

The effect of operational parameters on biosorption of Cd²⁺, Ni²⁺ and Cr⁶⁺ using *Glycine max* pod (Soya Bean).

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Abstract

The potential of *glycine max* pod (GMP) in removal of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions from aqueous solutions was examined in a batch adsorption process with respect to several experimental conditions including pH of solution, contact time, GMP dosage, initial metal ions concentration, and temperature, etc. The characterization of GMP was performed by using FTIR and SEM techniques. The maximum uptake of Cd²⁺ (1.445 mg/g), Ni²⁺ (1.585 mg/g) and Cr⁶⁺ (1.594 mg/g) was observed when used 2.0g of GMP biomass, 25 mgL⁻¹ of initial Cd²⁺, 50 mg/l of initial Ni²⁺ and 50 mg/l of initial Cr⁶⁺ concentration at pH 5, 6 and 3 and contact time of 90, 60 and 90 min at room temperature for Cd²⁺, Ni²⁺ and Cr⁶⁺ respectively. The experimental data were analyzed by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models. The monolayer adsorption capacity Of GMP was found to be 21.56 mg/g, 53.76 mg/g and 18.87 mg/g for Cd²⁺, Ni²⁺ and Cr⁶⁺ ions, respectively. The kinetics of the adsorption was tested using pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models. The results showed that the adsorption of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions onto GMP proceeds according to the pseudo-second-order model.

Keywords: *Glycine max*, biosorption, cadmium, nickel, chromium, kinetics.

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Introduction

Industrial wastewater contains high levels of heavy metals, and their potential health implications to man and his environment has been a subject of concern in environmental studies. Heavy metal ions discharged with industrial effluents usually find their way into receiving water bodies such as rivers, lakes and streams therefore increasing the amounts of these pollutants in such water bodies. This can have serious health implications on man ranging from cancer, hormonal imbalance to brain impairment. Therefore, industrial wastewater treatment for the removal of pollutants such as heavy metal ions, remains a challenge to both developed and developing countries of the world [1].

Cadmium ion (Cd²⁺), a non-essential, non-beneficial element to plants and animals is non-biodegradable and travels through the food chain. The major sources of Cd²⁺ released into the environment are effluents from electroplating, smelting and alloy manufacturing processes [2-4]. Cd²⁺ may be ingested through the food chain, through polluted soils in which food crops are grown and inhaled through smoking. The kidneys are the critical target organ after ingestion (renal dysfunction, hypertension and anemia). Cd²⁺ combines with sulfhydryl group in protein and restrains the activity of enzymes [2]. The permissible limits of Cd²⁺, Ni²⁺ is 0.05 mg/L [5].

Nickel ions (Ni²⁺) are non-biodegradable toxic heavy metals present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries. Acute poisoning of Ni²⁺ causes headache, dizziness, nausea and vomiting, chest pain, dry cough, respiratory problems and cyanosis [4]. The Ni²⁺ level in wastewater from mine drainage and metal finishing has been reported up to 130 mg/L [6,7].

Chromium (Cr⁶⁺) is a very toxic pollutant introduced into natural waters from a variety of effluents from dyeing and metal finishing industries [8]. Chromium occurs most frequently as Cr⁶⁺ or Cr³⁺ in aqueous solutions. Both valences of chromium are potentially harmful but hexavalent chromium poses a greater risk due to its carcinogenic properties [9]. High exposure of Cr⁶⁺ causes cancer in the digestive tract and lungs leading to cause gastric pain, nausea, vomiting, severe diarrhea, and hemorrhage [8]. Because its bioaccumulation in aquatic organisms, feeding on such aquatic organisms can lead to metal poisoning in man. According to the United Nation Environment Programme [10] the maximum permissible limits in wastewater and potable water are 1.0 mg/L and 0.05 mg/L for chromium (VI) respectively [11].

In waste water treatment, various technologies are available such as chemical precipitation, ion exchange, electrochemical precipitation, solvent extraction, membrane separation, coagulation, reverse osmosis, emulsion and adsorption are used. However, cost implication, huge sludge generation and environmental friendliness form the major techno-economic limitation of these techniques for water treatment. Therefore the development and improvement of absorption capacities of agricultural waste material for removal of toxic pollutants especially heavy metals is needed to reduce cost of purifying industrial wastewaters before disposal [12].

This research work is aimed at probing into the metal uptake ability of *Glycine max* pod (GMP) to ascertain potential of *Glycine max* pod (GMP) as a biosorbent in sequestering heavy metals from aqueous solution. For its objective, this study investigates the influence of some operating parameter such as

the effect of pH, contact time, initial metal ion concentration and sorbent dosage on the uptake of Cd²⁺, Ni²⁺ and Cr⁶⁺ by *Glycine max* pod. The kinetics and equilibrium modeling of the system were also investigated.

