ADSORPTION OF CHROMIUM (VI) BY *Delonixregia* (FLAME OF THE FOREST) PODS: KINETICS AND THERMODYNAMIC STUDIES

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Abstract: In this study we engaged the use of a low-cost adsorbent, *Delonixregia* in the adsorption and removal of Cr (VI) ions from synthetic wastewater. The effects of different experimental conditions such as solution pH, contact time and temperature were studied so as to optimize the adsorption process. An optimum pH of 1 and contact time of 240 min were obtained for the adsorption process. Modelling the kinetic data showed that pseudo-second-order kinetic model provided the best fit for. The study showed that *Delonixregia* have an adsorption capacity of 9.23 mg/g for chromium (VI) ions, increasing the adsorbent dose increased the uptake of chromium (VI) ions while the presence of Mg^{2+}, Ca^{2+} and Na^{+} reduced the capacity of *Delonixregia* for the uptake of chromium (VI) ions as verified here. The results from thermodynamic study revealed the process to be exothermic, with ΔH = -14813 kJ/mol, ΔS = -61.81 and positive values of Gibb's free energy at all temperature used in this study. This study has proven that *Delonixregia* biomass, an agro-waste could be used for removing Cr(VI) ions from wastewater.

Keywords: *Delonixregia*, chromium(VI), kinetic modelling, pseudo-second-order, enthalpy, Gibb's free energy

Introduction

Heavy metals are important pollutants in source and treated water and their presence has become a severe public health concern since industrial waste serves as the main point source into the environment (Pastircakova, 2004; Demirbas *et al.*, 2005; Celik and Demirbas, 2005; Demirbas *et al.*, 2006).

Chromium occurs as ores in natural deposits containing some elements such as ferric chromite ($FeCr_2O_4$), crocite ($PbCrO_4$) and chrome ochre (Cr_2O_3) (Mohana and Pittman, 2006). It is a common highly toxic metal in drinking water, and it naturally exists in various oxidation states ranging from +2, +3 and +6. The heavy metal chromium is used largely in industries such as electroplating, textile, steel production, chrome plating, wood conservation, tanning, leather, glass, pigment and fabrication. The metal is used also as cleaning agents, titrating agents and additives in the production of mold and magnetic tape fabrication process (Miretzky and Cirelli, 2010).

Various activities carried out in these industries produce waste product in which the hexavalent form of chromium (Cr (VI)) and the trivalent form (Cr(III)) are available (Atieh *et al.*, 2010). Cr (VI) is more harmful than the Cr (III) for plants, animals and other organisms (Ali *et al.*, 2013; Demim *et al.*, 2013). Cr (VI) is extremely toxic and its presence in various industrial wastewater result in severe vomiting, creation of ulcer, pulmonary congestions, skin inflammation, diarrhea, liver and kidney damage (Fang *et al.*, 2007; Mohan *et al.*, 2006; Hu *et al.*, 2009; Miretzky and Cirelli, 2010).

Discharge of industrial wastewater to the environment is the potential source of chromium release to drinking water. Much quantity of chromium metal due to its use in the industries must be considerably removed from the wastewater before it gets released into the environment or be modified into less toxic forms (Ihsanullah *et al.*, 2016).

Various researches have focused on the removal of pollutants which include heavy metals, biodegradable waste, nitrates and phosphates, dyes, heat, sediment, fluoride, pharmaceutical and personal care products and radioactive pollutants (Reddy *et al.*, 2013) with different treatment methods which include ion exchange, nano-filtration, oxidation/precipitation, coagulation/co-precipitation, solvent extraction, bioremediation etc. (Saha and Sarkar, 2012; Crini and Badot, 2008). Among these techniques, adsorption has been adjudged one of the most viable methods due to its simplicity of operation, easy recovery, cost effectiveness, sludge-free operation and regeneration capacity (Gusmão *et al.*, 2012).

However, the removal of heavy metal ions from wastewater is always a challenging task for environmentalists, even though some researchers have attempted to develop good performance adsorbents for the removal of heavy metal ions. Amongthese adsorbents, activated carbon is regarded as one of the most effective adsorbents for heavy metal ion removal because it has high specific surface area and adsorption capacity, but its use has been restricted because it is relatively expensive, thus the search for technique that make use of relatively cheap, indigenous and largely available adsorbent continues.

One of such techniques is biosorption, that is, the use of low-cost adsorbent like agricultural materials of no economic value and industrial by-products (Jeme, 1968; Inoue *et al.*, 1979) for the removal of heavy metal ions from polluted water.

