Global Scientific JOURNALS

GSJ: Volume 7, Issue 1, January 2019, Online: ISSN 2320-9186
www.globalscientificjournal.com

An Abridged Review on Biosorption of Heavy Metals Using *Aspergillus Niger* as Sorbent Material

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Highlights

- Isotherms and models frequently used for *A. Niger* biosorption
- Processes involved in biosorption
- Physiochemical factors that manipulate the biosorption property

Abstract

Due to technological and industrial advancement, rise in the number of pollutants bring serious environmental issues. Heavy metals are good example of pollutants that are dreadful due to their high toxicity. Along with variety of techniques studied to treat effluents containing hazardous materials, usage of biomaterial such as fungal biomass for removal of heavy metal was studied due to its high potential in reducing metal concentration on contaminated bodies of water through biosorption. Biosorption ability of *Aspergillus Niger*, factors involved in achieving optimal adsorption of heavy metals using fungal biomass; type and nature biomass, concentration of metal solution, and physiochemical factors affecting, and parameters used was reviewed including summarization and description of methods used in biosorption, result accumulated, and inferences on the effects manipulating the biosorption. It was concluded that, *Aspergillus Niger* biomass is an effective sorbent material that most likely follows pseudo-second-order reaction rate and best described using Langmuir isotherm model.

Keywords: Biosorption, heavy metals, biosorbent, kinetics, isotherm, isotherm model

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1. Introduction

The irrepressible generation of toxic wastes such as solutions containing heavy metals becomes a major environmental concern that society is currently facing[1].Usage of heavy metals contribute to increasing concentration of toxic materials that may impose threat to living organisms. Some hazardous organic compounds can be also harmful, for example, human consumption of phenol-contaminated water can cause severe pain leading to damage of the capillaries ultimately causing death [23]. Major sources of large effluents that discharges hazardous materials to the environment are electroplating and metal finishing industries, metallurgical industries, fertilizer industries, chemical manufacturing, and tannery operations [37], including educational institutes that dispose its wastes from their laboratory experiments. Experiments, researches and testing requires the use of the heavy metals but, the lack of storage for the generated toxic waste became a problem not only for the institutes but also to the environment. Treatments like ion exchange, evaporation, precipitation, membrane separation etc. are too expensive to treat low levels of heavy metal in wastewater [1]. Therefore, scientists had shift to a new method such as using living organisms such as fungi, bacteria, algae, plants, etc. as the sorbent material because of its ability to accumulate metal ions from aqueous solutions. Living and dead cells of an organisms can remove heavy metals ions from aqueous solutions but the use of dead cells seems to be more effective than using living cells [2]. The use of pretreatments, physical or chemical also discovered to improve the potential of the sorbent material. Physical pretreatment methods included heat treatment, autoclaving, freeze drying, and boiling while chemical pretreatment methods involves using acids, alkali and organic chemicals [1].

1.1 *Objectives*

This aim to review related studies and literatures regarding the capability of fungal biomass of *A. Niger* as sorbent material and scrutinize the factors associated to biosorption of heavy metals and *A. Niger*'s adsorption efficacy.

2. Heavy Metals

Heavy metals are used in various industries for their technological importance but beyond certain limit, heavy metals are toxic to living organisms and may cause serious hazard to public health [17]. Heavy metals like copper, mercury, chromium, nickel, cadmium, lead, and zinc cause serious threat to environment, animals and humans for their extreme toxicity [18].

Chromium

A number of chromium compounds have a great economic importance and are used extensively in chemical, metallurgical and refractory industries [20]. Chromium (Cr) occurs in different valence states, but Cr(III) and Cr(VI) are the most dominant. In comparison to Cr(III), the chromate anions of Cr(VI) are more toxic due to its carcinogenic and mutagenic properties. The metal compound is discharged to ground and surface water through wastewater of leather tanning, metal finishing, electroplating, and chromate preparation [3].The US EPA has set the discharge limit of Cr(VI) to surface water below 0.05 mg/L while the total Cr including Cr(III), Cr(VI) and its other forms to below 2 mg/L [21].