Materials and Methods

Preparation of the biosorbent

The *Glycine max* pods (GMP) were collected at different location within a farmland in Agbonle village, Saki-East LGA of Oyo State. The GMP sample was washed to removed dirt and debris, air dried. The dried sample was grounded in a mechanical grinder to form a powder. The powder was sieved using a 0.45 mm mesh screen and stored in air tight plastic bottle to protect it from moisture before use in all the experiments.

Characterization of the biosorbent

The Specific Surface Area (SSA) of the sample was determined using the methods of Sears [13] and Iler [14]. The bulk density and specific gravity of the GMP sample was determined as described by Olu-Owolabi *et al.* [15]. The pH at the point zero charge (pH PZC) was determined as described by Unuabonah *et al.* [16]. This is important because it marks the pH where the surface functional groups do not contribute to the pH of the solution, and in an applied electric field, the electrophoretic mobility of the particles would be zero [17].

The Fourier Transform Infrared (FTIR) spectra of the GMP biosorbent were obtained using Perkin Elmer Spectrum1 FTIR spectrophotometer. About 0.1 g of the processed dry GMP biosorbent in powder form along with KBr were ground into fine particles and compressed into pellets was used to obtain the FT-IR spectrum in the scanning frequency from 4100 to 400 cm⁻¹.

Biosorption experiments

The synthetic metal ion (Cd²⁺, Ni²⁺ and Cr⁶⁺) solutions were prepared from AnalaR grade of their salts (CdCl₂, Ni(NO₃)₂·6H₂O and K₂Cr₂O₇). A stock solution of 1000 mg/L was prepared by dissolving 1.5985 g, 4.9547 g and 2.8289 of Cd²⁺, Ni²⁺ and Cr⁶⁺ salts respectively in 200 cm³ distilled water and then made up to mark in a 1L standard volumetric flask. Working solutions of various concentrations were prepared from this stock solution as required. The pH of sorbate solutions were adjusted using 0.1 M HCl or 0.1M NaOH. All experiments were carried out in duplicates to enhance the integrity of analytical results. Blank experiments were conducted to estimate and correct for adsorptions to the walls of the apparatus used.

Batch experiments were carried out to determine metal sorption capacity *Glycine max* pod (GMP) at room temperature (28 ± 2)°C by suspending 2 g of GMP in separate 20 mL of 250 mg/L metal ion solution in a 60 mL polythene bottles. After the sorbent-sorbate mixtures were shaken on a mechanical shaker, biomass suspensions were filtered using whatman No.1 filter paper and concentration of metals in the clear supernatant filtrate solutions were analyzed using the Atomic Absorption Spectrometer (Buck Scientific 205) with air-acetylene flame on absorbance mode d equipped with hollow cathode lamps used for the metals.

After biosorption experiment, the metal ion concentrations adsorbed by GMP biomass in mg/g were calculated by using the following equation:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

Where; C_o and C_e are the initial and equilibrium sorbate concentrations in solutions; q_e , V and M are the amount of sorbate adsorbed (mg/g), volume of the solution (mL) used for incubation and mass (g) of biosorbent respectively.

Adsorption isotherms

Adsorption isotherms of Cd²⁺, Ni²⁺ and Cr⁶⁺ unto GMP biomass were obtained by batch experiments working at optimized adsorbent dose, pH and contact time as established after optimization of working parameters. Initial metal concentration was varied from 5 to 50 mg/L for all the metals. The amount of metal adsorbed q was determined using Equation 1. To obtain insights into the surface properties and degree of affinity of GMP for the metal ions and hence adsorption process, adsorption data were tested against the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) equilibrium isotherms using the linear forms of these models in Eqs. (2), (3) and (4).

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (2)$$

$$\text{Freundlich: } \log q_e = \log K_f + n \log C_e \quad (3)$$

where; Q_o is the maximum adsorption capacity per unit weight of sorbent, b is a solute-surface interaction energy-related parameter, while C_e and C_e are the amount of solute adsorbed per unit mass of the adsorbent (mg/g) and equilibrium metal concentrations in the solution (mg/L); where K_f and n are the Freundlich model capacity factor and the isotherm linearity parameter, respectively.

Dubinin-Radushkevich (D-R) isotherm [18]: This is a more general isotherm than the Langmuir and Freundlich and does not assume a homogeneous surface or constant adsorption potential. The linear form of the model is represented as follows:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (4)$$

Where β is a constant related to the mean free energy of adsorption per mole of adsorbate (kJ²/mol²), capacity (mg/g).

Kinetic models

In describing the mechanism of the biosorption of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions by GMP biomass and the potential rate determining steps, such as mass transport and chemical reactions, reaction-based and diffusion-based kinetic models were used to stimulate the experimental adsorption data, the pseudo-first-order, pseudo-second-order, Elovich, and Intra-particle diffusion models have been applied to the biosorption data. The Langergren pseudo first-order and pseudo second-order rate equations [19] were tested using their simplified equations in (4) and (5) respectively:

1. The pseudo first order kinetic model [19]:

$$\text{Log}(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303}\right) \quad (5)$$

Where q_e and q_t are the amounts of metals sorbed (mg/g) at equilibrium and at time t , respectively; and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). The q_e and rate constants k_1 were calculated from the slope and intercept of the plot of $\log(q_e - q_t)$ vs. t .