Various low cost biomaterials were reported, Owalude and Tella (2016) reported the use of ground nut hulls as adsorbent for the removal of chromium (VI) from aqueous solution; rice husk, Eucalyptus bark and bagasse were reported to have been used for treating industrial effluent in order to remove chromium and magnesium ions (Sarin and Pant, 2005). Neem leaf powder was also reported to have been used to remove hexavalent chromium from aqueous solutions (Jain, 2014). Furthermore, Aloe vera leaf was investigated by Jeyaseelan and Gupta (2016); Sugarcane leaf was used by Parlayici and Pehlivan (2012) to remove lead and chromium ions. The authors reported pH 2 as the optimum pH value for the removal of Cr^{6+} from a solution of 200 mg/L. Rane *et al.*, (2010) investigated the use of green coconut shell treated with or thophosphoric acid while Ali and Mabood (2016) worked on bamboo treated with potassium hydroxide in order to remove chromium (VI) ions. 83% adsorption of chromium (VI) ions by coconut shell at pH 1.5 optimum contact time of 10 hours, particle size 75 micro m was reported by Babel and Kurniawan (2004); Kumar *et al.* (2017); Pandhram and Nimbalkar (2013); Panda *et al.*, (2017). Gupta and Babu (2009) reported 81% as the maximum removal efficiency of sawdust for chromium (VI) ions at optimum pH 1, and contact time of 250 min.

This research work was carried out to investigate the potentials of an agro-waste *Delonixregia* pods for the removal of chromium (VI) ions from aqueous solutions. The kinetics and thermodynamics of the process was also studied. Desorption and possible recovery of adsorbed metal from the adsorbent using various concentrations of hydrochloric acid was considered.

Delonixregia is popularly grown in Africa and Hong Kong as a shade tree and for ornamental purpose. The tree has pods that can be as long as 60 cm in length and 5 cm wide, with a distinct bright green fern-like compound leaves. It belongs to the flowering plant family *Fabaceae* and commonly called the flame of the forest tree. The outcome of this research would be of great benefit to most industries in the developing countries of the world, the adsorbent would serve as cheaper adsorbent for the removal of chromium (VI) ions from wastewater.

Materials and Methods

Analytical grades of chemicals purchased from Sigma Aldrich, USA were used in this experiment. Potassium dichromate salt ($K_2Cr_2O_7$), sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium sulphate (Mg_2SO_4), Sodium hydroxide (NaOH) and concentrated hydrochloric acid (HCl) were used without further purification. 1000 mg/L of Cr^{6+} was prepared by dissolving potassium dichromate (VI) salt with deionized water in a 1L volumetric flask. HCl and NaOH (0.1M) were used to adjust the pH of the solution where necessary. NaCl, $CaCl_2$ and $MgSO_4$ were used for the study of interference of other ions on the adsorption process. *Delonixregia* pods, collected from The Federal University of Technology Akure were thoroughly washed with deionized water, sun dried, chopped into small pieces and blended. The blended component was sieved through a screen of mesh size 850 µm to obtain the fine powder that was used as the adsorbent for the removal of chromium (VI).

Sorption experiments

From the *Delonix regia* fine powder, 0.5 g was weighed into 150 ml tubes containing 100 ml of the Cr^{6+} solution of pH 1.0 to 7.0. The suspensions were stirred for 6 hours, after which they were centrifuged and analysed for the residual metal content using an atomic absorption spectrophotometer. From the analysis pH 1.0 was observed as the optimum for the removal of Cr^{6+} and thus was used for further experiments such as contact time study, adsorbent dose, ionic interference done to optimize the adsorption process.

Sorption kinetic was conducted by adding 0.5 g of *Delonixregia* pods to 100 mL of Cr^{6+} solution and shaken for the interval of 5, 15, 30, 60, 90, 120, 180, 240, 300, and 360 min. At the expiration of each time interval, the suspensions were centrifuged and analysed to determine the residual amount of Cr^{6+} in the aqueous solutions. In all experiments conducted in this research, an initial concentration of 100 mg/L of Cr^{6+} was used with the exception of isotherm modelling experiment where concentrations of 10, 20, 40, 60, 80, 100, 150 and 200 mg/L were used. In order to study the effect of temperature on the process, reaction temperature which normally was 25^{o}C was changed to 30, 40, 50 and 60^{o}C (Meena *et al*., 2008).

The percentage Cr(VI) ions removal was calculated using Equation 1 and the amount of Cr(VI) ions adsorbed (Q_e) was calculated using Equation 2.

$$\% \, removal = \frac{C_o - C_e}{C_o} \times 100 \quad Equation\ 1$$

$$Q_e = \frac{C_o - C_e}{W} \times V Equation\ 2$$

Where C_o and C_e (mg/L) are the initial and equilibrium concentration of Cr (VI) ions solution, respectively, V (mL) is the volume of the solution, W is the mass of *Delonixregia* used as adsorbent and Q_e (mg/g) is the mass of Cr (VI) ions adsorbed per unit mass of the adsorbent.

