World Applied Sciences Journal 5 (Special Issue for Environment): 32-40, 2009
ISSN 1818-4952

Study of Various Parameters in the Biosorption of Heavy Metals on Activated Sludge

[1]*Addagalla Venkata AjayKumar,* [2]*Naif A. Darwish and* [1]*Nidal Hilal*

[1]Centre for Clean Water Technologies, Department of Chemical and Environmental Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK
[2]Department of Chemical Engineering, American University of Sharjah, United Arab Emirates

Abstract: Heavy metal pollution has become one of the most serious environmental problems today. Billions of gallons of wastewaters containing oils and particulates are produced each year by metallurgical plants, ships, petroleum and gas operations, industrial washing operations and other processes. Unfortunately, water systems have long tended to be one of the neglected areas of the process plant. However, this situation is changing rapidly as environmental legislation tightens. An investigation has been undertaken to determine the removal of heavy metals (Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) of high environmental priority due to their toxicity, from dilute aqueous solutions studied in the present work by biosorption using inexpensive biomaterials like activated sludge. Activated sludge is used widely in water treatment plants and is easily available. To understand the action of bio metals uptake, the essential role played by extra cellular polymeric substance (EPS) needs to be understood. Factors influencing the biosorption of the heavy metals are cleaning of the sludge, pH, initial metal ion concentration, weight of the adsorbent, mixing index, time and temperature. The adsorption parameters were determined using both Langmuir and Freundlich isotherm models and showed a better fitting of experimental data. The maximum sorption uptake of the studied metal ions by activated sludge showed the following order Cd^{2+}> Cu^{2+}>Ni^{2+}>Zn^{2+}.

Key words: Biosorption · Heavy metals · Activated sludge · Extracellular polymeric substances (EPS) · Heavy metals · Inductively Coupled Plasma optical emission spectroscopy (ICP- OES) · Isotherms

INTRODUCTION

Water is considered to be a vital and limited resource; population growth, industrial developments and other pressures faced by developing countries have lead to structured measures to ensure sustainable management of this important source [1]. Many heavy metals and their compounds have been found toxic, while some are also subjected to biomagnifications [2]. The presence of these heavy metals (HMs) in wastewaters will pose an important problem for the environment as well as for the treatment process, because the disposal of both the treated water and activated sludge contaminated with heavy metals give rise to detrimental impacts on the environment. Metal ions present in the waste water are characterized by their mobility in the liquid phase of the eco-system and by their toxicity to higher life forms even at low concentrations. In addition these metal ions are non-degradable and thus persistent, leading to both ecological and health problems [3]. Penalties for the discharge of untreated waste water pose large financial pressures on industrialists and treatment of waste water containing heavy metals is becoming most popular and financially sustainable [4]. The efficient use of water and minimization of waste water generation is an area of increased interest, both for industrialists and environmentalists.

In view of the toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals from wastewater both to decrease the amount of wastewater produced and to improve the quality of treated effluent, before it is released in to the environment. Conventional processes in the field of wastewater treatment can be divided into two main phases: (1) generation of suspended solids from colloidal and dissolved solids by physical, chemical and biological means in addition to the already existing suspended solids; (2) separation of suspended solids by chemical and mechanical methods including sedimentation,

Corresponding Author: Professor Nidal Hilal, Centre for Clean Water Technologies, Department of Chemical and Environmental Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

flotation and filtration [5]. A number of physico-chemical methods have been developed over the years to remove toxic metal ions from aqueous solution which includes chelation extraction, chemical coagulation, evaporation, adsorption, extraction, chemical precipitation, ion exchange, electrochemical processes, flotation, flocculation and membrane processes [1] However, the applications of such processes are sometimes restricted because of technical or economic constraints. Among these methods ion-exchange is a highly popular one and has been used widely in industrial wastewater treatment process. But the application of such a processe is often restricted because it can be very expensive [6]. Biological wastewater treatment systems are chiefly designed for the removal of organic matter by activated sludge microorganisms and the removal of heavy metals in these systems may be regarded as a side-benefit [2].