Cadmium

Cadmium is one of the heavy metals with the greatest potential hazard to humans and the environment. It accumulates mainly in kidneys and liver, but is also found in skeletal system, muscular system, and reproductive system and also in endocrine glands leading to renal dysfunction, hypertension, mutagenesis, and anemia [4]. The major source of this metal are from

welding, electroplating, pesticide fertilizer, Cd and Ni batteries, nuclear fission plant.

Nickel

Nickel resists corrosion and is used to plate other metals to protect them and is mainly used in making alloy such as stainless steel. The IARC has determined that some nickel compounds are carcinogenic [22]. High nickel concentrations can cause gastrointestinal irritation and lung and bone cancers [5].

Lead

Lead are amassed from paints, pesticides, smoking, automobile emission, mining, burning of coal. This causes Liver, kidney and gastrointestinal damage, and mental retardation in children [6].Once it enters a person's system, it is distributed throughout the body just like helpful minerals. Young children are particularly vulnerable to the toxic effects of lead and can suffer profound and permanent adverse health effects, particularly affecting the development of the brain and the nervous system. Lead also causes long term harm for adults, including risks of high-blood pressure and kidney damage [22].

3. Biosorbent

Adsorption is a surface reaction [6]. Thus, the biosorption potential of the biosorbentdepends on the surface area and polarity. Biosorbent is the biological material whose adsorption potential is harness [25] and are prepared from the naturally abundant and/or waste biomass of algae, moss, fungi, or bacteria that have been killed while the biomass is pretreated by washing with acids and/or bases before finally drying granulation [17]. Among these, fungal biomass can be produced cheaply [24]. Living and dead cells of fungi are able to remove heavy metal ions from aqueous solutions [26].Because of this, the fungal biomass received much attentions from the researches. The huge percentage of

the presence of cell-wall material gives higher amount of functional groups that can be used in metal binding which also increases its metal uptake ability.The fungal cell-wall is composed of chitin, which is long linear chain of beta-1,4-linked N-acetylglucosamine and also possesses proteins, glucan, polymers and functional groups such as carboxyl, phosphoryl, hydroxyl, amino and imidazole on their surface [7].

The microbe is said to be an economical biosorbent because it can be easily grown in large amount using un-sophisticated fermentation techniques and inexpensive growth media such as Potato Dextrose Agar [8].

4. Process of Biosorption

4.1 Factors Affecting Biosorption of Metals

To achieve the maximum potential of the fungal biosorption or its maximum metal uptake, it is important to analyze and evaluate the factors which influences the adsorption. Type and nature of biomass, initial solute concentration, biomass concentration (biosorbent dose/solution volume) in solution and physicochemical factors like temperature, pH, and ionic strength are some of this factors [6].

Type and Nature of Biomass

The type and nature of the biomass includes the nature of application or how the biomass was applied is important to be evaluated. Biomass can be used in many forms, such as living or dead, free or immobilized, raw or pretreated, wild or mutant cells, engineered or non-engineered, lab culture or waste industrial biomass and biomass from different industries [6]. It is for the fact that different forms can give different results depending in its metal uptake mechanism.

Initial Concentration of Metal Solute

The initial solute concentration on the other hand brings impact unto biosorption. It was

studied that higher concentration of solute results in a high solute uptake, because the sites available for sorption are more compared with the moles of solute present. Thus, number of available binding sites is dependent with the initial concentration of the solute.

The concentration of metal and dosage of biosorbent greatly affects the extent of the biosorption. Increase in concentration increases the amount of the biosorbed solute, which also increases the surface area of the biosorbent. Thus, the number of binding sites increases then reached its saturation value [9]. Along with this, increase in the biosorbent dosage decreases the quantity of the biosorbed solute. It is because the interference between binding sites due to increased biosorbent dosages cannot be overruled and would results in a low specific uptake. But, other studies show that increase in adsorbent dosage would increase the percentage of adsorption. It suggests that the increase in the removal efficiency is due to the fact that, with an increase in the adsorbent dosage, more adsorbent surface is available for the solute to be adsorbed [5].

Physiochemical Factors

Physicochemical factors like temperature, pH, ionic strength, biomass concetration are the factors that also have influence in the running process.