Results and Discussion

Effect of pH

The effect of pH on chromium (VI) sorption by *Delonixregia* pods is very important in establishing the optimum sorption of metal ions at the solid/liquid interphase. Ionization and solubility of metal ions during sorption is pH dependent because at low pH, hydrogen ions tend to occupy some of the binding sites on the adsorbents (Vimala and Das, 2009). The result obtained for this aspect of the study is presented in Figure 1, from where it is shown that 92.35 - 25% of chromium (VI) was removed at pH range 1.0 to 7.0. Major decrease was found in the percentage of chromium (VI) adsorbed between pH 1.0 and 3.0, after these values the percentage adsorbed remained constant throughout the range tested in this study. At pH 1, which is the optimum for this work, 92% adsorption was recorded; this value decreased to 57% at pH 2 and 28% at pH 3. Further increase in pH had no effect on the percentage adsorbed. The sharp decrease in adsorption noticed as pH values increase may occur due to the formation of cadmium hydroxides. Similar report was given by Gupta and Babu (2009) and Ali and Mabood (2016).

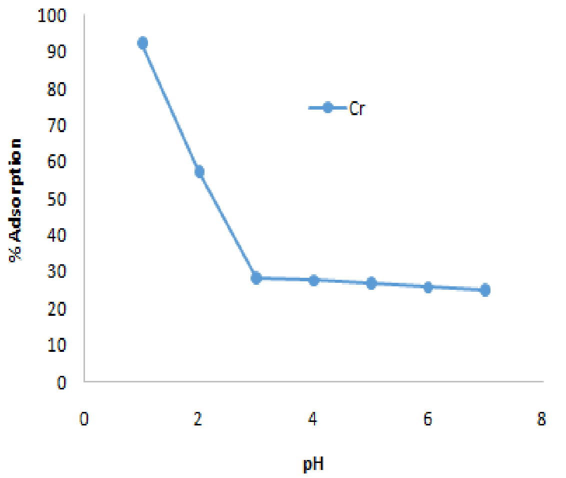

Fig. 1: Effect of pH on the adsorption of chromium (VI) ions by Delonixregia pods

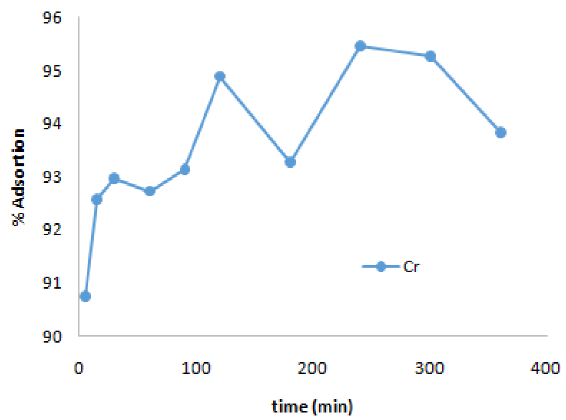

Fig. 2: Contact time on the adsorption of Cr^{6+}

Contact time and kinetic modelling

The result shown in Fig. 2 represent what was obtained from the contact time study that was done in order to determine the equilibrium time for the adsorption of Cr (VI) ions unto *Delonixregia* pods at time intervals between 5 and 360 min. The result showed a rapid uptake of about 90.7% (9.07 mg/g) chromium (VI) ions by the adsorbent occurred within 5 min of contact, after which series of adsorption and desorption of the adsorbate was observed between 30 and 60 min and also between 120 and 240 min of interaction after which a decline was observed at 300 min. At 240 min of contact, maximum uptake of 94.5% (9.49 mg/g) was achieved on the adsorbent which decreased to 93.8% at 300 min. This result showed the high potency of *Delonixregia* in removing chromium (VI) from solution. Thus in all subsequent experiments, the contact time of 240 min was used.

Adsorption kinetics describes the rate of metal uptake on *Delonixregia* and this rate in turn controls the equilibrium time. The kinetics of adsorbate uptake is necessary for choosing optimum operating conditions for full scale batch process (Ghomri *et al.*, 2013). The kinetic parameters give information for designing and modelling processes and are useful insight for prediction of adsorption rate.

The experimental data obtained from contact time study was used for the kinetic modelling and it fitted the pseudo-second order kinetic equation shown in Equation 3

$$\frac{t}{Q_t} = \frac{1}{k_{2,ad}Q_{eq}2} + \frac{1}{Q_{eq}t} \text{Equation 3}$$

where $k_{2,ad}$ is the pseudo-second-order rate constant for adsorption (g/mg/min); contact time, t, (min); Q_t, sorption uptake at any time t and Q_{eq} (mg/g) is the equilibrium sorption uptake.