The search for new technologies, involving the removal of toxic metals from wastewaters has directed attention to biosorption, due to the metal-binding capacities of various biological materials [7]. The sequestering of metal ions by solid materials of biological origin is known under the general term "biosorption". It is a process that utilizes inexpensive dead biomass like algae, bacteria, fungi and yeast which can easily isolate toxic heavy metals and is particularly useful for the removal of contaminants from industrial effluents [8]. Further more, many researchers suggested that biomass from biological pollution control processes, especially activated sludge systems could be effective in removing heavy metals from polluted waters [9]. Activated sludge process, the most commonly used biological wastewater treatment method, is the most abundant source of microbial biomass [10]. Non-living biomass is generally used for biosorption studies and many investigations are going on the use and selection of activated sludge for the removal of heavy metals [11], which eliminates the problem of heavy metal toxicity [12]. Compared to conventional methods for removing toxic metals from industrial effluents, biosorption offers the advantages of low operating cost, minimization of the volume of chemical or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents and no nutrients are required. These advantages have served as the primary incentives for developing full-scale biosorption process to clean up heavy-metal pollution. The adsorption of heavy metals on the sludge surface is usually attributed to the formation of complexes between metals and the carboxyl, hydroxyl and phenolic surface functional groups of the extracellular polymeric substances (EPS).

MATERIALS AND METHODS

Activated sludge was collected as slurry from the Severn Trent Water wastewater treatment plant (Nottingham, United Kingdom). The slurry was filtered and washed several times with distilled water to remove heavy metal contaminants. The washing process was continued until the filtrate contains no metal ions. This can be confirmed by taking a random sample and analyzed by using ICP-OES. The slurry was dried at 60 °C for 12 h to avoid the alteration of functional groups, grounded to very fine sized particles.

Modification of Activated Sludge: This step was made in order to increase the activity of activated sludge as a bioadsorbent. 50 g of very fine size activated sludge particles were taken and suspended in 500 ml of 0.2 M NaOH solution in a beaker with a magnetic stirrer for 12 hours at room temperature. The suspension was centrifuged at 3000 rpm for 5 min. The resulting cake was washed with deionized water until the pH of the wash solution was 7. The cake was oven dried again at 60 °C for 12 h, grounded and screened to remove oversized and under sized particles [3].

Preparation of Metal Ion Solutions: The aqueous solutions of metal ions used in the present investigation were prepared by using analytical grade chemicals. Individual stock metal ion solutions of 1000ppm concentration of Cu^{2+} from $CuSO_4.5H_2O$, Ni^{2+} from $NiCl_2.6H_2O$, Cd^{2+} from $Cd(NO_3)_2$ and Zn^{2+} $ZnSO_4$ respectively were prepared. In the case of Cd, nitrate is used instead of sulphate to avoid metal precipitation, though the effect of the anion was negligible. These stock solutions were used to prepare dilute solutions of these ions by dilution with double distilled water. The stock solutions were acidified to $4< pH<6$ using concentrated HCl in order to prevent the formation of metal hydroxide and to return the metal ion to the dissolve state [13].

Sample Preparation for Analysis: Samples (40 ml) were transferred into a micro centrifuge tube and centrifuged at 3000 rpm for 5 minutes, to remove activated sludge or other suspended materials in the samples. Supernatant (10 ml) was transferred to 100 ml volumetric flask and acidified with 90 ml of 10% nitric acid (HNO_3) to get a standard solution of 100ml. These samples were stored in a freezer to terminate the reaction until measurement [14]. These samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES).