Acidity (pH)

The pH value of the solution greatly influences the complexation and biosorption availability of the metals. Increase in pH resulting to an increase in biosorption capacity is related to the influence of functional groups present on cell surface. Therefore, when heavy metal removal was inhibited it will yield a positive charge density on metal binding sites due to a high concentration of protons in solution. Thus, the negative charge density on the cell surface increases due to deprotonation of the

metal binding sited and thus increases biosorption [1].

Temperature

Temperatures in the range of 20–35°C usually have little effect on the biosorption performance due to due to the exothermic reaction [10]. Increasing it usually enhance sorption since it increases the surface activity and kinetic energy of the solute but, high temperature causes physical damage to the biological sorbent. Thus, this reduce the biosorption capacity of the biomass.

Ionic Strength

Ionic strength influences adsorption of solute to the biomass surface because of the competition between ions which happened when the biomass surface and solute in aqueous solution are in contact. Thus, adsorption decreases with increase in ionic strength [11].

Biomass concentration

Studies on biomass dose showed that the amount of metal bound per gram of biomass in mg/g decreased as the biomass concentration increases. This was due to the restriction between binding sites at higher concentrations or inadequacy of metal ions in solution with respect to available binding sites. Higher uptake with lower biomass concentration could be due to an increased metal to sorbent ratio, which decreases upon an increase in biomass concentration. The highest uptake observed was 23.62 mg/g at metal to ratio biomass of 250:1000 [29].

Hence, at equilibrium concentration, low cell density sorbent materials adsorbs more metal ions than high cell density sorbent materials. Specific uptake of metals increases at lower biomass concentration because of less interference between the metal ions and the binding site [38].

4.2 Mechanism

Biosorption mechanisms can be classified according to various criteria but are not fully understood. The first one is according to the

dependence on the cells metabolism, biosorption mechanisms can be divided into:

- Metabolism dependent
- Non -metabolism dependent.

The second is according to the location where the metal removed from solution is found, biosorption can be classified as:

- Extra cellular accumulation/ precipitation
- Cell surface sorption/ precipitation
- Intracellular accumulation[36]

4.3 Equilibrium and Kinetic Studies

The Isotherm equilibrium studies describe the relationship between the mass of the adsorbed component per biosorbent mass and the concentration of this component in the solution. This is measured through tackling the effect of the amount of sorbent dosage the effect of increasing the metal concentration against the sorbent's efficiency and capacity. Whenever there was an increase in biomass concentration, there was an increase in efficiency and a decrease in sorption capacity [8].

4.3.1 Isotherm

The adsorption Isotherm also describes the capacity of an adsorbent to uptake the adsorbate. It is usually the ratio between the quantity that was adsorbed and what remained in the solution at fixed temperature and equilibrium. The equilibrium value of sorbate uptake (qe) by the biosorbent is plotted against the final equilibrium of sorbate concentration (C). Equilibrium sorption isotherms can also be used in comparing the different biosorbent and affinities of different substances for the same biosorbent, which is simplified by the equation;

$$q_e = V[C_i - C]/S$$

wherein V is the volume (L) of solution contacted with the sorbent; Ci and C are initial and equilibrium (final) concentrations of the sorbate (mg L−1); and S is the amount

of biosorbent usually expressed as dry weight which expressed q_e as weight per unit dry weigh [6].

4.3.2 Isotherm Models

Langmuir and Freundlich are some of the isotherm models which describes distribution of metal ions between the liquid phase and the solid phase. The Langmuir isotherm assumes monolayer adsorption onto a surface which contains a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface hence, if one site is filled, that site can no longer take up another sorbate. This indicates that the biosorbent's surface reaches saturation point and the maximum adsorption of the surface is achieved [12]. The isotherm is represented by;

$$\frac{C_e}{q_e} = \frac{1}{q_n} C_e + \frac{1}{K_L(q_n)}$$

Where Ce is concentration of adsorbate at equilibrium (mg g−1), KL is Langmuir constant related to adsorption capacity (mg g−1), which can be correlated with the variation of the suitable area and porosity of the adsorbent which implies that large surface area and pore volume will result in higher adsorption capacity.