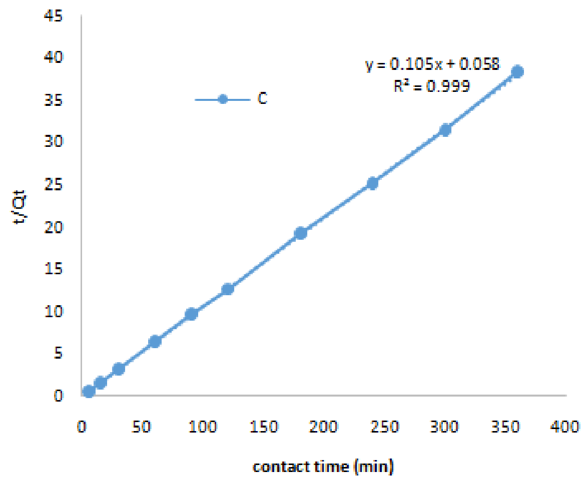

Fig. 3: Second-order kinetics plot for the adsorption of Cr^{6+}

The linearity of the plot of t/Q_t against t showed the applicability of the pseudo-second-order kinetic model to the adsorption process. From the plot Q_{eq} (9.50 mg/g) and $k_{2,ad}$ (0.19 g/mg/min) are obtained from the slope and intercept, respectively.

Furthermore, the experimental data from contact time study was tested to show the contributions of intra-particle diffusion mechanism using the Weber and Moris equation shown in Equation 4 (Abu Al-Rub *et al.*, 2004).

$$Q_t = k_{id}t^{1/2} \text{Equation 4}$$

where k_{id} is the intra-particle diffusion rate constant ($mg/min^{1/2}/g$), and $Q_t$is the amount of adsorbate adsorbed (mg/g) at any time t (min^{-1}).

The plot of Q_t versus $t^{1/2}$ shown in Fig. 4 should be linear if the only mechanism applicable is intra-particle diffusion. The plot obtained in Fig. 4 shows a non-linear curve and does not passes through the origin an indication that intra-particle diffusion mechanism is not the only mechanism involved in the sorption of chromium (VI) unto *Delonixregia*. It can be deduced from the two kinetic modelling used in this work that physisorption and chemisorption are involved in the adsorption of chromium (VI) ions unto *Delonixregia*.

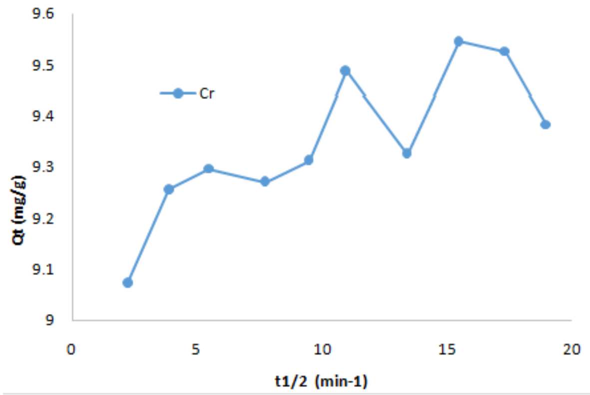

Fig. 4: Intra-particle diffusion plot for the adsorption of Cr $^{6+}$

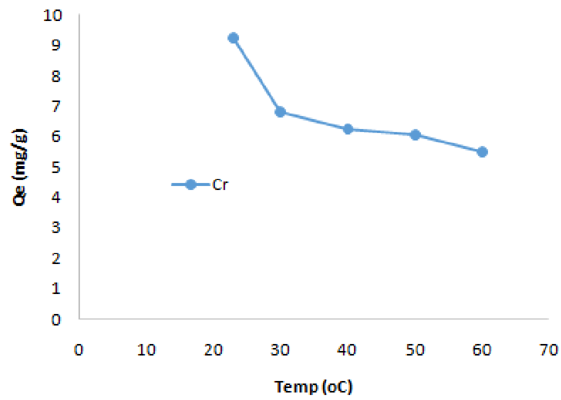

Fig. 5: Effect of temperatureon the adsorption of Cr^{6+}

Effect of temperature on adsorption of Cr^{6+}

It has been documented that increase in temperature leads to a decrease in the rate of adsorption (Kapoor, 1987). Fig. 5 showed that when the temperature was increased from 25 to 30°C, the uptake of chromium (VI) ions was reduced from 9.26 to 6.85 mg/g; further increase in temperature to 60°C reduced the uptake to 5.50 mg/g. The effect of temperature can be understood from the thermal energy of the adsorbate and the residual binding forces of the adsorbent surface. These two parameters are antagonistic to each other and thus if the temperature of a system is high, there will be large thermal energy which in consequence will lessen the number of molecules held to the solid surface and hence reduced adsorption will be observed; whereas at lower temperature, the opposite will occur (Kapoor, 1987).