RESULTS AND DISCUSSION

Effect of pH: Literature reports say that activated sludge presents a negative net charge at surface level which facilitates its binding with positive metal cations [15]. The metal ions are in competition with the protons in the solution at low pH values for the biosorption on active sites biomass surface [16]. The influence of pH on the biosorption capacity for the different metals is shown in Fig. 1. At very low pH metal uptake was less and this is due to the fact that cell walls are closely associated to H_3O^+ and access of metal ions to cell walls would be restricted as a result of repulsive forces. Metal uptake increased with pH from 3-4 this is due to more ligands with negative charge being exposed with the subsequent increase in attraction sites to positively charged metal ions [17]. Beyond this point there is not much further increase in efficiency until pH 6. After pH 6 the efficiency of the biosorption process increases drastically due to the formation of metal hydroxides with their respective metal ions. This is mostly due to the metal precipitation as hydroxides which depend on the pH and ion concentration [3] but not due to the biosorption. It was initially thought that, at higher pH values, metals may accumulate inside the cells or cell walls by a mechanism known as combined sorption-micro precipitation [18]. From the previous research it is a known fact that the heavy metals are taken up from water predominantly in exchange for counter ions present in the biomass [19].

Effect of Adsorbent Mass: The effect of varying the adsorbent mass on the biosorption of various metal ions is shown in Fig. 2. It is clearly seen that the removal efficiency increases as the sludge mass increases. As the sludge mass increases the number of binding sites for the ions also increases [3]. After some point, sorption capacity was steady or decreased with biomass concentration due to a screen effect between cells, this produced a block of the cell active sites by an increase of biomass in the system [13]. Removal efficiency increases for Cadmium from 37.61 to 61.11%, for Copper 23.36 to 50.28%, for Nickel 12.04 to 27.54% and Zinc is 9.2 to 36.28% as the mass increases from 0.5g to 3g. The rate of increase gradually decreases with increasing adsorbent mass. This difference in adsorption shows that the adsorbent has much affinity towards cadmium than copper, nickel and zinc respectively.

Effect of Contact Time: Contact time plays an important role in the efficient removal of heavy metals using activated sludge. The influence of contact time on the biosorption capacity for different metal ions is shown in Fig. 3. Removal efficiency increases for Cadmium from 39.12 to 52.31%, for Copper 31.24 to 82.13%, for Nickel 13.13 to 27.36% and Zinc is 10.26 to 40.74% as the contact time increases from 15 to 240 min.The results clearly revealed that rate of adsorption is higher at the beginning and this is due to availability of a large number of active sites on the adsorbent. As these sites are exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [20]. Maximum removals were attained with in the first 45 min of stirring time. There must not be seemed to be much benefit after 180 min. Therefore the equilibrium time was set to be 4 hours.

Effect of Initial Metal Ion Concentration: The feasibility and efficiency of a biosorption process depends not only on the properties of the biosorbents, but also on the concentration of the metal ion solution. The initial metal concentration provides an important driving force to overcome all mass transfer resistances of the metal between aqueous and solid phase [11]. The effect of initial concentrations of heavy metal ions was studied and illustrated in Fig. 4. The efficiency values decreases from 56.06 to 40.48% for Cadmium, 51.78 to 18.03% for Copper, 20.88 to 11.35% for Nickel and 40.61 to 15.97% for Zinc respectively. There are many factors which can contribute to the adsorbate concentration effect. The first and most important one is that adsorption sites remain unsaturated during the adsorption reaction. The second cause is the aggregation/agglomeration of adsorbent particles at higher concentrations. Such aggregation leads to a decrease in the total surface area of the adsorbent particles available for adsorption and an increase in the diffusional path length [21]. We can clearly see that copper and zinc are affected more, as the figure shows that % cumulative removal of heavy metals is stable until some point and starts to decrease as the heavy metals concentration increases. This is due to the fact that at initial stages, the metal ions are fully adsorbed at the active sites present in the activated sludge and later no free sites are available to adsorb. More over these results clearly indicate that metal ion concentration must be in the range of 200-600 ppm.