2. The pseudo second order kinetic model as proposed by Ho and McKay [20]:

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \quad (6)$$

Where k_2 is the rate constant of pseudo-second-order sorption. The pseudo-second-order rate constants k_2 and q_e values were calculated from the slope and intercept of the plots t/q vs. t .

3. Elovich model as described by Basha and Murthy as adopted by Olu-Owolabi et al. [21]:

$$qt = 1 \frac{1}{\beta} \ln(\alpha\beta) + 1 \frac{1}{\beta} \ln(t) \quad (7)$$

Where α is regarded to as the initial adsorption rate (mg/g min) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). (α and β are constants).

4. The linearized form of the intra-particle diffusion model equation [22] was used as shown in Eq. (7):

$$\text{Log}R = K_{id} + \alpha \log(t) \quad (8)$$

Where R is percentage metal ion adsorbed, t is contact time, α is gradient of linear plots and depicts the adsorption mechanism, K_{id} is intra-particle diffusion rate constant (h^{-1}).

Results and Discussion

Characterization of biosorbent

Some of the physicochemical characteristics of the *Glycine max* pod (GMP) adsorbent used in this study were determined using methods described by Unuabonah et al. [16]. The value of the PZC of GMP biomass was measured to be at pH 6.81. The PZC value obtained above for GMP adsorbent indicates that it could be used to efficiently adsorb metal ions at pH values as low as 6.81 as the adsorbent becomes more negative at values above the PZC. The GMP biosorbent gave Cation Exchange Capacity (CEC) of 36.51 meq/100 g).

When viewed under a Scanning Electron Microscope (SEM), GMP biosorbent gave particles with regular structures and showed some white particles indicative of porosity of the surface of the biomass (Figure 1b). The SSA of GMP has been determined as 27.280 m^2/g , while the bulk density and specific gravity are 0.575 g/cm^3 and 0.176 g/cm^3 respectively. The determination of GMP surface properties is necessary because

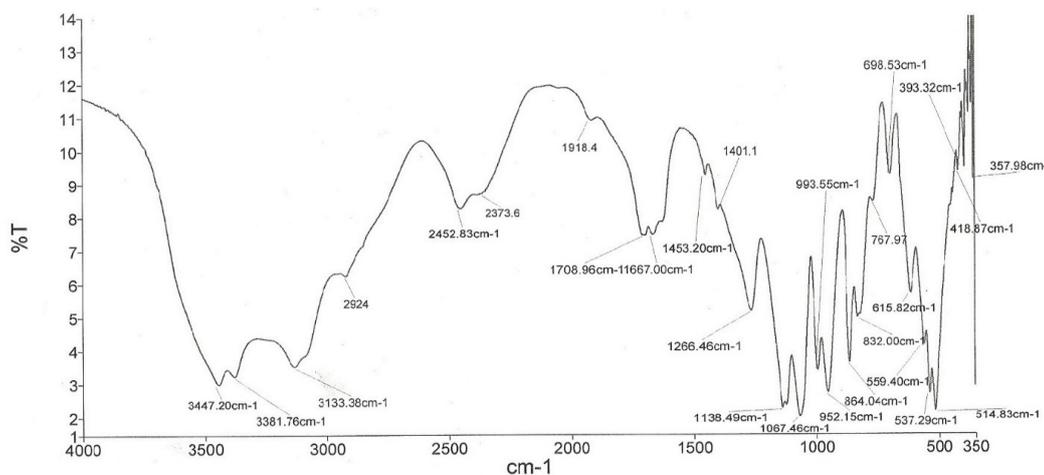


Figure 1a. Fourier Transform Infrared Spectra of Glycine max pod (GMP), T= Transmittance.

