EPH - International Journal Of Applied Science
ISSN (Online): 2208-2182
Volume 09 Issue 01 October 2023
DOI: 10.53555/eijas.v9i1.163

ISOTHERM, KINETIC AND THERMODYNAMIC STUDY OF THE EFFICACY OF ACTIVATED AND UNACTIVATED HUMAN HEAD HAIR FOR THE REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTION

Omituyaki, Paul Taye*

****Corresponding Author:***

Abstract

A systematic comparison of biosorption performance, based on the biosorption capacities of the two human hair samples (H1 and H2) for removing Cd(II) and Pb(II) ions under different conditions, has been checked. It was found that H2 and H1 showed high biosorption capacities ((93.5 and 77.99 %) and (84.25 and 66.5 %)) for lead and cadmium removal respectively. The phosphoric acid activated hair (H2) showed better biosorption capacity. This could be attributed to the higher surface area and more number of amines and sulfonate groups, which is confirmed by the SEM and FT-IR analysis, respectively. Lead was more effectively adsorbed than cadmium by both adsorbents. Adsorption increased with increase in adsorption temperature, contact time and adsorbent dosage and decreased with increase in initial concentration of the metal ions. Adsorption also increased with increase in pH of the metal solutions up to a pH value of 6, beyond which the metal ions were precipitated out of their solutions as their hydroxides. The pseudo-second order kinetic model is more likely to predict kinetic behavior of the metal biosorption process for whole contact time range, with the chemical sorption being the rate-controlling step. The metal sorption closely followed Freundlich and Temkin models. The Freundlich isotherm has R^2 values of 0.969 for H2 and 0.765 for H1, while Temkin has R^2 values of 0.969 for H2 and 0.856 for H1 which indicated that the adsorption behaviour was heterogeneously distributed. Negative standard Gibb's energy indicates that the heavy metal biosorption process is thermodynamically feasible and spontaneous. Thus, this work showed that activated human head hair has good potential as an adsorbent in the treatment of lead and cadmium contaminated waste water.

Keyword: *Human head hair, activated hair, biosorption, adsorption isotherm, kinetics and thermodynamic.*

INTRODUCTION

Exceptional arrival of heavy metals into nature through modern effluents and urbanization has represented an extraordinary issue worldwide and expulsion of such toxins has been an incredible fuss over the most recent couple of decades. In contrast to natural toxins, overwhelming metals are non-biodegradable and in this way, experience bioaccumulation in living beings bringing about numerous illnesses and scatters, for example, hypertension, frailty, lead harming, unconsciousness and host of others as documented by (Yu, *et al.,* 2000).

The most widely recognized wellspring of heavy metals contamination incorporate squanders from the electroplating and metal completing enterprises, tannery tasks, cowhide and tanning ventures, manure businesses, concoction producing, metallurgical ventures, mine seepage, battery fabricating, dirtied ground water from unsafe waste destinations, leachates from landfills and color producing businesses. These are known as anthropogenic sources (Faisal and Hasnain, 2004).

Metal particles in water can likewise happen normally from filtering of metal stores. The nearness of overwhelming metal contaminants in the treated or untreated waste water from the enterprises either delivering or utilizing these metal bearing items brings these metals into water bodies (Sudha and Abraham, 2003).

These metal toxins are traditionalist contaminants that are not effectively degradable, chemically or organically. They are along these lines lasting chemical overload in the environment. At the point when these metals are available in huge amounts in the environment, they comprise a wellspring of contamination and poisons and represent a danger to the environment, quatic and human lives (Kang *et al.,* 2008). The danger of metal ions is inferable from their capacity to bond with protein atoms and inhibit replication of DNA and in this way consequent cell division (Khaled *et al.,* 2005).

Lead is one of the four noteworthy most hazardous metals for human wellbeing (Satarug *et al.,* 2004). Lead is normally found in the environment yet is predominantly created by human activities, for example, use in gas generation (Mahdavian and Raouf, 2010). Lead salts enter the environment through the vehicle exhausts polluting the environment.

In kids, lead causes a lessening in intelligent quotient (IQ) score, hindrance of physical development, hearing impedance, hindered learning just as diminished consideration and homeroom execution (Satarug *et al.,* 2004).

In children, lead causes a lessening in intelligent quotient (IQ) score, hindrance of physical development, hearing impedance, hindered learning just as diminished consideration and homeroom execution (Satarug *et al.,* 2004).

Cadmium is another heavy metal with high toxicity when in excess. It is, also, an essential trace element for human beings. However, it can cause harmful and acute effects. The major effects of excessive large doses of cadmium in the human body include high blood pressure, severe mucosal irritation, widespread capillary damage, anemia, hepatic damage and necrotic changes in the liver and kidney (Malakootian *et al*., 2008).

As of late, activated carbon from various birthplace "regular waste or crude materials" are one of the materials that is been utilized to expel metal ions from industrial wastes (Khaled *et al.,* 2009).

The increasing variety and amounts of potentially hazardous impurities in water have led to the increased use of activated carbon as adsorbents (Bansode *et al.,* 2003).

Adsorption of heavy metals on surface of activated carbon materials is one of the more mainstream techniques for the expulsion of metals ions from the aqueous solutions. While, the adsorption is a surface phenomenon, where molecules of adsorbate (metals ions) are pulled in and held to the outside of an adsorbent (activated carbon materials) until equilibrium is accomplished between adsorbed molecules and those still freely circulated in the conveying gas or fluid (Bhattacharya *et al.,* 2006).

Regular techniques for expelling heavy metals from aqueous wastes include; chemical precipitation, ion exchange (Chiban and Sinan, 2006), adsorption (Sari *et al.,* 2007), sedimentation (Song *et al.,* 2004), electrochemical procedures (Falim *et al.,* 2006), coagulation/flocculation (Lai and Lin, 2003), filtration and membrane procedures and solvent extraction (Hossain *et al.,* 2012).

Among them, adsorption strategy demonstrates basic and financially savvy in both vitality necessity and environmental friendliness accordingly has caught the attention of researchers (Markovska *et al.,* 2006).

Last decade witnessed a growing knowledge in the subject as researchers guided exertion to discovering minimal effort, promptly accessible however efficient adsorbents. Ensuing upon that, most regular adsorbents have been profoundly examined (Kang *et al.,* 2008).

Agricultural wastes, for example, tea waste and coffee, hazelnut straws, Peanut frame, saw dusts, corncobs and apple squanders, fleece filaments, tea leaves banana, orange strips, papaya wood, maize leaf powder, grape stalk squanders and different agricultural by-products are mostly considered (Pehlivan *et al.,* 2006).

The above featured reports tend to suggest that adsorption, which uses plants and animals remains (agricultural waste) in their natural or preconditioned form as adsorbents, is a promissory strategy for the treatment of heavy metals contaminated water; particularly adsorbents gotten from animal remains (Arief *et al.,* 2008).

Be that as it may, very little has been done in the area of investigating the efficiency of utilizing human head hair for heavy metal removal from aqueous solution (Babarinde, 2002).

Hence, having identified the existing research gap and in line with the quest to discover a cheap and readily available adsorbent, it becomes imperative to investigate the capacity of human head hair as an adsorbent for heavy metal removal from aqueous solution as well as the mechanism behind the process, which is the cardinal point of this research.

STATEMENT Of PROBLEM

Water pollution caused by heavy metals has posed a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature (Bahadir*et al.,* 2007).

These metals are known to produce severe toxic damage to neuronal system, kidneys, reproductive system, liver and brain (Wang *et al.,* 2007; Gupta *et al.,* 2011). Since they don't degrade in the environment like organic pollutants (Li *et al.,* 2002), a safe and effective disposal of wastewater containing these metals (Cd^{2+} and Pb^{2+}) is always a challenge to industrialists and environmentalists (Sekar *et al.,* 2004).

Also human hair is considered as waste in many societies and accordingly is found in the metropolitan waste streams in practically all urban communities and towns of the world (Kumar, 2009).

In rural regions or zones with low population, the hair is discarded in nature where it gradually disintegrates more than quite a long while, in the end restoring the constituent components, in particular, carbon, nitrogen, sulfur, etc, to their separate regular cycles.

In urban regions or zones with high population, it frequently aggregates in huge sums in the waste streams, representing a multifaceted issue. As a result of slow degradation, it remains in the waste streams for long occupying large amount of space.

Burning of human hair or the waste heaps containing them, a practice observed in various part of the world, produces foul smell and poisonous gases, for example, alkali, carbonyl sulfides, hydrogen sulfides, sulfur dioxide, phenols, nitriles, pyrroles, and pyridines (Brebu&Spiridon, 2011). Open dumps of hair produce hair dust which makes uneasiness in individuals close them and, whenever breathed in huge sums, can bring about a few respiratory issues.

Having identified these problems arising from water pollution and indiscriminate disposal of hair, it becomes imperative to adopt a method of treatment of this polluted water using hair as an adsorbent.This has dual advantages; first, is producing a potentially low cost adsorbent for treatment of polluted water. The second advantage is minimizing the hazardous emissions produced from the treatment of these wastes.

OBJECTIVES OF THE STUDY

The objectives of the research include:

i. Preparation of aqueous solutions (simulated waste water).
ii. Determination of the concentrations of heavy metals in simulated waste water before and after biosorption.
iii. Preparation of activated carbon from the human head hair by chemical activation method using H_3PO_4 as activating agent.
iv. To carry out batch adsorption to determine efficacies of the activated and unactivated human head hair in the removal of heavy metals from aqueous solution.
v. To test the data obtained from the study on various kinetic, isotherm and thermodynamic models.