Effect of Mixing Speed: The effect of the mixing speed on the removal efficiency of all the metal ions using NaOH treated sludge is shown in Fig. 5. The efficiency values increase from 20.11 to 44.10% for Cadmium, 22.33 to 35.6%

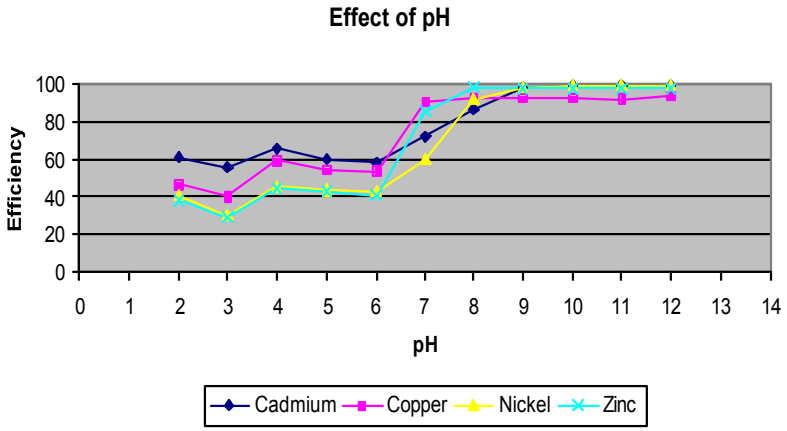


Fig. 1: Effect of pH on the adsorption of heavy metal ions onto activated sludge at Temperature= 20°C, mixing speed=600 rpm, solution volume=250 ml, contact time = 4 h and adsorbent mass=1g

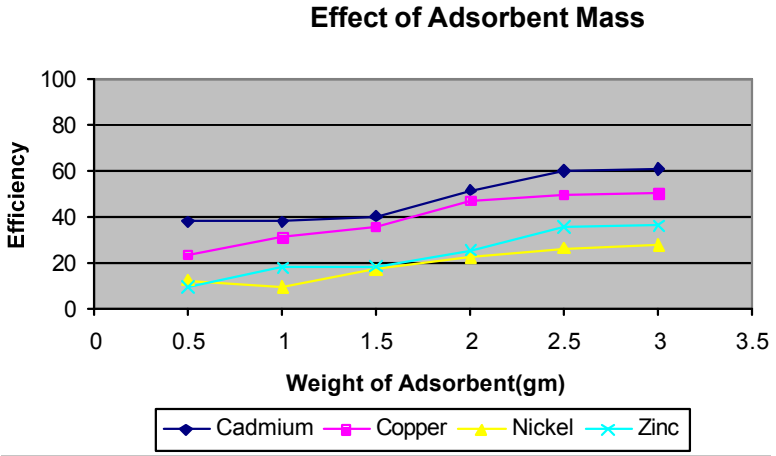


Fig. 2: Effect of Adsorbent mass on the adsorption of heavy metal ions onto activated sludge at Temperature=20°C, pH=4, mixing speed=600 rpm, solution volume=250 ml, contact time = 4 h

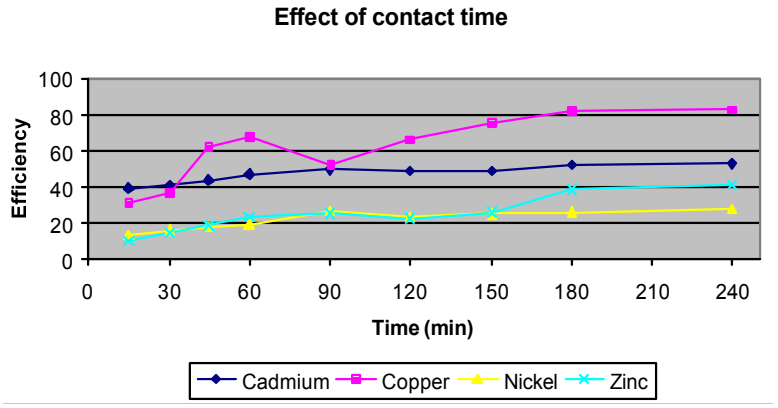


Fig. 3: Effect of contact time on the adsorption of heavy metal ions onto activated sludge at Temperature=20°C, pH=4, Mixing speed=600 rpm, Solution volume=250 ml, Adsorbent mass = 1g