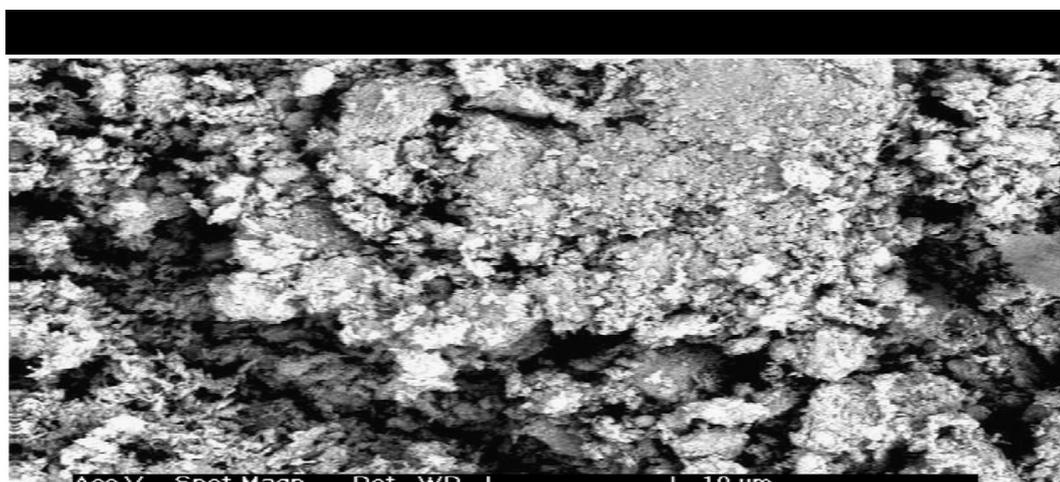


Figure 1b. SEM Micrograph of the Glycine max pod (GMP).

the particle sizes are most likely heterogeneous and these properties aid in estimating the degree of metal adsorption.

The FTIR (Fourier Transform Infrared Spectrograph) of the GMP biomass is shown in Figure 1a. Peaks appearing in the raw biomass were assigned various functional groups and bands in accordance with their respective wave numbers (cm⁻¹). The sharp vibration peak at 3447 cm⁻¹ was assigned to the stretching of O-H group due to inter- and intra-molecular bonding of polymeric compounds such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin. The broad range for this O-H band indicates the presence of 'free' hydroxyl groups of carboxylic acids [23]. The band 2924cm⁻¹ is assigned the asymmetric C-H vibration in -COOH group of aliphatic acid [24,21]. The peak in the region of 2452 and 1266 cm⁻¹ corresponding to the stretching vibrations of C-C or C=O or C-H or C-O in nonionic carboxyl groups such in esters and carboxylic acids is present in the GMP spectra. The peaks in the 1061 cm⁻¹ is due to the presence of the C-C stretching polysaccharides [25]. Upon loading of the GMP sample with Cd²⁺, Ni²⁺ and Cr⁶⁺ ions, the 1708 cm⁻¹ bands indicating the presence of a non-ionic carboxyl group appeared in the spectra. The appearance of the 1453 cm⁻¹ and 1401 cm⁻¹ band in the metal GMP-FTIR spectra may be attributed to a chemical interaction between the metals and the biomass. The shifts in the ionic carboxylate and hydroxylate anions observed after loading of the biomass may be attributed to changes in counter ions associated with these ions suggesting their contribution to metal uptake. Moreover, the structure of GMP biosorbent and presence of the outer -OH peak which suggests the possibility for the adsorption of Cd²⁺, Ni²⁺ and Cr⁶⁺ onto this site on this adsorbent [23].

Effect of pH of solution

For biosorption, the pH of the aqueous solution is an important controlling parameter in the metal uptake process. Metal adsorption on surface of biomass materials has been described in terms of molecular mechanisms which may include cation exchange in the interlayer, and specific adsorption resulting from surface complexation. Hydrogen ions affect metal complexation because they have great affinity for adsorption sites [21]. Hence, pH value of a solution strongly influences not only the site dissociation of the biomass surface, but also the solution chemistry of the heavy metals. For this reason, the effect of pH on the uptake of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions onto GMP was studied by varying pH values in range of 1 to 9 and the results were presented in Figure 2 respectively. It is clear that

Cd²⁺ ion was effectively adsorbed in the pH range 4 and 5 with the highest amount adsorbed at pH 5. While for Ni²⁺ ion there was continuous increase in the amount metal ions adsorbed from pH 2 to 6 with the highest removal at pH 6. Similar trends were reported by Jimoh *et al.* [26-29]. In these cases, pH 5 was reported as the optimum pH for Cd²⁺ adsorption. This result therefore shows weak acidic pH favours Cd²⁺ biosorption onto GMP. The increase in the amount of metal ion adsorbed due to increase in pH may be explained on the basis of decrease in the competition between proton (H⁺) and the positively charged metal ion at the surface sites and by decrease in positive charge near the surface resulting in a lower repulsion of the adsorbing metal ion. This means that at higher H⁺ concentration, the sorbent surface becomes more positively charged thus reducing the attraction between the sorbent and metal cations [30]. In contrast, as pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake and therefore metal sorption tends to increase significantly by increasing pH. Thus, Cd²⁺ and Ni²⁺ at pH values 5 and 6 have 98.7% and 96.0% removal respectively by GMP biosorbent.

However, for Cr⁶⁺ the highest amount of the metal ion adsorbed was at slightly strong acidic pH 3 which decreases significantly as solution pH increases. Similar trend was reported by Kaiser [31] This unusual adsorption at such low pH was explained to be as a result of the presence of HCrO₄ as the dominant form of Cr⁶⁺ which was attracted by positively charged sites [32]. The further justification for higher removal of chromium at low pH is the reduction of Cr⁶⁺ to Cr³⁺ which was then sorbed by the biosorbent [32]. As a result of this reduction reaction, H⁺ was consumed and an increase in pH was observed at the end of the experiments. Thus, Cr⁶⁺ at pH 3 have 79.8% removal by the GMP biosorbent.