LITERATURE REVIEW

HEAVY METAL POLLUTION

Heavy metals are elements having atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 (Hasar & Cuci, 2001). Most of the heavy metals are dangerous to health or to the environment (Satarug *et al.,* 2004). Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold and nickel (Pehlivan *et al.,* 2009).

Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers (Soleimani & Kaghazchi, 2008).

So far, various effective techniques have been developed for heavy metal expulsion. Fenglian *et al.* (2011), looked into different techniques for the removal of heavy metals, for example, chemical precipitation, electro dialysis, ultra filtration, nano filtration, coagulation, flocculation, floatation, and so forth.

However, chemical processes produce a large amount of metallic sludge, making metal recovery difficult (Yadanaparthi *et al.,* 2009).

At the point when connected to weaken metal waste or lower groupings of metal particles, these procedures are either incapable or not financially savvy and require abnormal state of aptitude; thus they are not connected by many end-clients (Srivastava *et al.,* 2006).

Also, most of these methods are costly and require high level of expertise; hence they are not applied by many end-users. For these reasons, adsorption technology has gained a wider application due to its inherent low cost, simplicity, versatility and robustness (Kwon *et al.,* 2010).

Also, most of these techniques are expensive and require high level of skill; thus they are not applied by many end-users. Thus, adsorption innovation has increased a more extensive application because of its intrinsic ease, low-cost, flexibility and availability (Kwon *et al.,* 2010).

Low-cost adsorbents derived from agricultural by-products, keratin biomaterial and industrial solid wastes could be used to remove recalcitrant wastes from synthetic wastewater (Kongsuwan *et al.,* 2006).

Change of these materials into adsorbents for wastewater treatment would lessen the expense of waste disposal. The adsorption of toxic waste from industrial wastewater using agricultural waste and industrial by-products has been massively investigated (Ismadji, 2011).

The technical feasibility of various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed (Babel *et al.,* 2003). Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as chitosan, zeolites and other adsorbents which have high adsorption capacity and are locally available.

REMOVAL OF HEAVY METALS BY HAIR

Just a few research investigations have been reported in the literature related to the biosorption of heavy metals by hair from aqueous solutions. Madhavi *et al*. (2013) used different hair samples including human and hog, in general from cattle and tannery to remove Hg(II). They found that the adsorption capacity of tannery hair for Hg(II) was better than others, probably because the crystalline regions in cattle hair were changed to be amorphous during the swelling in the tannery dehairing process.

Kulkarni & Rane (1980), reported a maximum adsorption capacity of 41.6 and 50.5 mgg^{-1} of Hg(II) by tannery hair pretreated in alkali and alkaline Na_2S solution, respectively.

Fergusson (1990), studied the sorption of Cu(II), Mn(II), Zn(II) and As(III) from aqueous solution by using human hair. At equilibrium, metal concentration was 0.3 $\mu g/cm^3$. The sorptions were relatively low for Mn and As but higher for Zn and Cu.

Fergusson considered that the greater sorption of Cu(II) probably was due to its greater potential binding capacity and stability, specially of the Cu-S interaction, and also due to the greater electrostatic interactions between Cu(II) and hair (Fergusson, 1990).

Adsorption capacities of untreated hair, inorganic acid treated hair and alkaline treated hair were compared by Tan *et al.* (2007). Among the pretreatment processes checked, hair with an alkaline treatment was more effective for the adsorption of Cu(II) than others. A favorable pretreatment of the human hair in a 0.1 MNaOH/0.1 M Na_2S solution for 20 min gave the best adsorption capacity for Cu(II). The adsorption capacity was found to increase as pH increased from 1.0 to 5.0. Moreover, the uptake capacity was significantly affected by the presence of other metal ions. Anionic effect was found to be more pronounced for a mixed ions system than for a single ion system.

The use of readily available natural materials as adsorbents of heavy metals from industrial wastewaters was investigated by Asubiojo & Ajelabi (2009). The natural adsorbents also contained human hair. Two modes of removal; column and batch experiments were carried out and their adsorption efficiencies were compared. It was found that in terms of the efficiency of heavy metal scavenging (heavy metal adsorbed per unit weight of adsorbent) it followed: bagasse and human hair > com cob and peanut skin > wheat bran > paddy husk. Moreover, efficiency of heavy metal removal by the natural adsorbents increased with column height and decreases with the increase in particle size of adsorbent and residual heavy metal concentration in the effluent (Romera *et al.,* 2007).

Gilbert *et al.* (2011) examined and compared the ability of different keratin-composed biosorbents (chicken feathers, hair and horn) for the removal of heavy metal ions from aqueous solutions. Among them, hair was an effective biosorbent and showed a higher Zn(II) ion uptake over Cu(II). The absolute amount of metal adsorbed increased with an increase in the initial metal concentration and in the pH of the aqueous initial solution. Intra-particle diffusion was involved in the adsorption processes but was not the rate-controlling step.

The studies by Jung *et al.* (2008) showed that perm-lotion-treated human hair can be efficient in the removal of Pb(II) and Cu(II) from diluted aqueous solution. The maximum metal removal at pH 4.2 was greater than 90% for both metals. This confirmed the ability of human hair to adsorb heavy metals due to the presence of reduced disulfide bonds. The perm-lotion-treated hair satisfactorily removed heavy metals from solutions with high concentrations. Although hair, especially human hair has shown excellent adsorption efficiency for the removal of heavy metals, the research based on human hair is still rare (Hasar & Cuci, 2000).

More importantly, the kinetic and isotherm studies on the biosorption by using human hair are quite rare. However, there is still big room to enhance the adsorption ability though the chemical modification of human hair (as it has been done with other keratin biomaterial) (Kongsuwan *et al.,* 2006).

STRUCTURE AND CHEMICAL COMPOSITION OF HUMAN HEAD HAIR

Human hair is a complex tissue consisting of several morphological components, and each component consists of several different chemical types (Rogers, 2004). Hair is an integrated system in terms of its structure and its chemical and physical behavior wherein its components can act separately or as a unit (Gao & Bedell, 2001).

Human hair contains numerous peptide bonds and CO- as well as NH- group which forms hydrogen bonds between neighboring molecules on the human organic follicle surface and has a highly porous cortex (Kumar, 2009).

Also human hair is considered as waste in many societies and accordingly is found in the metropolitan waste streams in practically all urban communities and towns of the world (Kumar, 2009).

In rural regions or zones with low population, the hair is discarded in nature where it gradually disintegrates more than quite a long while, in the end restoring the constituent components, in particular, carbon, nitrogen, sulfur, etc, to their separate regular cycles.

In urban regions or zones with high population, it frequently aggregates in huge sums in the waste streams, representing a multifaceted issue. As a result of slow degradation, it remains in the waste streams for long occupying large amount of space.

Burning of human hair or the waste heaps containing them, a practice observed in various part of the world, produces foul smell and poisonous gases, for example, alkali, carbonyl sulfides, hydrogen sulfides, sulfur dioxide, phenols, nitriles, pyrroles, and pyridines (Brebu&Spiridon, 2011). Open dumps of hair produce hair dust which makes uneasiness in individuals close them and, whenever breathed in huge sums, can bring about a few respiratory issues.

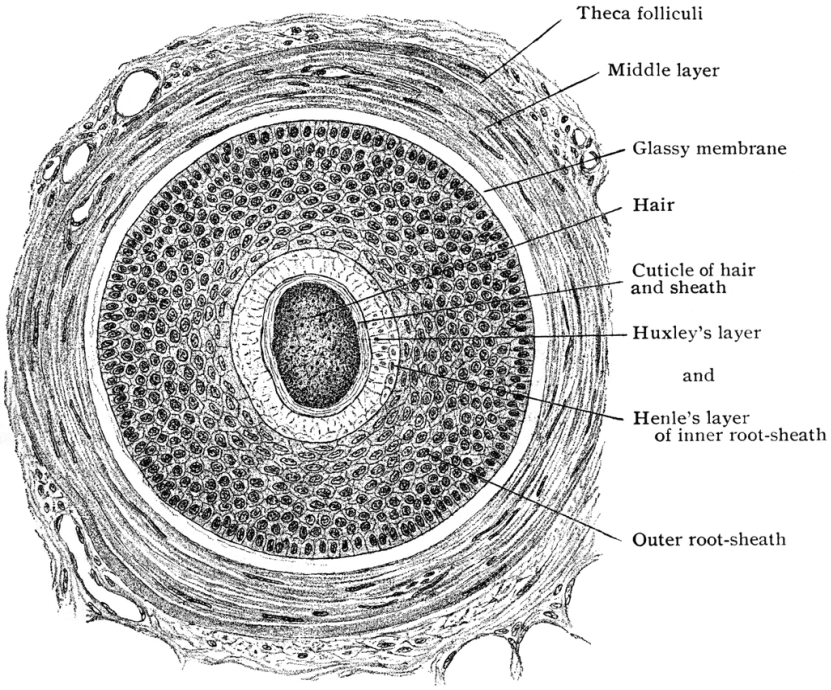


Figure 2.1: Structure of human head hair (Rogers & Koike, 2009).

METHODOLOGY

Untreated human head hair sample was obtained from barber shops in Abuja municipal council Abuja, Nigeria, washed with commercial detergent, rinsed several times with de ionized water and dried in an oven until a constant weight was achieved. The dried head hair was grinded into small particles using grinder and sieved using conventional sieves to get the desired particle size (0.5 mm – 1 mm) which was then divided into two portions and stored at room temperature in an airtight container for future use. A portion of the human hair was (80 g) soaked in 500 cm^3 beaker containing 200 cm^3 of 85 % of H_3PO_4 with continuous stirring for 2 min and then allowed for 24 hours. The reaction mixture was then mixed with of di ionized water to wash away the unreacted H_3PO_4, tested with litmus paper, filtered and the residue collected.