Figure 5 showed clearly that the adsorption of chromium (VI) ions to *Delonixregia* pods is an exothermic process, by applying the Vant Hoff's equation (Equation 5) the change in enthalpy (ΔH) = -14,813.05 kJ/moland change in entropy (ΔS)= -61.81 J/K/molof the adsorption systemwereobtained from the slope and intercept of the plot of Ln k against 1/T shown in Fig. 6.

$$Ln\ k = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{Equation 5}$$

where k is the distribution coefficient (ml/g), R is the gas constant (8.313 J/K/mol), ΔH is the enthalpy (kJ/mol), ΔS is the entropy (J/mol) and T is temperature in Kelvin. It is possible to calculate the Gibb's Free energy (ΔG) of the system (Equation 6) at various temperatures used in this work since the values of ΔH and ΔS have been determined.

$$\Delta G = \Delta H - T\Delta S \qquad \text{Equation 6}$$

The numerical value of G increases with increase in temperature implying that the reaction is non-spontaneous and not favourable at higher temperature.

Table 1: Thermodynamic parameters for the adsorption of Cr (VI) ions on *Delonixregia*

∆H (kJ/mol)	∆S (J/mol)	∆G (KJ/mol) 288K	293K	303K	313K
- 14,813.05	-61.81	32,614.33	32,923.38	33541.48	32,923.05

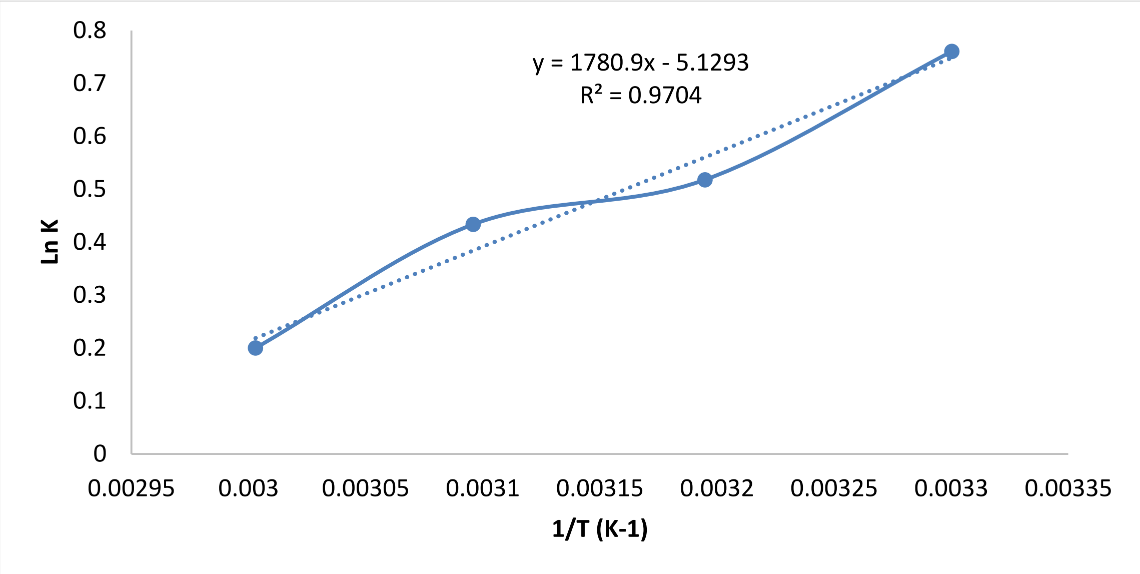

Fig. 6: Plot of Ln K versus 1/T for the adsorption of chromium (VI) ions

Adsorbent dose study

The surface of contact between sorbents dose and liquid phase plays an important role in adsorption. The plot in Figure 7 is the result obtained from the study of adsorbent dosage on the adsorption of chromium (VI) ions unto *Delonixregia* pods, it showed that at 0.2 grams of adsorbent, 48.51% equivalent to 4.82 mg/g was adsorbed while an increase in adsorbent dosage to 1.0 grams showed an increase in percentage adsorbed to 98.99 grams (9.89 mg/g). The main factor responsible for the observed increase in amount of chromium (VI) ions adsorbed is that the number of adsorption sites available for adsorption increased with increasing adsorbent dosage.