Effect of adsorbent dosage

Figure 3 shows the effect of adsorbent dose on the percentage removal of Cd²⁺, Ni²⁺ and Cr⁶⁺ respectively. The percentage of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions adsorbed by GMP increased with an increase in the weight of adsorbent from 0.5 to 3g of GMP after which the percentage adsorbed remained constant.

From the analysis of the experimental data obtained for metal ions, it was observed that the adsorption efficiency increased progressively with increase in adsorbent dose for Cr⁶⁺ ion up to a mass of 2 g after which the amount of metal adsorbed remain almost constant while for Ni²⁺, it was observed that

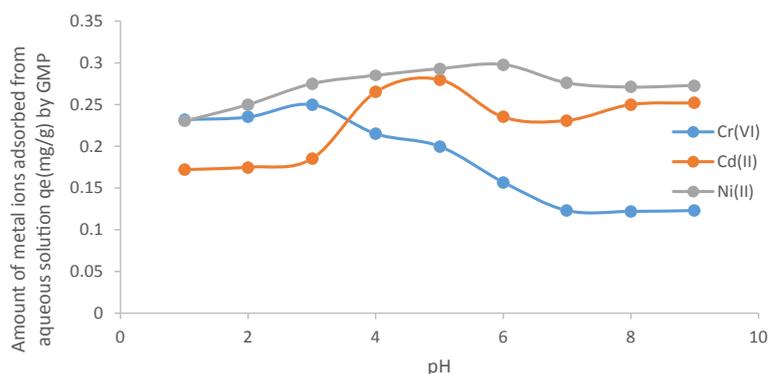


Figure 2. Effect of pH on biosorption of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions GMP Adsorbent.

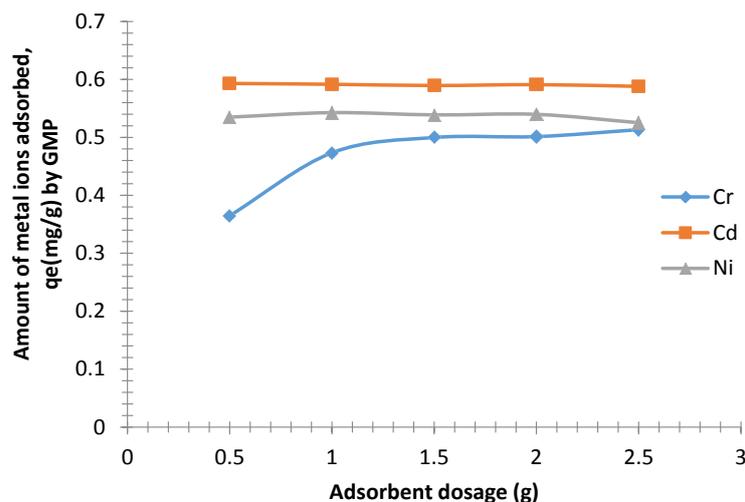


Figure 3. Effect of biomass dosage on the adsorption of Cd^{2+} , Ni^{2+} and Cr^{6+} onto glycine max pod.

the adsorption efficiency increased with increase in adsorbent dose up to a particular dosage (2 g) above which the efficiency reduced. An increase in biomass dosage generally increases the amount of biosorbed metal ion because of an increase in surface area of the biosorbent, which consequently increases the number of available binding sites [33]. However, adsorption capacity q_e of Cd^{2+} decreases continuously up to a particular dosage (1.5 g) above which efficiency increased slightly as the biosorbent was increased to 2 g and later decreased again as the biomass dosage increases to 2.5 g. This reduction in metal uptake with increasing biomass dose can be attributed to a relative amount of metal ions in solution with respect to available binding sites [34,35].

Effect of contact time

The effect of contact time on biosorption of Cr^{6+} , Cd^{2+} and Ni^{2+} ions by GMP are shown in Figure 4. The rate of metal uptake was rapid within different time of 90 min, 60 min and 90 min respectively for Cr^{6+} , Cd^{2+} and Ni^{2+} ions respectively. The observed fast metal ions uptake is consistent with biosorption of metal involving non-energy mediated reactions, where metal removal from solutions is purely physico-chemical interaction between biomass and metal solution. This fast metal uptake from solution indicates that binding might have resulted from interaction with functional groups on the cell wall of the biosorbent rather than diffusion through the cell wall of the biomass. Additional increase in time after the optimum time of each metal ion resulted in alternating decrease and increase in the amount of metal ions adsorbed. This implied that the active sites on the adsorbent were exhausted and further agitation resulted in desorption or the adsorption sites became saturated to maximum uptake capacity. The adsorptive capacities of Cr^{6+} , Cd^{2+} and Ni^{2+} ions uptake by GMP at equilibrium were 1.034 mg/g, 1.485 mg/g, and 0.849 mg/g corresponding to a percentage adsorption of about 68.9%, 99.0% and 56.6% at 45, 60 and 20 min contact time. Similar trends was observed for the biosorption of Cd^{2+} and Cr^{6+} ions [26,36]. Nuhoglu and Malkoc [37] reported similar trend for Ni^{2+} ions adsorption which occurred in two steps; an initial fast step which lasted for about 60 min followed by a lower second phase which continued until the end of experimental period.