Batch adsorption process was employed for the adsorption tests. 0.5 g of adsorbent was added to 100 mg/dm^3 metal solution at pH 5 and agitated using a magnetic stirrer set at 300 rpm for 4 hours at room temperature. The adsorbents were removed by filtration using ash-less and fine crystalline filter paper. The filtrates were subsequently analyzed for the residual metal concentration using atomic absorption spectrometry. All experiments were carried out in triplicates.

To determine the effect of activating conditions on the resulting activated carbon (human hairs), 0.5 g of the biosorbent was used for the adsorption. 20 cm^3 of the metal solution with initial metal concentration of 100 g/dm^3 was added to the biosorbent at pH 5.0 and was agitated using a magnetic stirrer for 30 minutes and allowed for 24 hours, which is sufficient time to reach equilibrium. The temperature is kept constant at 25±1 ºC. Same amount from the second portion of the human hair (unactivated) was used as blank.

Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) images were used to demonstrate the surface topography of the different biosorbent samples (activated and unactivated human hair).

RESULTS

Comparison of Biosorption Efficacy between Unactivated and Activated Human Hair

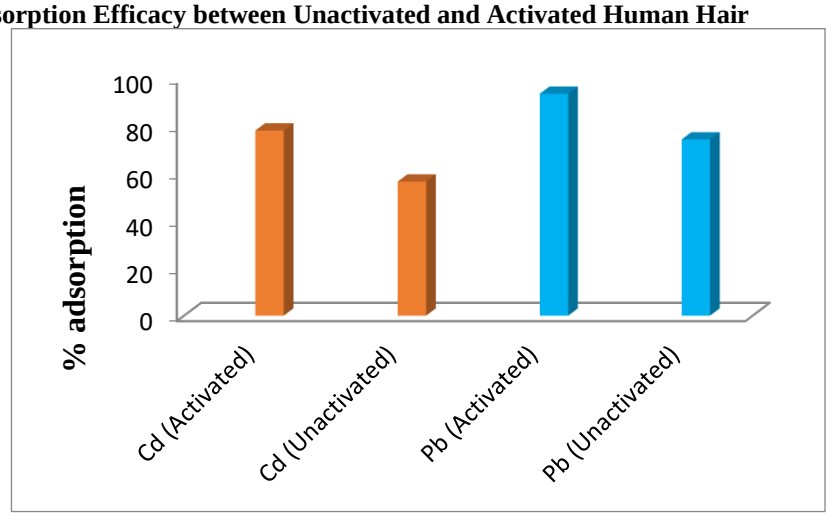
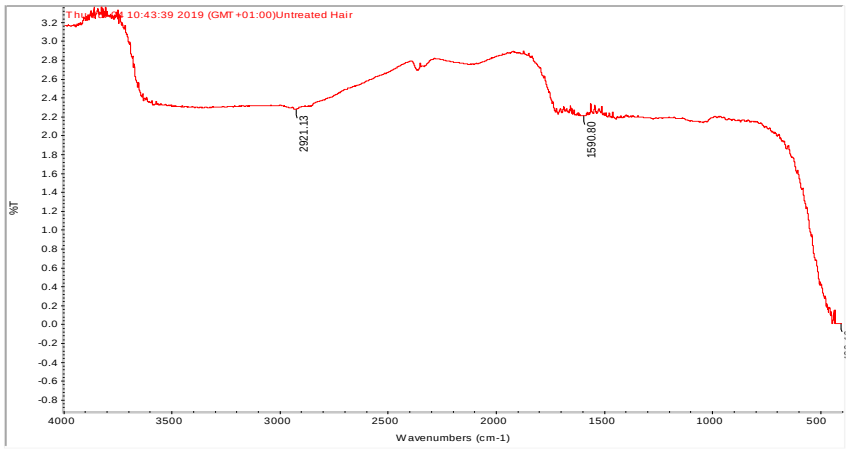
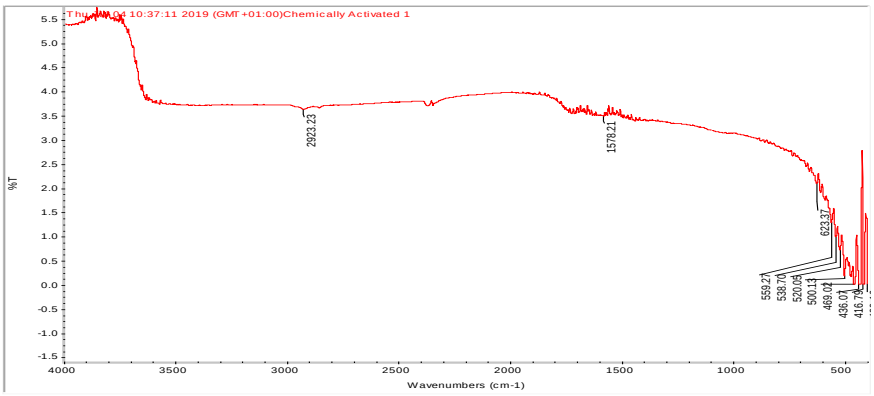


Figure 4.1: Comparison of biosorption capacity between unactivated and activated human hair in metal system. The initial metal concentration is 100 mg/cm^3, the contact time is 24h, the pH is 5.0, and the biosorbent is 0.5 g.

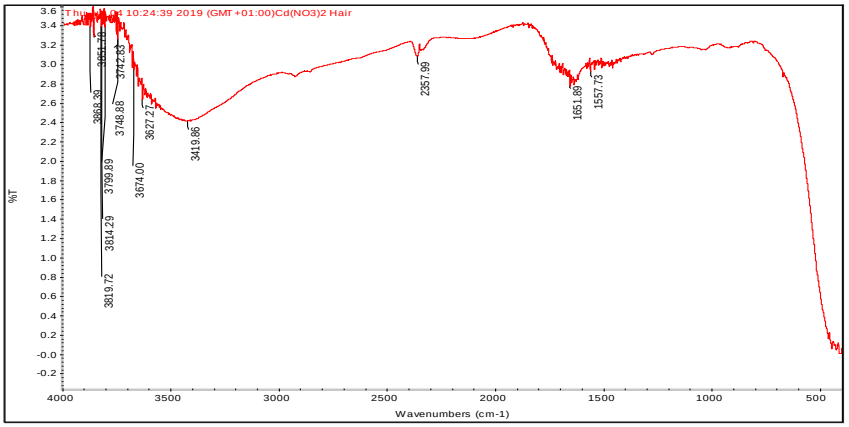
FT-IR Characterization



Unactivated hair



activated hair



Metal loaded-activated hair

Plate 4.1: FT-IR spectra for unactvated, activated and metal loaded activated hair respectively.

SEM Characterization

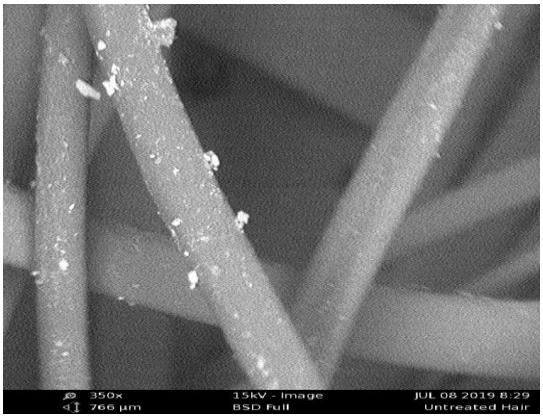


Plate 4.2: Scanning Electron Microscopy (SEM) micrographs of unactivated human hair (H1).

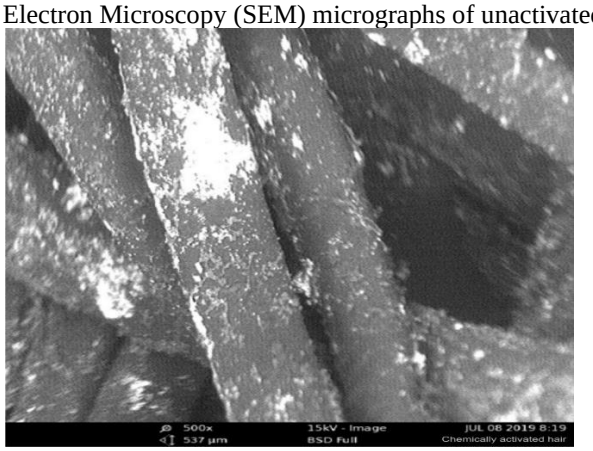


Plate 4.3: Scanning Electron Microscopy (SEM) micrographs of activated human hair (H2).

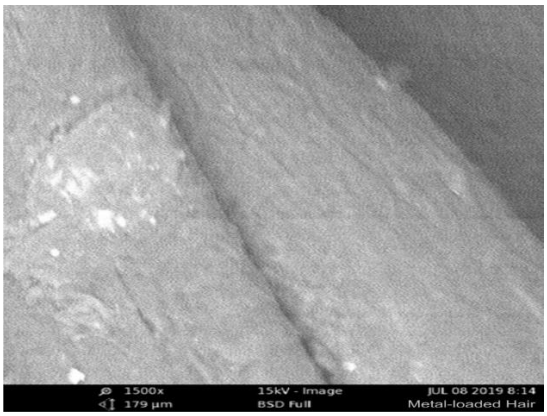


Plate 4.4: Scanning Electron Microscopy (SEM) micrographs of metal-loaded human hair (H3).