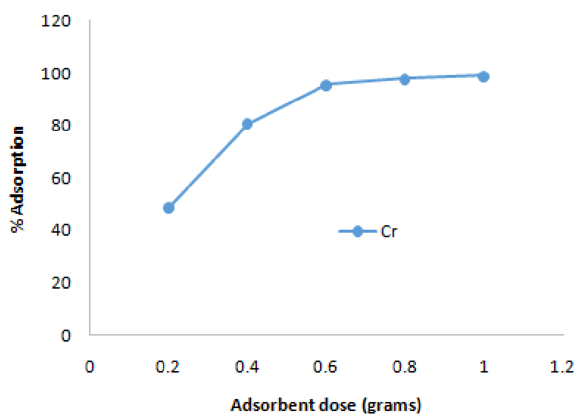

Fig. 7: Effect of adsorbent dose on the adsorption of Cr^{6+} unto *Delonix regia*

Effect of ionic interference

Some cations such as sodium, magnesium and calcium are mostly found co-existing with other metals in wastewater and their interference in the adsorption process is one major problem that is frequently encountered in adsorption systems. The result for the interference study presented in Fig. 8 showed that the presence of each of the tested cations in the adsorbate solution decreased the uptake of metal ions by the adsorbent. Within the concentration range of interfering ions (20 – 250 mg/L) used in this study the decrease in uptake recorded for sodium ions were 9.33 to 7.43 mg/g (%?) while that of magnesium and calcium ions were 8.33 to 7.43 and 8.23 to 4.13 mg/g, respectively. This showed clearly that the reduced uptake of the adsorption of chromium (VI) ions by *Delonix regia* is more pronounced in the presence of Ca^{2+} especially at high concentration, the trend observed in uptake could be written as $Ca^{2+} > Mg^{2+} > Na^{+}$.

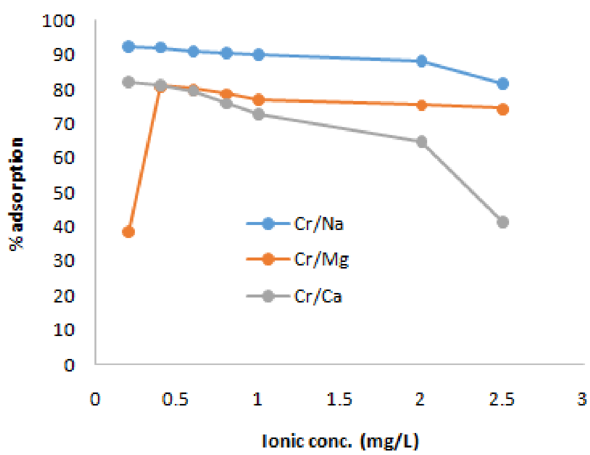

Fig. 8: Effect of ionic interference on the adsorption of Cr^{6+}

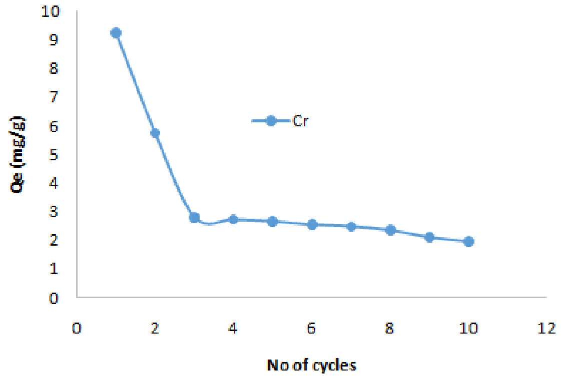

Fig. 9: Plot of the adsorption capacity of Delonix regia for Cr^{6+}

Adsorption capacity

With the view of establishing the carrying capacity of *Delonix regia* pods for chromium (VI), an adsorption capacity experiment was conducted by carrying out batch adsorption in ten consecutive cycles; the result obtained is shown in Fig. 9. The efficiency of the biomass to remove chromium (VI) ions gave 9.23 mg/g uptake in the first cycle, this is an amount close to the value (9.55 mg/g) obtained in the contact time of 120 minutes, but at the tenth cycle, the biomass removed 1.94 mg/g of chromium (VI) from the solution. Thus, the adsorption capacity of *Delonix regia* pods for chromium (VI) ions is 9.23 mg/g.

Desorption

Desorption study of the adsorbed Cr (VI) ions from the biomass was carried out to assess the potency of the biomass for possible re-use and to attempt the recovery of the adsorbed metal ions for other usage. The result obtained from the experiment revealed low desorption of chromium ions from *Delonix regia* pods (Fig. 10).