Effect of initial metal ion concentration

The result of the effect of initial metal ion concentration shows the relationship between concentrations and the amount of metal ion adsorbed at fixed adsorbent dosage (2 g). Increase in the initial metal ion concentration led to increase in amount of metal ion adsorbed. The experimental data illustrating the effect of initial metal ion concentration on rate of metal uptake of Cd^{2+} , Ni^{2+} and Cr^{6+} ions are presented in Figure 5 respectively. The result showed a similar trend for Cr^{6+} and Ni^{2+} ions in their removal by the biosorbent mass as initial metal ion concentration increases from 15-25 mg/l, the amount adsorbed increases from 1.314 mg/g to 1.594 mg/g and 1.334 mg/g to 1.585 mg/g respectively after which a slight decrease was observed but a progressive increase was seen in the amount of Cd^{2+} adsorbed from 0.441 mg/g to 1.445 mg/g as the initial metal ion concentration increases from 15 to 50 mg/L. The trend of adsorption was $\text{Cd}^{2+} > \text{Cr}^{6+} > \text{Ni}^{2+}$. It is generally expected that as the concentration of the adsorbate increases, the metal ions sequestered should increase according to Okeimen and Onyenkpa [38] and Elaigwu *et al.* [39].

This adsorption characteristic indicates that surface saturation was dependent on the initial metal ion concentrations. At low concentrations of these metal ions solution, adsorption sites took up the available metal more quickly. However, at higher concentration, metal ions need to diffuse to the biomass surface by intra-particle diffusion and greatly hydrolyzed ion will diffuse at a lower rate [40].

Effect of temperature

The influence of temperature on the adsorption of Cd^{2+} , Ni^{2+} and Cr^{6+} onto GMP are shown in Figure 6. Adsorption of Cr^{6+} onto the biomass increased from 0.703 mg/g to 0.841 mg/g as the temperature rises from 35°C to 50°C. The increase in adsorption efficiency with rise in temperature may be an indication of chemisorption process [41]. However, the biosorption of Cd^{2+} and Ni^{2+} ion onto GMP showed similar trend, adsorption decreases slightly from 1.490 mg/g to 1.444 mg/g for Cd^{2+} and 0.950 mg/g to 0.852 mg/g for Ni^{2+} as temperature rises from 35°C to 50°C and increased from 1.444 mg/g to 1.462 mg/g for Cr^{6+} and 0.852 mg/g to 0.877 mg/g for Ni^{2+} and Cr^{6+} with further

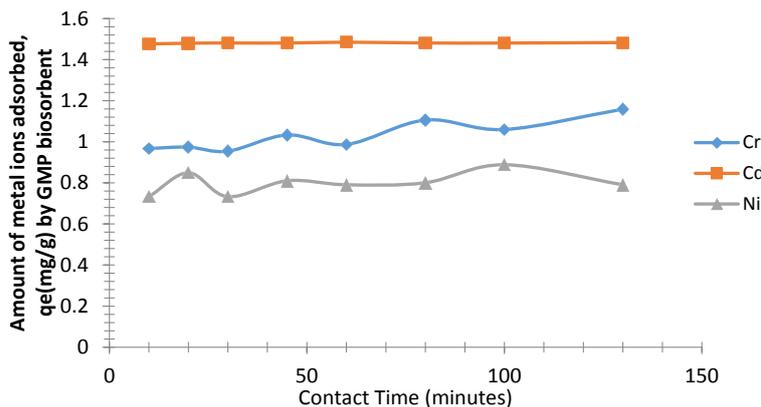


Figure 4. Effect of contact time on adsorption of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions onto GMP Biosorbent.

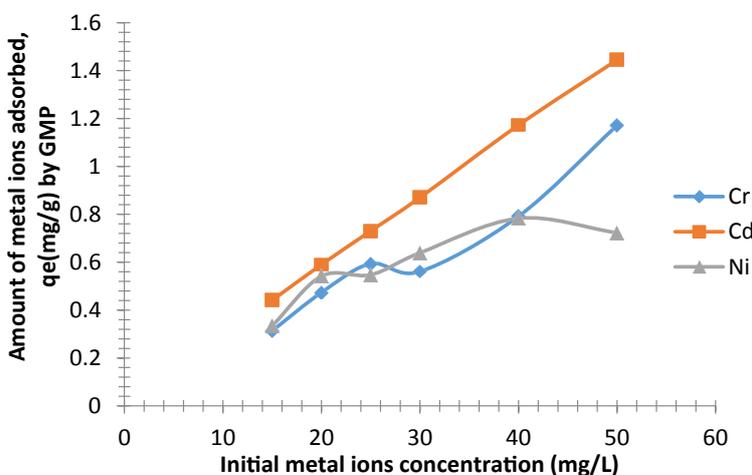


Figure 5. Effect of initial metal concentration on adsorption of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions onto GMP Biosorbent.