Effect of pH

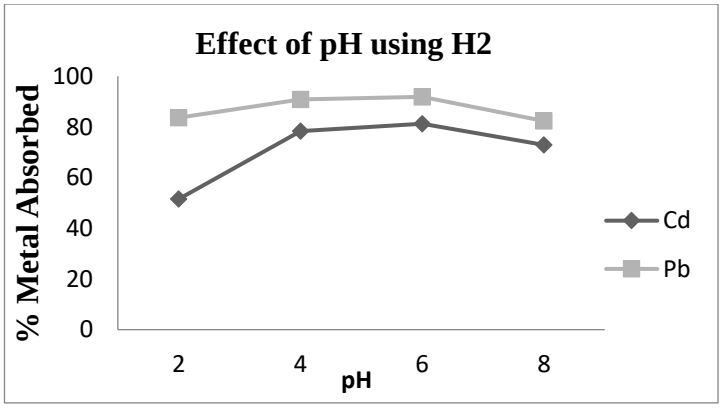


Figure 4.2: Effect of pH on the biosorption of Cd(II) and Pb(II) using H2. The initial metal concentration is 100 mg/dm^3, the contact time is 24 h, and the biosorbent is 0.5 g.

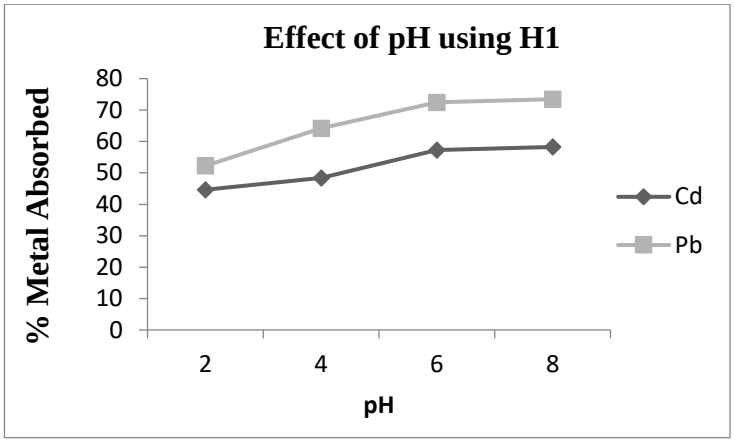


Figure 4.3: Effect of pH on the biosorption of Cd(II) and Pb(II) using H1. The initial metal concentration is 100 mg/dm^3, the contact time is 24 h, and the biosorbent is 0.5 g.

Effect of Contact Time

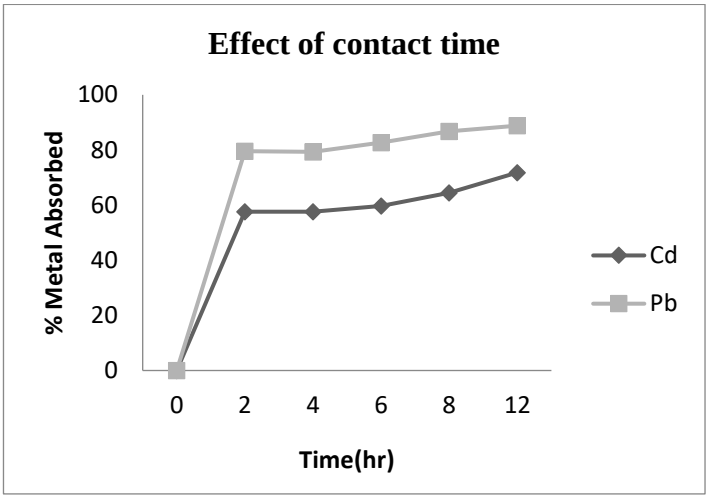


Figure 4.4: Effect of contact time onbiosorption Cd(II) and Pb(II) in metal system at different contact time using H2. The initial metal ion concentration is 100 mg/dm^3, the pH is 5.0, and the biosorbent is 0.5 g.

Effect of Initial Metal Concentration

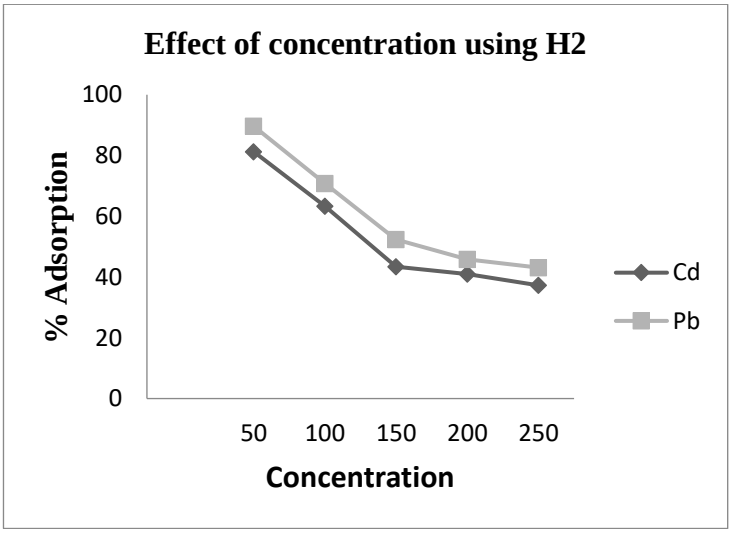


Figure 4.5: Effect of concentration on biosorption of Cd(II) and Pb(II) using H2 at different initial metal ion concentration. The contact time is 24 h, the initial pH is 5.0, and the biosorbent is 0.5g.

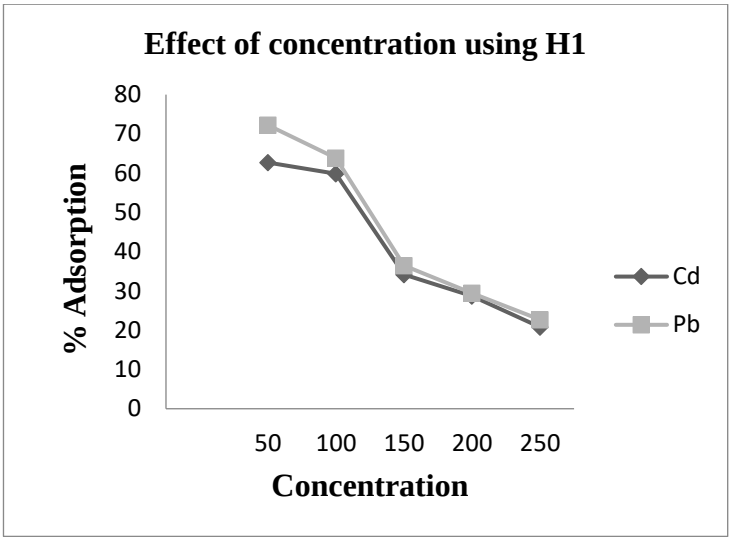


Figure 4.6: Effect of concentration onbiosorption of Cd(II) and Pb(II) using H1 at different initial metal ion concentration. The contact time is 24 h, the initial pH is 5.0, and the biosorbent is 0.5g.

Effect of Biosorbent Dosage

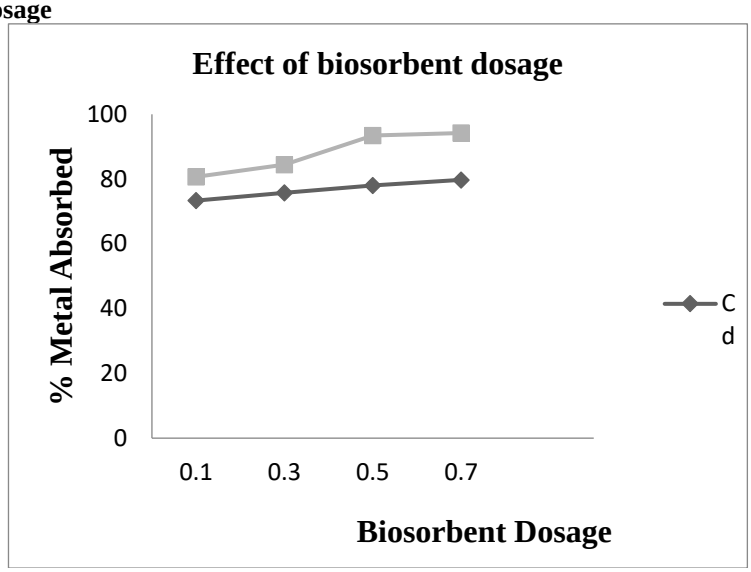


Figure 4.7: Effect of biosorbent dosageon the biosorption of Cd(II) and Pb(II) using H2. The contact time is 24 h, the initial pH is 5.0, and the initial metal concentration is 100 mg/ dm^3.