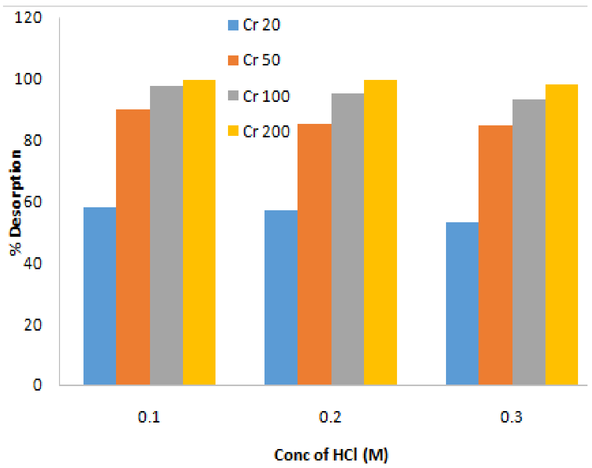

Fig. 10: Desorption of adsorbed chromium (VI) ions from *Delonix regia*

This could be attributable to very high binding affinity of chromium (VI) ions to *Delonix regia* pods. Desorbing the spent biomass with three different concentrations of HCl (0.1, 0.2, 0.3M) yielded 41.65, 43.05 and 47.05% desorption. This further confirmed the type of association that might be involved in the adsorption of chromium (VI) ions unto *Delonix regia* to be chemical bonding.

Conclusion

The results of this study indicated that *Delonixregia* can be successfully used to remove Cr (VI) ions from aqueous solutions especially at low temperatures;it will present a major advantage of wastewater treatment at low cost. We have optimized the conditions for adsorption and obtained optimum pH of 1, equilibrium time of 240 minutes and that the pseudo-second-order kinetic model provided the best fit for the kinetic data. From the adsorption capacity experiment, the adsorption capacity of *Delonix regia* for chromium (VI) ions was 9.23 mg/g.

The values of enthalpy ΔH and ΔS evaluated from the variation of temperature revealed that the adsorption of chromium (VI) ions unto *Delonixregia* to be an exothermic process while the values obtained for G showed the non-spontaneity of the adsorption process. The presence of interfering ions reduced the capacity of *Delonixregia* for the uptake of chromium (VI) ions; the reduction was more evident with the divalent Ca^{2+} and Mg^{2+}. The desorption of adsorbed metal ions might not be feasible at low concentrations of desorbing solution. This study has shown the potential of *Delonixregia* pods for the removal of chromium (VI) ions from aqueous solution and thus could be a viable option for reducing chromium (VI) ions in wastewater thus reducing water pollution.

Conflict of Interest

Authors declare that there is no conflict of interest related to this study.

References

Ali A, Saeed K & Mabood F 2016. Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent. *Alexandria Engr. J.*, 55(3): 2933-2942.

Abu Al-Rub FA, El-Naas MH, Benyahia F & Ashour I 2004. Biosorption of nickel on blank alginate beads free and immobilized algal cells. *Process Biochemistry*, 39(11): 1767-1773.

Ali H, Khan E & Sajad MA 2013. Phytoremediation of heavy metals – Concepts and applications. *Chemosphere*, 91(7): 869-881.

Atieh MA, Bakather OY, Tawabini BS, Bukhari AA, Khaled M, Alharthi M, Fettouhi M & Abuilaiwi FA 2010. Removal of chromium (III) from water by using modified and nonmodified carbon nanotubes. *Journal of Nanomaterials*, p. 17.

Babel S & Kurniawan TA 2004. Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 54(7): 951-967.

Celik A & Demirbaş A 2005. Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes. *Energy sources*, 27(12): 1167-1177.

Crini G & Badot PM 2008. Application of chitosan, a natural amino polysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Progress in Polymer Science*, 33(4): 399-447.

Demim S, Drouiche N, Aouabed A, Benayad T, Dendene-Badache O & Semsari S 2013. Cadmium and nickel: Assessment of the physiological effects and heavy metal removal using a response surface approach by *L. gibba*. *Ecological Engineering*, 61: 426-435.

Demirbas A, Pehlivan E, Gode F, Altun T & Arslan G 2005. Adsorption of Cu (II), Zn (II), Ni (II), Pb (II), and Cd (II) from aqueous solution on Amberlite IR-120 synthetic resin. *J. Colloid and Interface Sci.*, 282(1): 20-25.

Demirbas A, Sari A & Isildak O 2006. Adsorption thermodynamics of stearic acid onto bentonite. *Journal of Hazardous Materials*, 135(1-3): 226-231.

Fang JUN, Gu Z, Gang D, Liu C, Ilton ES & Deng B 2007. Cr (VI) removal from aqueous solution by activated carbon coated with quaternized poly (4-vinylpyridine). *Envtal. Sci. & Techn.*, 41(13): 4748-4753.

Ghomri F, Lahsini A, Laajeb A & Addaou A 2013. The removal of heavy metal ions (copper, zinc, nickel and cobalt) by natural bentonite. *LARHYSS Journal ISSN 1112-3680*, (12).