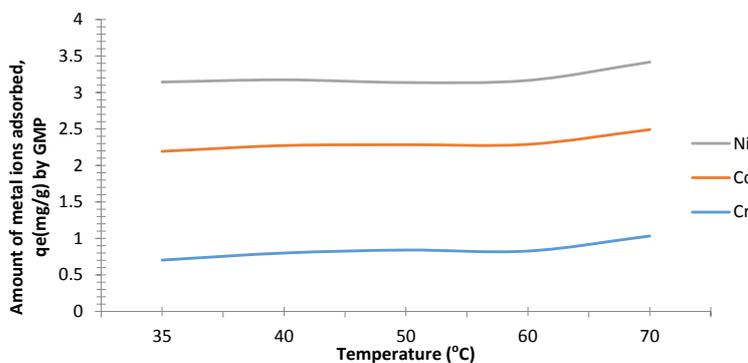


Figure 6. Effect of temperature on adsorption Cd²⁺, Ni²⁺ and Cr⁶⁺ onto glycine max pod (GMP).

increase in temperature from 50°C to 60°C. Similar trend was also reported for Cd²⁺ onto cocoa pod by Ahmet and Mustafa [42]. This decrease in the amount of Cd²⁺ uptake may be attributed to many parameters such as the relative increase in the dissociation tendency of the Cd²⁺ ions from the solid phase to the bulk phase; deactivating the biosorbent or destroying some active sites on the biosorbent surface due to bond ruptures. It may also be due to the weakness of biosorptive forces between the active sites of the biosorbent and the sorbate species and between the adjacent molecules of sorbed phase at such temperature [42].

Isotherms of the adsorption process

The results obtained from the biosorption of Cr⁶⁺, Cd²⁺ and Ni²⁺ ions on GMP were tested using Langmuir, Freundlich

and isotherms to describe the equilibrium between the metal ions sorbed on the biomass as shown in table 1. The Langmuir isotherm showed good correlation for the adsorption of Cd²⁺, Ni²⁺ and Cr⁶⁺ ions onto GMP with a regression R² > 0.98. This indicates that Cd²⁺, Ni²⁺ and Cr⁶⁺ ions do not form a monolayer coverage over the interface between the adsorbent GMP. The equilibrium parameter RL often referred to as dimensionless separation factor was calculated for the adsorption of the metal ions on GMP [43,44].

Where K_L is the Langmuir constant obtained from the initial Langmuir plot, and C_i is the initial concentration (mg/L). The values of RL obtained from Equation 4 all fall within 0 and 1 (0 < R_L < 1), indicating that the adsorption process is favorable [21].

The adsorption of Cr^{6+} , Cd^{2+} and Ni^{2+} ions onto GMP was equally described by the Freundlich model. The Freundlich adsorption isotherm supports the heterogeneity of the surface and the exponential distribution of the sites and their energies. The K_F and $1/n$ values obtained for adsorption of Cd^{2+} , Ni^{2+} and Cr^{6+} ions were (1.047, 4.282 and 7.102) and (0.759, 0.563, 0.403) respectively. $1/n$ is an empirical parameter relating to the biosorption intensity and varies with the heterogeneity of the material. Values between 0 to 1 for Cd^{2+} , Ni^{2+} and Cr^{6+} ions indicated that biosorption of the metal onto GMP was favorable at studied conditions.

The D-R isotherm assumes a fixed volume or 'adsorption space' where adsorption takes place. It also describes heterogeneity of adsorption energies within this space independent of temperature. It was observed that the D-R isotherm gave a good fit for the adsorption of both metals to both biomasses when compared with Langmuir, Freundlich. The E values obtained of the biosorption processes were all in the range of ion exchange reactions [16].

Kinetics of biosorption process

Kinetic data obtained in this study was fitted to Equations 5 to 8. Kinetic parameters obtained are shown in Table 2. The results obtained indicate that only the pseudo-second order equation was able to satisfactorily fit the kinetic data for GMP on Cr^{6+} , Cd^{2+} and Ni^{2+} ions in the whole data range. R^2 values are very high (0.9998, 1.0, 0.9919) respectively. Also, the theoretical $q_{e, \text{cal}}^2$ values were closer to the experimental $q_{e, \text{exp}}^2$ values. In this model, the rate-limiting step is a biosorption mechanism involving chemisorption, where metal removal from solution is due to physicochemical interactions between biomass and metal solution [21]. According to the pseudo-second order kinetic model, the rate of biosorption reaction non-linearly decreases with time [45].