Effect of Temperature

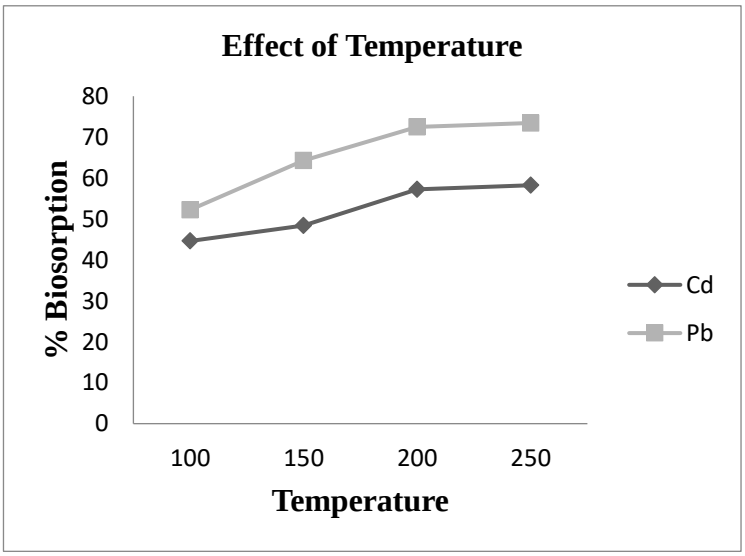


Figure 4.8: Effect of temperature on biosorption of Cd(II) and Pb(II)using H2. The contact time is 24 h, the pH is 5.0, the biosorbent dosage is 0.5 g and the initial metal concentration is 100 mg/dm^3.

Kinetic Study

Table 4.1: Parameters ofPseudo-first and Pseudo-second-order metal equations parameters for the biosorption of Pb^{2+} and Cd^{2+} by the treated human head hair.

Metal		Pb^{2+}	Cd^{2+}
Pseudo First-Order	K_1	2.06	0.13
	R^2	0.903	0.889
	q_e	0.11	0.91
Pseudo Second Order	K_2	1.08	0.60
	R^2	0.997	0.985
	q_e	3.58	2.87

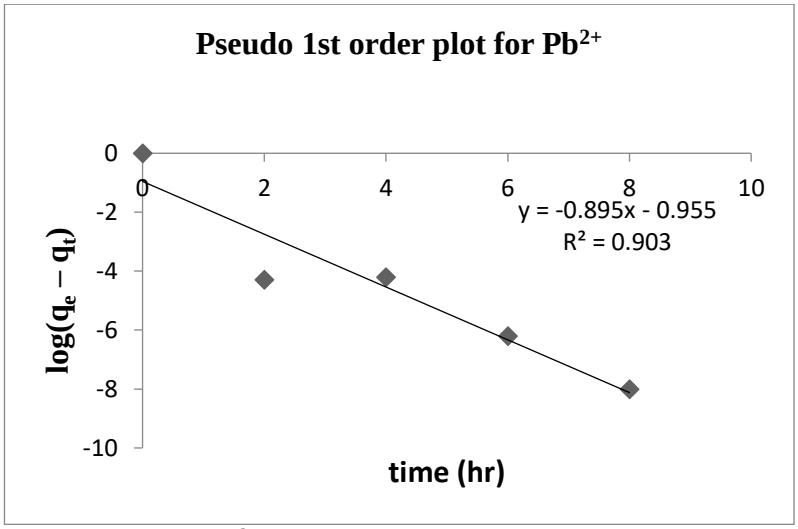


Figure 4.9: Pseudo First Order plots for Pb^{2+}at pH = 4, Adsorbent dosage = 0.5g, 20mL solution and concentration = 100mg/L.

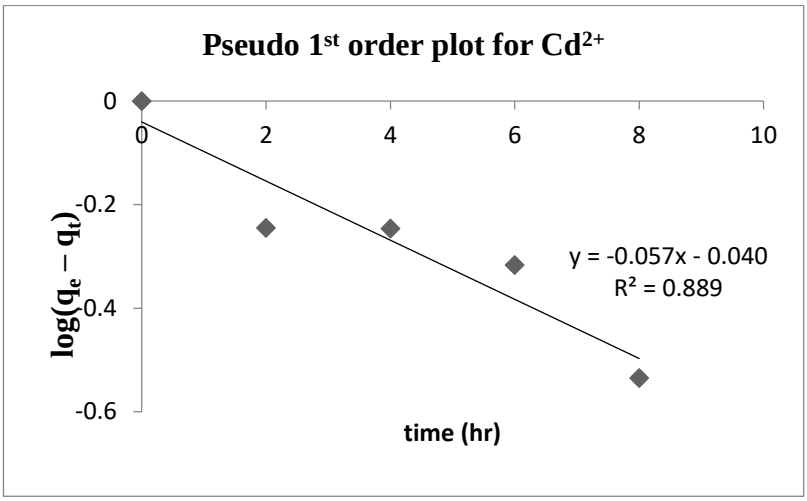


Figure 4.10: Pseudo First Order plots for Cd^{2+} at pH = 4, Adsorbent dosage = 0.5g, 20mL solution and concentration = 100mg/L.

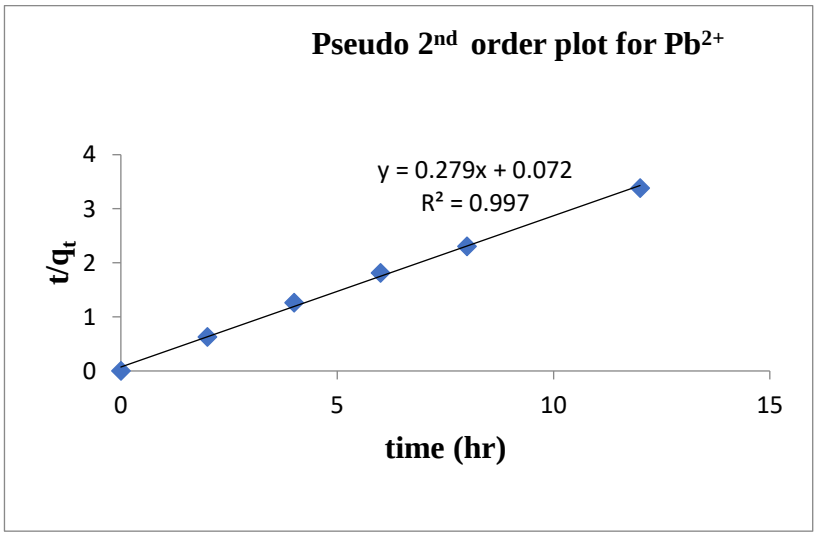


Figure 4.11: Pseudo second order plots for Pb^{2+}at pH = 4, Adsorbent dosage = 0.5g, 20mL solution and concentration = 100mg/L.

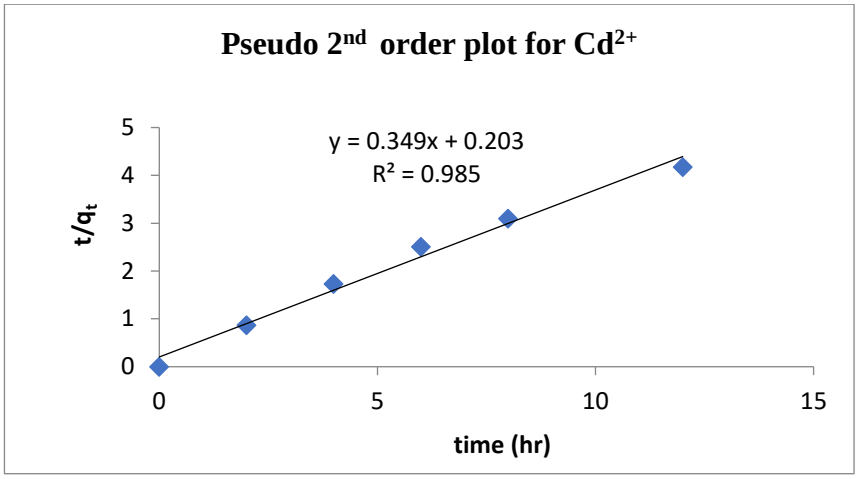


Figure 4.12: Pseudo second order plots for Cd^{2+}at pH = 4, Adsorbent dosage = 0.5g, 20mL solution and concentration = 100mg/L.

Isotherm Study

The equilibrium data were analyzed using Freundlich, Langmuir and Temkin Isotherm models.

Table 4.2: Parameters of three adsorption isotherms for Pb^{2+} and Cd^{2+} adsorption on treated human hair.

Isotherm Model	Constant	H2	H1
Freundlich	K_f (mg/g)	1.21	0.99
	n (g/l)	3.13	6.21
	R^2	0.969	0.765
Langmuir	Q_h (mg/g)	4.57	3.70
	K_L (L/mg)	0.054	0.027
	R^2	0.652	0.598
Temkin	K_T (L/mg)	0.16	0.81
	B_T (KJ/mol)	1.419	0.432
	R^2	0.969	0.856

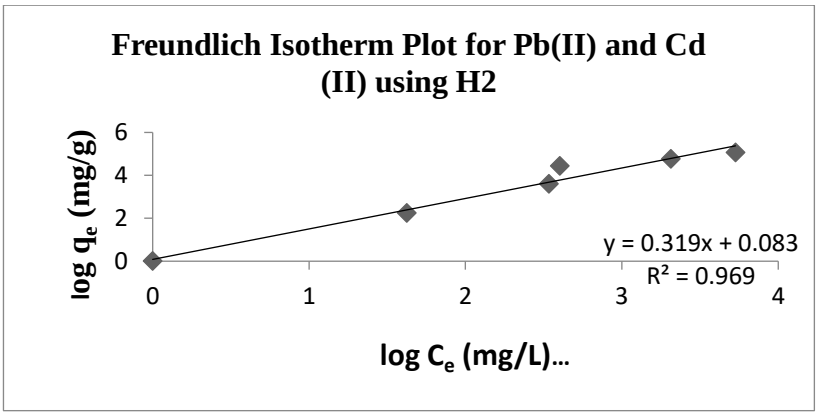


Figure 4.13: Freundlich isotherm plot forPb(II) and Cd(II) removal using H2.