Freundlich isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies.

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e)$$

Wherein KF is adsorption capacity (L/mg) and $1/n$ is adsorption intensity. This also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites.

4.3.3 Kinetics

For the kinetic studies, the most common kinetic models are: pseudo-first, pseudo-second, Elovich, and Intraparticle-diffusion [19].

4.4 Methodology

Successful biosorption requires the need for a good biosorbent [6]. The process starts in the selection of biomass to be used as a sorbent material. Then, pretreatments and immobilization improves its sorption ability yielding for more acquired metal ions. The study can be carried out by batch and column processes to study for adsorption mechanism. Lastly, the metal that was absorbed may be removed using desorption processes and biomass can be reuse again for adsorption.

4.4.1 Preparation of Biosorbent

P. Raja Rao et. al. (2013), had isolated fungus *Aspergillus Niger* from the soil samples in their adsorption study. It was done by serial dilution methods. Soil samples were first passed through 2mm mesh sieve and mix thoroughly. Then, 10 gm portion of soil was weighed out into the dilution bottle containing 95ml of distilled water. After that, glass beads were added to this dilution blank to facilitate mixing. The bottle was capped on the mechanical shaker and shake for 10 min. then performed serial dilution of 10^{-7} is reached. Using pour plate method, 0.1ml aliquot of this dilution was transferred into potato dextrose Agar medium plates. The plates were then incubated at 37^{o}C for 48 hrs. and pure cultures were obtained. The Fungi were identified by morphological structures observed by lactophenol staining under 100X lens. Flask (250 ml capacity) containing 50 ml sterile medium (potato dextrose broth) were inoculated by 0.1ml of fungal spore suspension prepared from 3-5days old culture fungal mycelium and incubated at 25°C for 7 days in a rotary shaker at 150rpm. The fungi grew in a filamentous (mold like) form under air, with fragmentation of some hyphae into spherical cells. They separated the fungi and medium through filtration and washing with Deionized water then pretreated it with 0.5N Sodium Hydroxide solution for 15 min. and

autoclaved it for 15min at 121°C. Lastly, biosorbent is dried in an oven at 80ºC for 24 hours and powdered and sieved to size 0.125mm.

The treated *Aspergillus Niger* yielded maximum removal of lead around 75-80% at pH 6-7 with maximum adsorbent dose of 0.2g/ml. Nickel was observed to have maximum biosorption of around 50-60% at pH 5-8. The results showed that fungal biosorption has very good potential to be used in removal of metal ions [1].

Study conducted by P. B. Kodolikar et. al. (2013) on the other hand obtained their pure cultures of fungus *Aspergillus Niger* of NICM grade from National Chemical Laboratory. It was obtained on slants, which was then cultivated in liquid medium using shake flask method. The spores and mycelium from these slants were transferred to 250 ml Erlenmeyer flasks containing 100 ml of growth medium.

Growth medium of following composition for 1 lt of medium was used; (all weights in g) Bacto Dextrose 20; Peptone 10; NaCl 0.2; CaCl2HO 01; KCl 0.1; KHPO 0.5; NaHCO 0.05; MgSo 0.25; Fe(SO)HO 0.005. The second type of medium that was prepared was called Sabouraud Broth. It was of the following composition for 1 lt of medium; (all weights in g) Dextrose 40; Peptone 10. Both the mediums were prepared in distilled water and were autoclaved adjusting the pH value to 5.0 using 1N HCl. Flasks containing the growth medium were kept in autoclave. Then the pressure in the autoclave was maintained at 15 kg/cm2 for 15 minutes. The biomass was inoculated in this sterilized growth medium. Then the flasks with the culture were kept on the shaker incubator at 25^{o}C and 160 rpm. The culture was incubated for 96 hrs. when sufficient growth was observed.

The grown biomass was then killed in the autoclave. The killed biomass was then

separated from its growth medium by centrifuge. Then the biomass was dried at 60^{o}C in the drier for 24 hrs. The dried biomass was then powdered in mortar and pestle and used for further experimentation.