The pseudo first order kinetic model did not appropriately describe the kinetic data in the whole data range. The other three kinetic models (intra particle diffusion model, Elovich model and the fractional power model) also did not give satisfactory fits when fitted for their applicability to the kinetic data. However, it was observed that the biosorption process presented by these

Table 1. Isotherm constants of two-parameter models for Cr^{6+} , Cd^{2+} and Ni^{2+} biosorption by GMP.

Adsorbents	Cr^{6+}	Cd^{2+}	Ni^{2+}
Langmuir			
K_L (L mg ⁻¹)	0.623	0.316	0.174
q_{max} (mg/g)	24.12	1.702	1.224
R^2	0.989	0.9686	0.9923
K_R	0.765	0.402	0.531
Freundlich			
KF (Lg ⁻¹)	7.102	1.047	4.282
$1/n$	0.759	0.563	0.403
R^2	0.674	0.822	0.747
q_{exp} (mg/g)	1.0335	1.485	0.849
Dubinin-Redushkevich			
q_{RD} (mg/g)	22.94	22.8	28.31
β (kJ/mol ²)	4.93×10^{-7}	6.21×10^{-7}	9.14×10^{-7}
E (kJ/mol)	1.007	0.707	0.739
R^2	0.897	0.905	0.913

Table 2. Kinetic model parameters for Cr^{6+} , Cd^{2+} and Ni^{2+} biosorption by GMP.

Adsorbents	Cr^{6+}	Cd^{2+}	Ni^{2+}
Pseudo first order			
K_1 (min ⁻¹)	-5.5×10^{-3}	8.01×10^{-3}	6.04×10^{-3}
q_{cal} (mg/g)	0.027	0.0013	0.094
R^2	0.6702	0.0285	0.2915
Pseudo second order			
K_2 (min ⁻¹)	1.59×10^{-3}	1.77×10^1	1.8×10^{-1}
q_{cal} (mg/g)	16.37	28.28	32.54
R^2	0.9998	1	0.9919
q_{exp} (mg/g)	16.85	28.5	34.93
Elovich			
a (mg/g min)	8.44×10^{10}	1.55×10^{19}	1.97×10^{11}
b (g/mg)	0.979	1.174	1.231
R^2	0.9932	0.9354	0.961
Intraparticle diffusion			
k_p (mg/g min ^{0.5})	6.781×10^{-1}	5.862×10^{-1}	1.36×10^{-1}
R^2	0.9756	0.9209	0.9195

models comprised of two phases suggesting their applicability to a particular period of the adsorption process. The three models were then tested on the two phases presented. It was observed that all data obtained before the saturation point of the biomass followed the assumptions of these models as indicated by their regression values. A similar method had been adopted for describing kinetic data for biosorption [46].

Conclusion

The potential application of *Glycine max* pod in removal of Cd^{2+} and Ni^{2+} and Cr^{6+} from wastewater effluents was tested in present study using batch adsorption process. Adsorption characteristics of Cd^{2+} and Ni^{2+} and Cr^{6+} onto GMP were found to be influenced by initial pH of aqueous solution, contact time, initial metal ions concentration, temperature, and GMP dosage. Perfect metal uptake efficiencies were obtained under operating conditions such that for Cd^{2+} and Ni^{2+} ions by Keeping the experimental conditions as follows; initial pH: 5.0 and 6.0, Contact time $\text{Cd}^{2+}/\text{Ni}^{2+}$: 90/60 min, GMP dosage: 2 g and initial $\text{Cd}^{2+}/\text{Ni}^{2+}$ concentration: 25/50 mgL⁻¹, nearly 100% removal efficiency was obtained. And for Cr^{6+} ions, the removal efficiency was reached to 79%, while the experimental conditions were as follows; initial pH: 3.0, contact time: 90min, GMP concentration: 2.0g and initial Cr^{6+} concentration: 50 mgL⁻¹ [47-50].

Kinetic models evaluated include Intraparticle diffusion model, Elovich model and pseudo-first and second order models. While the kinetic data for all the adsorption experiments satisfactorily fitted to the pseudo-second order model, the assumptions of the Elovich and intra-particle diffusion were apparently important before and after the saturation points of the biosorbents. The fast kinetics of the adsorption process and the high percentage removal from concentrated solutions under optimized conditions are useful properties of the adsorbent which can be developed by modification.

Equilibrium adsorption of all the metals could not be described by the simple Langmuir and Freundlich models alone. However, a combination of other two-parameter equilibrium models suggestively describes the nature of the adsorption processes. The R-D model, amongst the evaluated models gave the best fit for all the adsorption processes studied.

In the view of these results, it can be concluded that the GMP can be utilized as a low cost and effective biosorbent in removal of Cd²⁺ and Ni²⁺ and Cr⁶⁺ ions from wastewater and industrial effluents.

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