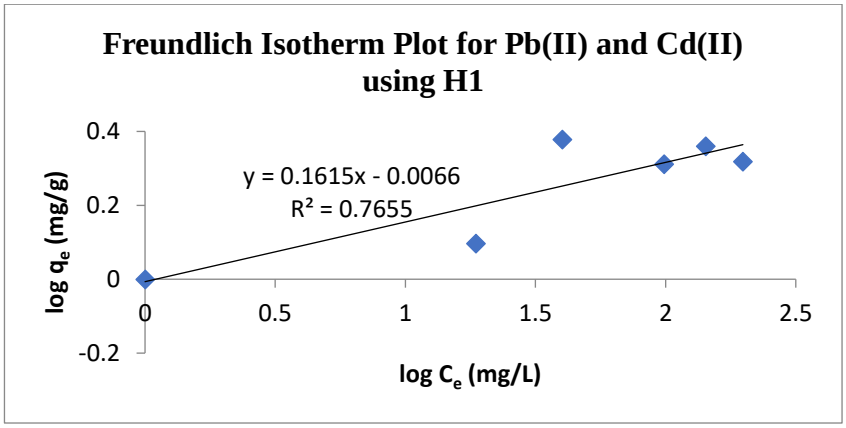


Figure 4.14: Freundlich isotherm plot for Pb(II) and Cd(II) using H1.

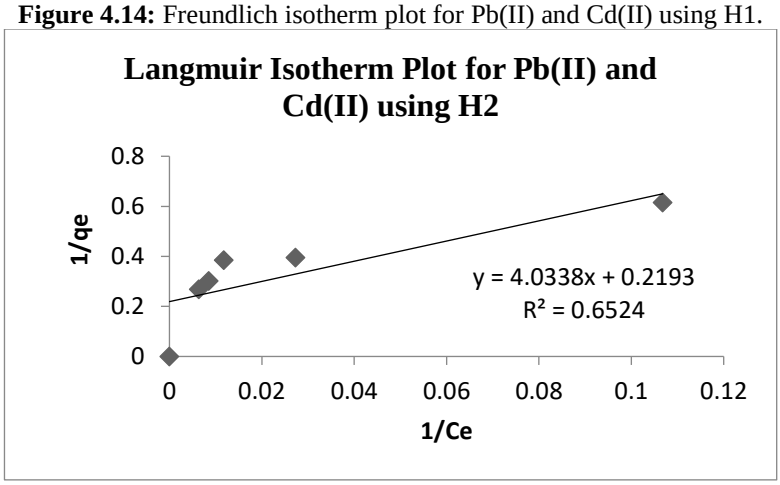


Figure 4.15: Langmuir isotherm for Pb(II) and Cd(II) removal using H2.

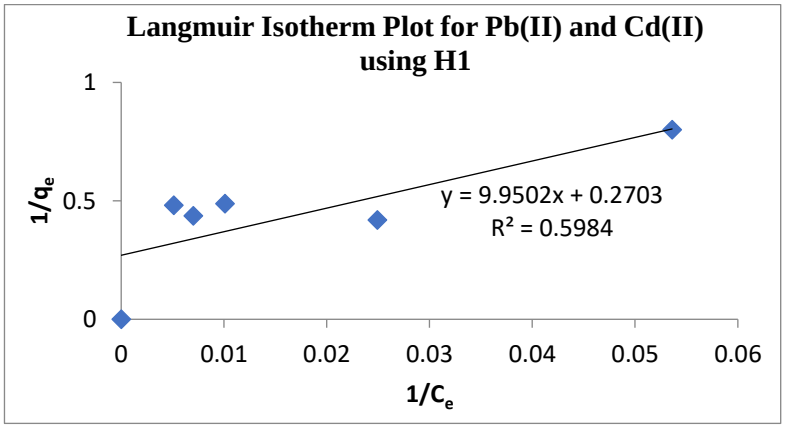


Figure 4.16: Langmuir isotherm plot for Pb(II) and Cd(II) removal using H1.

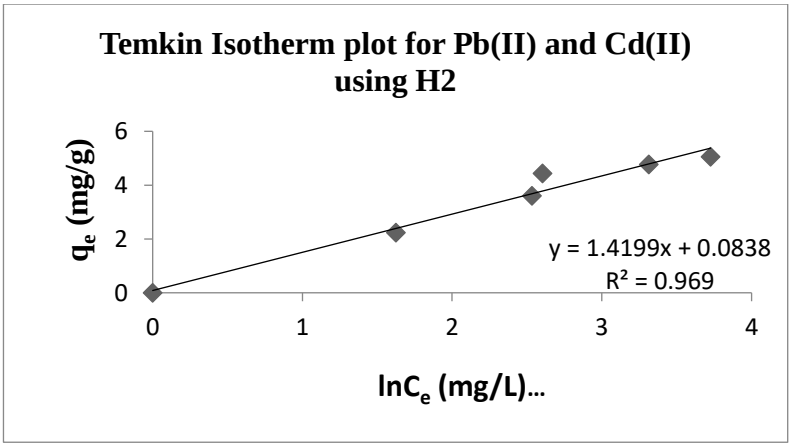


Figure 4.17: Temkin isotherm plot for Pb(II) and Cd(II) removal using H2.

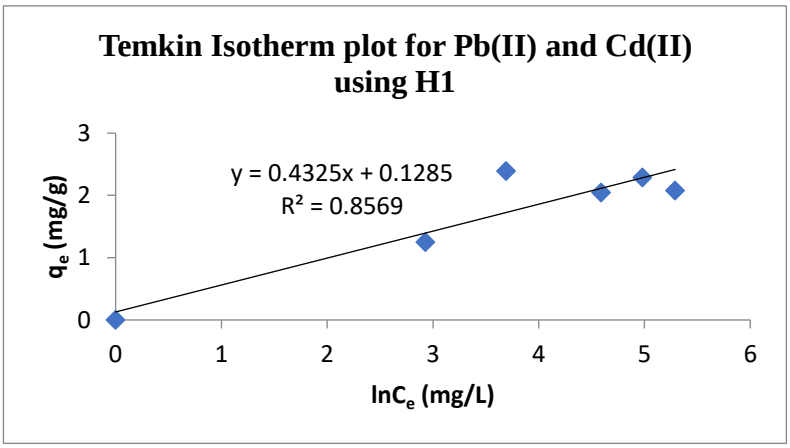


Figure 4.18: Temkin isotherm plot for Pb(II) and Cd(II) removal using H2.

Thermodynamic Study

The experimental data obtained at different temperatures were used in calculating the thermodynamic parameters of sorption;

Table 4.3: Values of ΔH, ΔSand ΔGcalculated from the sorption data of Pb^{2+} and Cd^{2+} on activated human hair (metal ion concentrations = 100 mg/L, biosorbent dosage = 0.5g, solution volume = 20 mL).

Sample	ΔH (KJmol^{-1})	ΔS(Jmol^{-1}K^{-1})	ΔG (KJmol^{-1})			
			373K	423K	473K	523K
Pb^{2+}	13.68	49.62	-4.83	-5.48	-6.13	-6.77
Cd^{2+}	16.66	57.61	-4.83	-5.48	-6.13	-6.77

CONCLUSION

The removal of heavy metals from aqueous solution using treated and untreated human head hair was investigated. Two biosorbent samples including unactivated hair (H1) and activated hair (H2) were selected for the biosorbtion study.

As expected, the activated human hair with a chemical modification shows betterbiosorption capacity for the removal of heavy metals. The maximumbiosorption capacities of the activated human hair for Cd(II) and Pb(II) at 295 K were 77.99% and 93.5%, respectively, while that of unactivated hair were 56.5% and 74.25% respectively.

FT-IR analysis of the hair samples confirm that abundant metal binding groups such as hydroxyl, amines and sulfonate groups are responsible for the metal removal. The sulfonate groups formed during the modification process of the human hair using phosphoric acid play a great role in the removal of heavy metals.

Biosorptionwas investigated to determine the influence of various parameters such as pH of solution, biosorbent dosage, contact time and initial metal concentration.Results showed that biosorption of Pb(II) and Cd(II) are highly dependent on the pH of the solution, contact time, biosorbent dose, initial metal concentration and temperature.Increase in biosorbent dose, contact time, pH and temperature let to corresponding increase in the percentage metal removed. While an increase in concentration led to decrease metal biosorption percentage.

The kinetic study shows that the biosorption of metal ions using human hair follows well the pseudo-second order kinetic model, which is in agreement with the chemical sorption being the rate controlling step. The biosorption equilibrium of metal ions is better fitted with Freundlich isotherm model, followed by Temkin model, while Langmuir model is least fitted.

The Freundlich isotherm model is considers heterogeneous surface and is not restricted to the formation of a monolayer while Temkin, takes into account the effects of indirect adsorbate/biosorbate interactions on the adsorption process.

The calculated standard Gibb's free energy (ΔG) indicates the thermodynamically feasible and spontaneous nature of the biosorption process.

Thus, taking into consideration the present findings, it can be stated that the activated human hair is an effective and low-cost biosorbent for the removal of heavy metals from aqueous solutions. Activation treatment would be quite useful in modifying human hair to enhance the removal of heavy metals from contaminated effluents.

RECOMMENDATIONS

1. Based on the obtained results, activated human head hair can be used as an alternative adsorbent to treat waste water containing lead and Cadmium. It can be applied in bioreactor design or large-scale batch biosorption systems.