Data obtained revealed that the maximum removal capacity at room temperature of Lead ions is about 24.60 mg/g of *Aspergillus Niger*. Adsorption is also said to be best fitted in Langmuir adsorption model and kinetics of sorption process followed a pseudo second order kinetics [13].

4.4.2 Selection of pretreatment

In the study conducted by Amna Javaid et. al. (2011), fungal biomass *Aspergillus Niger*, was pretreated with different types of alkaline/salts such as NaOH, $NaHCO_3$, Na_2CO_3, NaCl and $CaCl_2$, acids HCl and H_2SO_4 and detergent. This is to find which would yield most increase in metal uptake. It was proventhat pretreated biomass using Na_2CO_3 and NaOH increases and improves the biosortion potential *Aspergillus Niger* compare to untreated biomass. On the other hand, pretreatment with $NaHCO_3$, detergent, NaCl and $CaCl_2$ significantly reduce by 10-40%, metal sequestering efficiency of the adsorbent and acids HCl and H_2SO_4 resulted to drastic loss by 80% efficiency of metal uptake of biomass. Thus, Na_2CO_3 and NaOH is the best chemical pretreatment for the biomass [14].

In the study done by Al-Garni et al. (2009), for each 500 mg dry weight of the biomass, following treatments were carried out for 15 min such as autoclaving, 0.5 N NaOH and boiling, 0.5 N NaOH and autoclaving, 0.5 N KOH and autoclaving, 0.5 M NaCl, detergent, 10% formaldehyde, 10% acetic acid and 0.1 N HCl. Then, biomasses were separated by centrifugation and then washed with generous amounts of deionized water till the pH of the wash solution was in the near neutral range (7.0 - 7.2). After washing the biomass was dried at 65°C for 12 h, weight, powdered and sieved to pass

through a 100 mesh sieve. It was reported in that 0.5 N NaOH and autoclaving was the most efficient treatment with 197.6%, 3 folds increase as compared to untreated. Other pretreatment such as KOH and autoclaving, formaldehyde and detergent also showed significant increase in adsorption of Cadmium metal with 56.83%, 95% and 2.9 folds respectively. Whereas pretreatment with Acids such as 10% acetic acid and 0.1 N HCl showed drastic decrease in adsorption [2].

Another Study about effect of pretreatments was the research conducted by Ahmet ÇABUK et. al. (2005), which is about the effect of pretreatment on the Pb^{2+} biosorption capacity of fungal biomasses. The following physical and chemical pretreatments are investigated such as drying at 60 °C for 12 h in an incubator, autoclaving for 15 min at 121 °C and15 psi, boiling for 15 min in 500 ml of 0.5 N sodium hydroxide solution, boiling for 15 min in 500 ml of 15% (vol/vol) formaldehyde solution, boiling for 15 min in 200 ml of 10% (vol/vol) acetic acid solution, boiling for 15 min in 500 ml of 2% (vol/vol) gluteraldehyde solution, boiling for 15 min in 300 ml of 10% (vol/vol) hydrogen peroxide solution, boiling for 15 min in 500 ml of water in which 2.5 g of commercial laundry detergent that was dissolved, boiling for 15 min in 200 ml of 50% (vol/vol) dimethyl sulfoxide solution and lastly,boiling for 15 min in 200 ml of 10% (vol/vol) σ-phosphoric acid solution.

After each pretreatment with chemicals the biomasses were washed with generous amounts of deionized water and then dried at 60 °C for 12 h. The sodium hydroxidepretreated biomass was washed with deionized water until the pH of the solution was in a near neutral range (pH 6.8-7.2).

It was stated that the increase in metal biosorption after pretreating the biomass

could be due to the removal of surface impurities and to the exposure of available binding sites for metal biosorption. Study showed that pretreatment with formaldehyde, gluteraldehyde, hydrogen peroxide, commercial laundry detergent and dimethyl sulfoxide resulted in an improvement in Pb^{2+} biosorption. On the other hand, Acetic acid and σ-phosphoric acid pretreatment reduced biosorption of Pb^{2+} to a certain extent while autoclaving, heat, and sodium hydroxide pretreatment significantly reduced biosorption of Pb^{2+} [15].

