{-1}$	R^2
Adsorbent dosage/g	1.0	1.18×10^2	6327	0.9773	7.83×10^{-6}	3333	0.3254
	2.0	2.83×10^{-2}	6498	0.9195	2.30×10^{-5}	185	0.3385
	4.0	5.18×10^{-2}	4973	0.7811	1.33×10^{-4}	5000	0.9807
Solution pH	3.0	1.62×10^{-1}	1049	0.9683	1.09×10^{-4}	1429	0.8849
	4.0	2.83×10^{-2}	6498	0.9195	2.30×10^{-5}	185	0.3385
	5.0	2.12×10^{-1}	8164	0.5685	1.96×10^{-6}	10000	0.0557
Solution temperature/°C	28	2.83×10^{-2}	6498	0.9195	2.30×10^{-5}	185	0.3385
	35	1.19×10^{-1}	3320	0.8296	2.86×10^{-5}	5000	0.8582
	40	1.56×10^{-2}	2311	0.4318	5.33×10^{-4}	1250	0.9206

Figure 5: Intra-particle diffusion models for the interaction of Cr(III)-NSCW (a) Different adsorbent concentrations. ● 1 g ▲ 2 g ■ 4 g (b) Different temperatures ● 28 °C ▲ 35 °C ■ 40 °C.

diffusion-controlled mass transfer from the solution phase to the solid adsorbent phase, making the adsorption kinetics complicated. Values of R^2 obtained for both the pseudo first order and the pseudo second order being deviated far from unity, would thus explain the conformity of experimentally obtained results with neither of the kinetic models.

Although the Cr(III)-NSCW adsorption system follows the pseudo first order kinetics at the ambient

temperature of 28 °C as stated earlier, the situation is changed at warmer temperatures. The system tends to follow pseudo second order kinetics at 40 °C with a high R^2 value of 0.9206. The transition from pseudo first order to pseudo second order occurs between these two temperatures as observed at the solution temperature of 35 °C at which none of the models has a satisfactory R^2 value, and hence, the adsorption capacity determined from the models at this temperature would have a high uncertainty (Table 3). The

lower adsorption capacity for Cr(III) on NSCW of 1250 mg kg⁻¹ determined at the solution temperature of 40 °C, as compared to that at ambient temperature, is probably related to having a contribution of desorption due to warmer solution conditions. Further, the average energy of activation within the temperature range of 35 - 40 °C, determined using the rate constants obtained according to the pseudo first order model is 158 kJ mol⁻¹. Such a high energy of activation energy is indicative of chemisorption, which is further supported by the validity of the Langmuir adsorption model.

Intra-particle diffusion model

The basic assumption of the intra-particle diffusion model is that the film diffusion is negligible and intra-particle diffusion is the only rate-controlling step. The equation that governs intra-particle diffusion is given in Equation (10),

$$q_t = k_p t^{0.5} \quad (10)$$

where q_t is the extent of adsorption at time t , and k_p is the intra-particle diffusion rate constant. According to Equation (10), plots of q_t versus $t^{0.5}$ should yield a straight line passing through the origin, if the sorption process follows the intra-particle diffusion model. Although the relationships obtained for adsorption of Cr(III) on to NSCW are mostly linear over the first 15 min time interval, they do not pass through the origin indicating that the intra-particle diffusion is not the only rate-controlling step (Figure 5). The negative intercept observed at lower adsorbent dosages is indicative of boundary layer retarded diffusion (Tan and Hameed, 2017). Another important observation made is that, with increase in solution temperature, intercept becomes positive suggesting a rapid adsorption within a short time period. This also indicates that the boundary layer thickness is decreased with increasing temperature.

CONCLUSION

According to Fourier transform infrared spectra Scraped coconut waste (SCW) contains -OH, -NH and -COO functional groups. Following treatment of SCW with aqueous NaOH solution, ester groups, and carboxylic acid group undergo hydrolysis and deprotonation, respectively, forming negatively charged functionalities which would favorably attract positively charged Cr(III) adsorbate ions. Sorption of Cr(III) on NaOH-treated SCW (NSCW) obeys the Langmuir adsorption isotherm, indicating that monolayer formation is predominant. Data on adsorption kinetics gathered during early stages of interaction are in conformity with pseudo first order for lower adsorbent dosages under ambient solution temperature conditions, leading to average adsorption capacity of 6413 mg kg⁻¹. However, adsorption kinetics is changed to pseudo second order condition for higher dosages. Further, warmer solution temperatures promote adsorption of Cr(III) on NSCW to fulfill conditions of pseudo second order kinetics, resulting in lower adsorption capacity indicating the contribution from desorption. The average energy of activation within the temperature range of 35 - 40 °C is determined at 158 kJ mol⁻¹, giving strong evidence that

Cr(III) is chemisorbed on to NSCW. Transfer of Cr(III) adsorbate species towards the NSCW adsorbent is not solely controlled by intra-particle diffusion, and moreover, boundary layer retarded diffusion is observed at lower adsorbent dosages under ambient temperature conditions.

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DECLARATION OF CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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