2. It was noted in the experiment that pH played a pivotal role in the adsorption process, and that metals have the ability to precipitate upon addition of NaOH. This would mean that some metals were not solely removed by adsorption but also by precipitation. An investigation into the exact mechanism and quantities (either adsorption or precipitation) under which the metals were removed could be carried out.
3. Since chemical activation was used determine the efficiency of the adsorption process, use of other activation methods like two –step impregnation and microwave method and the use of other activating agents like H_2O_2, H_2SO4, KOH and HCl among others.
4. The durability of the produced activated hair and the ability to regenerate it for further use while recovering adsorbed metals should be more thoroughly investigated to improve the economic potential of the product and process.

REFERENCES

[1]. Abdulkarim, M., and Al-Rub, F.A., (2004). "Adsorption of Lead Ions from Aqueous Solution onto Activated Carbon and Chemically-modified Activated Carbon Prepared from Date Pits." Ads.Sci and Tech. 22(2):119 – 134.

[2]. Acharya, J.; Sahu, J.N.; Mohanty, C.R.; Meikap, B.C. (2009)."Removal of lead(II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation". *Chem. Eng. J. 149*, 249–262.

[3]. Agarwal, A. and Gupta, P.K., (2014). 'Removal of Cu and Fe from Aqueous Solution by Using Eggshell Powder as Low Cost Adsorbent'. *Advanced Applied Science Research*, *5*(2), pp.75-79.

[4]. Ahluwalia S., and Goyal, D., (2005). 'Removal of heavy metals by waste tea leaves from aqueous solution'. Engineering in Life Science, 5: 158-162.

[5]. Aksu, Z., and Kabasakal, K., (2004). 'Batch adsorption of 2,4 dichlorophenoxyacetic acid (2,4-D) from aqueous solution by granular activated carbon'. Separation and Purification Technology, 35: 223-240. 54.

[6]. Alluri H., Ronda S., Settalluri V., Bondili V., Suryanarayana V., and Venkateshwar P., (2007), 'Biosorption: An eco-friendly alternative for heavy metal removal'. *Afr. J. Biotechnol.* 6, 11,2924-2931.

[7]. Amarasingha, B.M.W.P.K., and Williams, R. A., (2007). 'Tea waste as a low cost adsorbent for the removal of Cu and Pb from waste water'. *Journal of Chemical & Engineering,* 132(1-3): 299-309.

[8]. Arief, V.O., Trilestari, K., Sunarso, J., Indraswati N., and Ismadji, S., (2008). 'Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: Characterization, biosorption parameters and mechanism studies': a review. Clean, 36: 937-962.

[9]. Arunlertaree, C., Kaewsomboon, W., Kumsopa, A., Pokethitiyook, P. and Panyawathanakit, P., (2007). 'Removal of lead from battery manufacturing wastewater by egg shell'. *Songklanakar in Journal of Science and Technology, 29*(3), pp.857-868.

[10]. Babarinde, N.A.A., Babalola J., and Adebowale, R., (2006). 'Biosorption of lead ions from aqueous solution by maize leaf'. *International Journal of Physical Sciences,* 1: 23-26.

[11]. Bailey, S.E., Olin, T.J., Bricka R.M., and Adrian, D.D., (1999). 'A review of potentially low cost sorbents for heavy metals'. Water Research, 33: 2469-2479. 63.

[12]. Bahadir, T.; Bakan, G.; Altas, L. and Buyukgungor, H. (2007). "The investigation of lead removal by biosorption: An application at storage battery industry wastewaters". *Enzyme Microb. Technol. 41*, 98–102.

[13]. Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M., and Portier, R.J., (2003). 'Adsorption of metal ions by pecan shell-based granular activated carbons.' Biores. Technol. 89: 115 – 119.

[14]. Bhattacharya, A.K., Mandal, S.N., and Das, S.K., (2006). 'Adsorption of Zn(II) from aqueous solution by using different adsorbents'. *Chemical Engineering Journal,* 123: 43-51.

[15]. BharathiIranica, (2012). A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions, *Iranica Journal of Energy and Environment,* 3(2): 143-156.

[16]. Borba C., Guirardello R., Silva E., Veit M., and Tavares, C., (2006). 'Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves'. Biochem. *Eng. J.* 30, 184e191.

[17]. Chavan, N., Daniels, S., Rajdeo, K., Tambe, S. and Mulani, K., (2013). 'Adsorption of chromium (VI) from aqueous solutions by coffee polyphenol-formaldehyde/acetaldehyde resins'. *Journal of Polymers.*

[18]. Chiban, M., and Sinan, F., (2011). 'Removal of Cu(II) ions from aqueous solution by micro-particles of dried Carpobrotusedulis plant in a column system'. *Water Quality Research Journal of Canada*, 46: 259- 267.

[19]. Debnath, S and Ghosh, U. C, (2008) "Kinetics, isotherm and thermodynamics for Cr (III) and Cr (VI) adsorption from aqueous solutions by crystalline hydrous titanium oxide", *J.Chem. Thermodynamics*. 40: 67–77.

[20]. Ekpete, O.A., Kpee, F., Amadi, J.C., and Rotimi, R.B., (2010). 'Adsorption of Chromium(VI) and Zinc(II) Ions on the Skin of Orange Peels *(Citrus sinensis)'.Journal of Nepal Chemical Society [Online],* 26: 31-39.

[21]. Faisal, M., and Hasnain, S., (2004) 'Microbial conversion of Cr (vi) into Cr (iii) in industrial effluent. *African J. Biotechnol*. 3(11): 610 – 617.

[22]. Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y., Indraswati. N., and Ismadji, S., (2009). 'Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies'. *Journal of Hazardous Materials,* 162: 616-645.

[23]. Gao, T., and Bedell, A., (2001). 'Ultraviolet damage on natural gray hair and its Photoprotection'. *J CosmetSci* 52:103–118

[24]. Gilbert, U.A., Emmanuel, I.U., Adebanjo, A.A., and Olalere, G.A., (2011). 'Biosorptive removal of Pb(II) and Cd(II) onto novel biosorbent: Defatted Carica papaya seeds'. Biomass & Bioenergy, 35(7): 2517-2525.

[25]. Gottipati, R., and Mishra, S., (2012). 'Application of response surface methodology for optimization of Cr(III) and Cr(VI) adsorption on commercial activated carbons'. *Research Journal of Chemical Sciences*, 2(2), 40-48
[26]. Gueu, S., Yao, B., and Adouby, K., (2007). 'Kinetics and thermodynamics study of lead adsorption the activated carbon from cocoanut and seed hull of palm tree' *Int. J environ, Sci. technol*, 2007, 1(4), 11-17.
[27]. Gupta, V.K.; Agarwal, S. and Saleh, T.A. (2011) Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *J. Hazard. Mater. 185*, 17–23.
[28]. Gupta, S. and Babu, B.V., (2009). Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies. *Chemical Engineering Journal*, 150: 352-365.
[29]. Han, R., Lu, Z., Zou, W., Daotong, W., Shi J., and Jiujun, Y., (2006). 'Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand: II. Equilibrium study and competitive adsorption'. *Journal of Hazardous Materials*, 137: 480-488.
[30]. Hasar, H., and Cuci, Y., (2000). 'Removal of Cr (VI), Cd(II) and Cu(II) by activated carbon prepared from almond husk'. Environ. Tech. 21: 1337 – 1342.
[31]. Helan, Z. (2014), "Biosorption of heavy metals from aqueous solutions using keratin biomaterial". Bellaterra; Cerdanyola del Valles. 79-160.
[32]. Hossain, M.A., Ngo, H.H., Guo W.S., and Nguyen, T.V., (2012). 'Biosorption of Cu(II) from water by Banana peel based biosorbent: Experiments and models of adsorption and desorption'. *Journal of Water Sustainability*, 2(1): 87-104.
[33]. Ho, Y.S., (2006). 'Review of second-order models for adsorption systems', *Journal of Hazardous Materials,* 136: 681-689.
[34]. Igwe, J.C., and Abia, A.A., (2006). 'A bioseperation process for removing heavy metals from waste water using biosorbents'. *Afr. J. Biotechnol.* **5**(12):1167-1179.
[35]. Ipeaiyeda, R. and Tesi, G.O. (2014). 'Sorption and desorption studies on toxic metals from brewery effluent using eggshell as adsorbent'. *Advances in Natural Science*, *7*(2), pp.15-24.
[36]. Ismadji, M., (2011). 'Performance of durian shell waste as high capacity biosorbent for Cr(VI) removal from synthetic wastewater'. Ecological Engineering, 37(6): 940-947.
[37]. Kang, K.C, Kim, S.S, Choi, J.W., and Kwon, S.O., (2008). 'Sorption of $Cu2^{+}$ and Cd^{2+} onto acid- and base- pretreated granular activated carbon and activated carbon fiber samples."*Journal of Ind. and Eng. Chem*. 14 (1): 131 - 135.
[38]. Kanyal, M. and Bhatt, A.A., (2015). 'Removal of heavy metals from water (Cu and Pb) using household waste as an adsorbent'. *Journal of Bioremediation & Biodegradation*, *2015*.
[39]. Khaled, A., Nemr, A.E., El Sikaily, A., and Abdelwahab, O., (2009). 'Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon'. Desalination, 238: 210-232.
[40]. Koel Banerjee, S.T., Ramesh, R., Gandimathi, P.V., Nidheesh H., and BharathiIranica, K.S., (2012). 'A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions'. *Iranica Journal of Energy and Environment,* 3(2): 143-156.
[41]. Kongsuwan, A., Patnukao, P., and Pavasant, P., (2006). 'Removal of Metal Ion from Synthetic Waste Water by Activated Carbon from Eucalyptus camaldulensis'. 99(8): 3162-3165.
[42]. Kwon J.S., Yun S.T., Lee J.H., Kim S.O., and Jo H.Y., (2010). 'Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic (III) from aqueous solutions using scoria: kinetics and equilibrium of sorption'.*J. of Hazard Mater*, 174, 307–313.
[43]. Kongsuwan, A., Patnukao, P., and Pavasant, P., (2006). 'Removal of Metal Ion from Synthetic Waste Water by Activated Carbon from Eucalyptus camaldulensis'. 99(8): 3162-3165.
[44]. Kurniawan, A., Sisnandy, V., Trilestari K., Sunarso, J., and Indraswati, N., (2006). 'Comparison of low-cost adsorbents for treating wastewater laden with heavy metals'. Science Total Environment, 366(2-3): 407-424.
[45]. Kumar, P.S., and Kirthika, k., (2009). 'Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder'. *Journal of Engineering Science and Technology,* 4: 351-363.
[46]. Lagergren S., (1998). 'About the theory of so-called adsorption of soluble substances'. KungligaSvenskaVetenskapsakademiens. Handlingar, 24(4): 1-39.
[47]. Liu, Y., (2006). 'Some consideration on the Langmuir isotherm equation'. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 274: 34-36.
[48]. Li, Y.; Wang, S.; Wei, J.; Zhang, X.; Xu, C.; Luan, Z.; Wu, D.; Wei, B. (2002) 'Lead adsorption on carbon nanotubes'. *Chem. Phys. Lett.357,* 263–266.
[49]. Low, K.S., Lee, C.K and Liew, S.C. (2000) 'Adsorption of cadmium and lead from aqueous solutions by spent grain'. *Process Biochem. 36,* 59–64.
[50]. Malkoc, E., and Nuhoglu, Y., (2005). 'Investigations of Ni(II) removal from aqueous solutions using tea factory waste'. *Journal of Hazardous Materials,* 127: 120-128.
[51]. Mahdavian, L., and Raouf, M., (2010). 'Thermodynamic and Electronic Investigation About Remove of MTBE from Environment by Single- Walled Carbon Nano tube (SWNT)'. Integrated Ferroelectrics, 114: 1, 7 -16.
[52]. Malakootian, M., Almasi, A., and Hossaini, H., (2008). 'Pb and Co removal from paint industries effluent using wood ash'. *Int. J. Environ. Sci.Tech.,* 5(2): 217-222.
[53]. Markovska, L.T., Meshko, V.D., and Marinkovski, M.S., (2006). 'Modeling of adsorption kinetics of zinc onto granular activated carbon and natural zeolite'. *J. Serb. Chem. Soc*. **71** (8 - 9): 957 - 967.