Fu & Viraraghavan studied the effect of pH by shaking 0.2 g of the biomass (NaOH-pretreated) in 75 mL of the dye solution for 30 hours over a range of initial pH values 2 to 12. 1N HCl or 1N NaOH was used for pH adjustment. The pH value corresponding to the highest adsorption capacity was the effective initial pH [28].

Studies conducted by P. Raja Rao et. al. (2013), Kapoor et. al. (1999), and A. Sugasini et. al. (2014) which also used NaOH and autoclaving for biomass treatment also resulted to an increase in adsorption potential of the biomass [1, 16, 32].

4.4.3 Immobilization of Biosorbents

Having low mechanical strength and small particle size of the free cells of biosorbents requires a need for excessive hydrostatic pressures to generate suitable flow rates, which can cause disintegration of free biomass. Though free cells can provide valuable information in laboratory experimentation these are not suited for column packing in industrial applications. Thus, several immobilization techniques were discovered to make biosorbents suitable for process applications. Such techniques are entrapment and cross linking which have been found to be practical for biosorption [6].

A research done by Kumar KK el. at. (2009), showed the advantage of immobilizing the biomass. The fungus *Rhizomucor tauricus* was first cultured in Potato Dextrose Agar, incubating it for 72 hours at temperature 30°C. To separate the unused nutrient broth, the biomass was then filtered through vacuum filtration unit and was rinsed twice with distilled water. it was filtered again through vacuum filtration unit and re-suspended in distilled water. to immobilized the biomass, the researchers used Sodium alginate (4%) solution which was prepared in hot distilled water at room temperature. Predetermined weighed biomass (Wet weight) in alginate solution were mixed thoroughly with magnetic stirrer. Then, uniform mixture of fungus and sodium alginate solution (2%) was pumped through the peristaltic pump into the 0.5 M $CaCl_2*2H_2O$ solution. The beads were stored at 4°C for overnight for cured with 0.25 M $CaCl_2*2H_2O$ solution, beads were (4 mm) washed twice with distilled water to avoid the excess $CaCl_2*2H_2O$.

After various analyzation, it was discovered that the binding capacity of immobilized live fungal biomass was very high compare to dead powdered fungal biomass. The maximum experimental biosorption capacities for entrapped live and dead powdered fungal of *Rhizomucor tauricus* were found to be 79.9 ± 2.2 mg Cd (II) L-1, 57.29 ± 3.4 mg Cd (II) g-1 respectively. Thus, entrapped biomass is better [4].

4.4.4 Batch/Column Biosorption Studies

Batch and continuous modes are the modes which can be performed for Biosorption process. Both of operation are frequently employed to conduct laboratory scale biosorption processes. But, most industrial applications prefer some kind of flow-through or continuous mode of operation [6].

4.4.4.1 Batch Biosorption

Batch experiments evaluates the required fundamental information, such as biosorbent efficiency, optimum experimental conditions which are the pH, temperature, ionic strength, biosorbent dosage, biosorbent size, initial solute concentration and agitation rate, biosorption rate and the possibility of biomass regeneration [6].

R. Isaac el. at. (2011), conducted their study by batch experiment which were carried out using non-living mycelial suspensions. Suspended *Aspergillus Niger* weighing 1g was added in Erlenmeyer flasks with 100ml of aqueous chromium solution at desired concentrations. The flasks were agitated on a reciprocating shaker (150 rpm) at constant temperature (25-30^{o}C) and at constant pH (60). Then, the samples were taken at regular intervals of 15 min until the equilibrium was reached. After that, the biosorbent was separated and the supernatant liquid was analyzed using spectrophotometer at 540 nm for calculation of q_e from remaining chromium concentrations and the amount of metal ion adsorbed onto per unit weight of biomass.

The effect of contact time was analyzed in a batch reactor for different contact times from 15-30 mins with 15 mins interval having 25 mg/l initial concentration of Cr (VI) ion.

The effect of initial chromium concentrations was analyzed through the varying initial chromium (VI) concentration (25, 50, 100 and 150 mg/l) in a batch reactor until equilibrium was reached.