Gupta S & Babu BV 2009. Removal of toxic metal Cr (VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies. *Chem. Engr. J.*, 150(2-3): 352-365.

Gusmão KAG, Gurgel LVA, Melo TMS & Gil LF 2012. Application of succinylated sugarcane bagasse as adsorbent to remove methylene blue and gentian violet from aqueous solutions–kinetic and equilibrium studies. *Dyes and Pigments*, 92(3): 967-974.

Hu J, Chen C, Zhu X & Wang X 2009. Removal of chromium from aqueous solution by using oxidized multiwalled carbon nanotubes. *Journal of Hazardous Materials*, 162(2-3): 1542-1550.

Ihsanullah Al-Khaldi FA, Abu-Sharkh B, Abulkibash AM, Qureshi MI Laoui T & Atieh MA 2016. Effect of acid modification on adsorption of hexavalent chromium (Cr (VI)) from aqueous solution by activated carbon and carbon nanotubes. *Desalination and Water Treatment*, 57(16): 7232-7244.

Inoue Y & Munemori M 1979. Coprecipitation of mercury (II) with iron (III) hydroxide. *Envtal. Sci. & Techn.*, 13(4): 443-445.

Jain RN, Patil S & Lal D 2014. Adsorption of Cr-(VI) from aqueous environment using neem leaves powder. *Int. J. Res. in Engr. and Techn.*, 3(9): 25-28.

Jeme EA 1968. Controls of manganese, iron, cobalt, nickel, copper and zinc concentrations in soils and water. *Adv. Chem. Ser.*, 7: 33-37.

Jeyaseelan C & Gupta A 2016. Green tea leaves as a natural adsorbent for the removal of Cr (VI) from aqueous solutions. *Air, Soil and Water Research*, 9: ASWR-S35227.

Kapoor KL 1987. Elements of Physical Chemistry. Part III, Macmillan India Ltd., New Delhi, pp. 61-62.

Kumar R, Arya DK, Singh N & Vats HK 2017. Removal of Cr (VI) using low cost activated carbon developed by agricultural waste. *IOSR J. Appl. Chem.*, 10(1): 76-79.

Meena AK, Kadirvelu K, Mishraa GK, Rajagopal C & Nagar PN 2008. Adsorption of Pb (II) and Cd (II) metal ions from aqueous solutions by mustard husk. *Journal of Hazardous Materials*, 150(3): 619-625.

Miretzky P & Cirelli AF 2010. Cr (VI) and Cr (III) removal from aqueous solution by raw and modified lignocellulosic materials: A review. *Journal of Hazardous Materials*, 180(1-3): 1-19.

Mohan D & Pittman Jr. CU 2006. Activated carbons and lowcost adsorbents for remediation of tri-and hexavalent chromium from water. *Journal of Hazardous Materials*, 137(2): 762-811.

Mohan D, Singh KP & Singh VK 2006. Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. *Journal of Hazardous Materials*, 135(1-3): 280-295.

Owalude SO & Tella AC 2016. Removal of hexavalent chromium from aqueous solutions by adsorption on modified groundnut hull. *Beni-suef Univ. J. Basic and Appl. Sci.*, 5(4): 377-388.

Panda H, Tiadi N, Mohanty M & Mohanty CR 2017 .Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution. *South Afr. J. Chem. Engr.*, 23: 132-138.

Pandhram P & Nimbalkar Shubhangi 2013. Adsorption of chromium from industrial waste water by using neem leaves as a low cost adsorbent. *Int. J. Chem. Phy. Sci.*, 2: 149-158.

Parlayici-Karatas S & Pehlivan E 2012. Removal of hexavalent chromium using modified pistachio shell. *Advances in Environmental Research*, 1(2): 167-179.

Pastircakova K 2004. Determination of trace metal concentrations in ashes from various biomass materials. *Energy Education Science and Technology*, 13: 97-104.

Saha S & Sarkar P 2012. Arsenic remediation from drinking water by synthesized nano-alumina dispersed in chitosan-grafted polyacrylamide. *Journal of Hazardous Materials*, 227: 68-78.

Sarin V & Pant K 2006. Removal of chromium from industrial waste by using eucalyptus bark. *Bioresource Technology*, 97(1): 15-20.

Rane NM, Sapkal RS, Sapkal VS, Patil MB & Shewale SP 2010. Use of naturally available low-cost adsorbents for removal of Cr (VI) from waste water. *Int. J. Chem. Sci. and Applic.*, 1(2): 65-69.

Reddy DHK & Lee SM 2013. Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions. *Advances in Colloid and Interface Science*, 201: 68-93.

Vimala R & Das N 2009. Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: A comparative study. *Journal of Hazardous Materials*, 168(1): 376-382.