[54]. Marshall W.E, Akin D.E, Wartelle L.H, Annis P.A (2007) 'Citric acid treatment of flax, cotton and blended nonwoven mats for copper ion absorption'. Ind Crop Prod 26(1):8–13
[55]. Metcalf and Eddy (2003). 'Wastewater Engineering Treatment and Re-use'.6th Edition John Wiley.
[56]. Mohan, M., and Pittman J., (2007) 'Arsenic removal from water/wastewater using adsorbents- A critical review'. *Journal of Hazardous Materials* 142, 1–53.
[57]. Naiya, T.K., Chowdhury, P., Bhattacharya, A.K., and Das, S.K., (2009). 'Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions'. *Chemica Engineering Journal*, 148: 68-79.
[58]. Nasim, A.K., Shaliza I., and Piarapakaran, S., (2004). 'Review paper; Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents' *Malaysian Journal of Science*, 23: 43-51.
[59]. Naseem, R., and Tahir S., (2001). 'Removal of Pb(II) from aqueous solution by using bentonite as an adsorbent'. Water Research, 35: 3982-3986.
[60]. Oboh, I., Aluyor, E. and Audu, T., (2009). 'Biosorption of heavy metal ions from aqueous solutions using a biomaterial'. *Leonardo Journal of Sciences*, (14), pp.58-65.
[61]. Olayinka, O., Oyedeji O., and Oyeyiola, A., (2009). 'Removal of chromium and nickel ions from aqueous solution by adsorption on modified coconut husk'. *African Journal of Environmental Science and Technology*, 3(10): 286-293. 66.
[62]. Okoye, A. (2010) 'Preparation, Characterization and Adsorptive evaluation of Activated Carbon from *Telfairia Occidentalis* and *Gambeya Albida* seed shells' UNN. pp62.
[63]. Pavan, F.A., Mazzocato A.C., and Gushiken, Y., (2008). 'Removal of methylene blue dye from aqueous solution by adsorption using yellow passion fruit peel as adsorbent'. Bioresources Technology, 99(8): 3162-3165.
[64]. Pehlivan, M., Sulaiman O., Hashim, H., and Ahmad, A., (2009). 'Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust'. *Journal of Hazardous Materials*, 170: 969-977.
[65]. Pettinato, M., Chakraborty, S., Arafat, H.A. and Calabro, V., 2015. 'Eggshell: A green adsorbent for heavy metal removal in an MBR system'. *Ecotoxicology and environmental safety*, *121*, pp.57-62.
[66]. Pollard S., Fowler G., Sollars C., and Perry R., (1992). 'Lowcost adsorbents for waste and wastewater treatment' a review, Sci. of Total Environment, 116, 31–52.
[67]. Rafatullah, M., Sulaiman O., Hashim R. and Ahmad A., 2009.Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. *Journal of Hazardous Materials*, 170: 969-977.
[68]. Rao, K.S.; Anand, S. and Venkateswarlu, P. (2010) 'Adsorption of cadmium (II) ions from aqueous solutions by TectonaGrandis L.F. (Teak leaves powder)'. *Bio Resources*, *5*, 438–454.
[69]. Rogers, G.E., and Koike, K., (2009). 'Laser capture microscopy in a study of expression of structural proteins in the cuticle cells of human hair'. ExpDermatol 18:541–547
[70]. Rogers, G.E., (2004). 'Hair follicle differentiation and regulation'. *Int J DevBiol* 48:163–170
[71]. Romera, E., Gonzalez, F., Ballester, A., and Blazquez J.A., (2007). 'Comparative study of heavy metals using different types of algae'. Bioresource Technology, 98: 3344-335.
[72]. Satarug, S., and Michael, R.M., (2004). 'Adverse Health Effects of Chronic Exposure to Low-Level Cadmium in Foodstuffs and Cigarette Smoke'. Environmental Health Perspectives.112 No.10, 1099-1103.
[73]. Satapathy, D., and Natarajan, G.S., (2006). 'Potassium bromated modification of the granular activated carbon and its effect on nickel adsorption' Adsorption, 12, 147-154.
[74]. Schiewer, S. and Volesky, B., (1997). 'Biosorption of Heavy Metals by Low Cost Adsorbents', Technical Report No. 112.
[75]. Sekar, M.; Sakthi, V.; Rengaraj, S. (2004) Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *J. Colloid Interf. Sci*. *279*, 307–313.
[76]. Sharma, S., (2012). 'Bioremediation: features, strategies and applications'. *Asian Journal of Pharmacy and Life Science ISSN*, *2231*, pp.4423.
[77]. Sheng, P.X., Ting, Y.P., Chen, J.P., and Hong, L., (2004). 'Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: Characterization of biosorptive capacity and investigation of mechanisms'. *Journal of Colloid and Interface Science*, 275: 131-141
[78]. Soleimani, M., and Kaghazchi, T., (2008). 'Activated hard shell of apricot stones: a promising adsorbent in gold recovery.' *Chinese Journal of Chem*. Eng. **16** (1): 112 – 118.
[79]. Sudha, R., and Abraham, T.E., (2003). 'Studies on chromium (VI) adsorption and desorption using immobilized fungal biomass'. Biores. Tech. **87**: 17 – 26.
[80]. Taha, M., Kiat, C., Shaharun, M., and Raml, A., (2011). 'Removal of Ni(II), Zn(II) and Pb(II) ions from Single Metal Aqueous Solution using Activated Carbon Prepared from Rice Husk'. World Academy of Science, Engineering and Technology 60
[81]. Volesky, B., (2001). 'Detoxification of metal-bearing effluents: biosorption for the next century'. Hydrometallurgy, 59 (2-3), 203-216.
[82]. Wang S., Ang, H.M., and Tade, M.O., (2008). 'Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes.' Chemosphere, 72, 1621–1635.
[83]. Wang, S.; Gong, W.; Liu, X.; Yao, Y.; Gao, B.; Yue, Q. (2007) 'Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes'. *Sep. Purif. Technol*. *58*, 17–23.

[84]. Wilson, K., Yang H., Seo, C., and Marshall, W., (2006). 'Select metal adsorption by activated carbon made from peanut shells'. Bioresource Tech., 97; 2266–2270.
[85]. Tumin, NajuaDelaila, A., Luqman, C., Zawani, Z., and Suraya., A. (2008). 'Adsorption of Cupper from Aqueous Solution by ElaisGuineensis Kernel Activated Carbon'. *Journal of Engineering Science and Technology*. 3, No.2, 180-189.
[86]. Yadanaparthi, S., Graybill, D., and Wandruszka, R., (2009). 'Adsorbents for the removal of arsenic, cadmium, and lead from contaminated waters'. *J. of Hazard Mater*., 171, 1-15.
[87]. Yu, B., Zhang, Y., Shukla, A., Shukla, S., and Dorris, K.L., (2000). 'The removal of heavy metals from aqueous solution by sawdust adsorption- Removal of lead and comparison of its adsorption with copper'. *Journal of Hazardous Materials*, 84(1): 83-94.
[88]. Zhu B, Fan TX, Zhang D (2008) 'Adsorption of copper ions from aqueous solution by citric acid modified soybean straw'. *J Hazard Mater* 153(1–2):300–308