To study the effect of pH, the chromium solution of 100ml of 150 mg/l was adjusted to various pH (1, 2, 3, 4, 5, 6 and 7) for the equilibrium batch experiments.

For the effect of biomass loading studies 100 ml of 150 mg/l concentration of chromium solution was loaded with different biosorbent dosages (1, 2, 3, 4 and

5g) by keeping pH and temperature as 6.0 and 30^0C respectively.

The results of the study proved that the *Aspergillus Niger* as biosorbent was successful in removing hexavalent chromium with 88% efficiency from aqueous solution. It was also discovered that sorption highly depends in pH. The percentage removal of chromium increases with increase in pH from 1.0 to 2.0 and thereafter decreases with further increase in pH. It also shows that adsorption is best fitted to Langmuir isotherm and first order kinetic model [33].

Melvin S. et. al. (2015) also used biosorption experiment to study the fundamental information of the adsorption processes for the removal of Cr(VI) from the aqueous solution was studied by *Aspergillus Niger.* The fungus was isolated from the contaminated soil of an industrial effluent area in Vellore, Tamil Nadu, India and was designated as the MSR4 strain. The fungi were cultured in a filamentous form under the aerobic condition for 3 days in a yeast extract peptone glucose (YPG) media, which consists of yeast extract of 3g/L, peptone 10g/L and dextrose (a-D-glucose) 20g/L. The pH of the growth media was adjusted to 4.5. After three days of incubation, the biomass was collected and dried at 60°C temperature in an oven for 24 hours. The dried biomass was then sieved through a150-mesh sieve and used for biosorption experiments.

Batch experiments was designed by RSM (Response surface methodology), were conducted in 250ml Erlenmeyer flasks at pH 2.0 and 27°C in order to study the effect of biomass dosage, initial Cr(VI) concentration and contact time, which could improve the removal of Cr(VI) onto the MSR4 biomass from the solution. Biosorption studies were performed by varying the biomass dosage (1–3g/L), Cr(VI) concentration (25–100mg/L) and contact time (15–60min).

After biosorption, the solution was filtered through a Whatmann filter paper no.1, and the Cr(VI) concentration was analyzed by Atomic Absorption spectroscopy (AAS).

It was proven that the isolated fungus was efficient for removal of Cr(VI) from an aqueous solution. Data acquired also shows that Langmuir isotherm model is best fitted and pseudo-second order kinetic model fitted best among the other kinetic models tested for the adsorption processes [7].

Torab et. al. (2010), Desta (2013), A. Shoaib et. al. (2013), and Farhan et. al. (2015) also conducted biosortion experiments wherein the influence of contact time, pH, Temperature, and adsorbent dose on the adsorption process was studied. It yielded to understanding the effect in optimum conditions, suitable Isotherm equilibrium model such as Langmuir and Freundlich model and Kinetic Model such as pseudo first and pseudo second order for Adsorption processes [5, 12, 34].

Kapoor, Viraraghavan, and Roy Cullimore studied the batch biosorption of the experiment. Batch forms of kinetic and isotherm sorption experiment were conducted separately to evaluate the effects of pH, time, and biomass concentration on removal of cadmium, lead, copper and nickel ions. Stock metal solutions (1000 mg/L) were prepared using nitrate salts of the metals. An initial metal concentration approximately 10 mg/L was used. pH values of the metal solutions were adjusted using 1 N NaOH and HNO_3. The heavy metal concentrations were determined with a Varian AA-10 spectrophotometer. All biosorption experiments were conducted in 125 mL Erlenmeyer flasks on a rotary shaker 9at 125 rpm) at room temperature. All the experiments were conducted in duplicate and mean values were used in the analysis of data [30].

4.4.4.2 Column Biosorption

Continuous biosorption is considered to be the best study for evaluating the technical feasibility of a process for real applications. There can be three basic types of sorption solid–liquid contact system in continuous flow [6]:

- the packed bed column (fixed bed system)
- the fluidized bed system
- the completely mixed system

Research conducted by Mukhopadhyay et. al.(2008) shows the mechanism of biosorption of pretreated *A. Niger,* in packed bed column system. The column experiment was carried out in a glass column of 1.5 cm outside diameter with 0.3 cm wall thickness and 11 cm (total height is 22 cm) length. The packed Bed experiments were carried out at 33 °C. A perforated polymeric plate was fitted at the top and bottom of the column.

Pretreated biomass weighing 1, 2, and 3g were then packed in the glass column and sorption experiment was performed corresponding to 2.1, 3.1, and 4.1 cm of initial height of the column. The column was conducted at the flow rates between 1.6 and 9.8 ml/min. Cu(II) solution of concentration 10mg/l, was fed from the top of the column. Afterwards, effluent samples were collected with varying times from the bottom of the column and were analyzed using AAS.

It was reported that the breakthrough was measured as a function of influent flow rate and bed height of for a feed solution at 10 mg/l metal ion concentration. Breakthrough was also described by bed depth service time and Thomas models. It was also reported that the pretreated *A. Niger* adsorbed around 13.4 mg/g yielding higher metal adsorption than untreated. Comparing the usage of packed bed column reactor to using bed reactor, it stated that packed bed column reactor results to higher metal uptake [35].

5. Results and Discussion

Effect of pH

Barros Junior et. al. (2003) had proved that the cadmium metal adsorption of pretreated *Aspergillus Niger* would rapidly increase when pH is increased from 3 to 4. Same result happened in the study conducted by Kapoor et. al. (1999). This is due to the increase of the negative charge density on the cell surface which increases the biosorption [8, 16].

Kinetic Analysis

The study conducted by Barros Junior et. al. (2003) also concluded that with increasing contact time, the concentration of cadmium decreases and reached equilibrium after 6 h at pH 4, 5 and 6. It was also verified that in one hour the biomass reached 91% of its saturation capacity at pH = 5.0 and from the 6th to the 10th hours, there was no significant removal of cadmium. The adsorption for cadmium metal also showed that it was fitted to a pseudo-second-order reaction-rate model indicating that it follows chemisorption [8]. According to Rostami and Joodaki, increasing processing period approximately more than 8 and 15 minutes has no effect on the adsorption extent of the cadmium removal by *A. Niger and P. austurianum* using cadmium concentration of 112 ppm strength. This shows that the cell wall texture of *A. Niger* may differ from that of *P. austurianum* which consequently affect the rate and extent of cadmium sorption [27].

Effect of Biomass Concentration

$$\frac{C_e}{q_e} = \frac{1}{q_n} C_e + \frac{1}{K_L(q_m)}$$

The study also showed that increase in biomass concentration, also increases the efficiency and decreases sorption capacity. The sorption efficiency curve defined 0.4 and 0.7 g/L as the lower and upper levels of biomass concentration to be used in the experimental design [8].

Effect of initial concentration of Cadmium solution

Experimental data from their study also showed that increasing the initial concentration of the metal, increased the sorption capacity up to 30 mg/L and then decreased it from this point on. But, it was also observed that the increased in initial concentration of the metal caused the sorption efficiency to decrease. Thus, to achieve greater efficiency in the removal of the heavy metals, it is important to maintain the effluent at a low metal concentration less than 5 [8].

Biosorption Isotherm Analysis

Barros Junior et. al. (2003) study used Langmuir modeland Freundlich model:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e)$$

to describe biosorption equilibrium.
It resulted that the Langmuir model parameters obtained were statistically significant at all pH values studied at a confidence level of 95%. The Freundlich parameters estimated were not significant at all pH values studied at a confidence level of 95% [8]. Thus, adsorption of cadmium metal using *Aspergillus Niger* is fitted with Langmuir model indicating that that it is a monolayer biosorption mode onto a surface containing a finite number of identical sites.

6. Conclusion

It was concluded that the fungus *Aspergillus Niger* can be used as sorbent material for adsorption. Increased in pH would result to increase the adsorption potential. Adsorption follows a pseudo-second-order reaction-rate model that assumes chemisorption. Lastly, adsorption is best fitted at Langmuir Isotherm suggesting a monolayer adsorption.

7. Recommendation

Further study on other *Aspiregillus* specie as candidate sorbent materialfor biosorption of heavy metals

8. References

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