for Copper, 5.63 to 18.56 for Nickel and 6.72 to 21.45% for Zinc respectively. It can be clearly seen that mixing speed increases the removal efficiency until it reaches a certain value and further increase is then of no benefit. The increase in efficiency is due to the increase in turbulence and as a consequence, the decrease in the external mass transfer resistance thickness around the adsorbent particles with increase in mixing speed [3]. At higher mixing speed the decrease in efficiency may be due to improper contact between the metal ions and the binding sites. More over these results clearly indicate that a mixing speed of 600-800 rpm is sufficient to obtain maximum removal efficiency by reducing the boundary layer thickness to a minimum value.

Effect of Temperature: Temperature plays a major role in the adsorption of heavy metals on activated sludge. Although, the magnitude of the heat effect for the biosorption process is one of the most important criteria for the efficient removal of heavy metals from the wastewater. Temperature changes will affect a number of factors which are important in heavy metal ion biosorption. Some of the factors include: (i) the stability of the metal ion species initially placed in solution; (ii) the stability of micro organism-metal complex depending on the biosorption sites; (iii) the effect of temperature on the micro organism cell wall configuration; (iv) the ionization of chemical moieties on the cell wall [22]. The temperature has two major effects on the adsorption process. One is that increasing the temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles because liquid viscosity decreases as temperature increases and the other one is that it effects the equilibrium capacity of the adsorbate depending on whether the process is exothermic and endothermic [3]. Figure 6. shows that the adsorption of heavy metals ions namely Cd^{2+},Cu^{2+}, Ni^{2+}, Zn^{2+}onto NaOH treated sludge at five different temperatures of 20°C, 25°C, 30°C, 35°C and 40°C. As the temperature increases, the adsorption capacity of cadmium, zinc and copper all decrease drastically where as with Nickel it has much less effect on temperature. As a whole, it is clearly seen that as the temperature increases the loading capacity for the same initial adsorbate concentration decreases. This means that the rate of desorption was more significant than the rate of adsorption, which implies that adsorption is an exothermic reaction, a well known scientific fact.

Sorption Isotherms: An adsorption isotherm is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium. It maps the distribution of absorbable solute between the liquid and solid phases at various equilibrium concentrations [23]. The Langmuir and Freundlich models are the most widely used models in the case of adsorption of metal ions by adsorbents even though the metal uptake may no exactly follow the monolayer adsorption mechanism. The Langmuir adsorption isotherm has been used traditionally to quantify and contrast the performance of different biosorbents. The Langmuir isotherm is based on the assumptions: (i) all sites are equivalent; (ii) adsorption results in a monomolecular layer of coverage; (iii) a molecule is adsorbed on a site independent of the neighbouring adsorbed molecules; (iv) coverage is independent of binding energy [24] and (v) constant temperature. The rate of attachment to the surface should be proportional to a driving force times an area. The driving force is the concentration in the fluid and the area is the amount of bare surface. The affinity between the biomass and the different metals was quantified by fitting the obtained sorption values to the Langmuir isotherm. In this case, the following form of the Langmuir equation is applied:

$$q = q_{\max}\left(\frac{bC_e}{1+bC_e}\right) \quad (1)$$

Where q_{max} is the maximum sorption uptake per unit mass of adsorbent in mg/g, C_e is the equilibrium concentration of heavy metal ions in mg/L and b is the Langmuir constant of sorption and desorption rate. q_{max} and b have been calculated from the intercept and slope of the plots. Figure 7 (a) shows plots of Langmuir isotherms for the bio adsorption of Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}respectively.

The Freundlich model is perhaps the most popular adsorption model for a single solute system and is an empirical relation equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium [25]. The linear form of the Freundlich equation is

$$x/m = Kc_e^{1/n} \quad (2)$$

Where x/m is concentration of metal ion adsorbed; C_e is equilibrium concentration of metal ion in solution; K and 1/n are empirical constants and have been calculated from

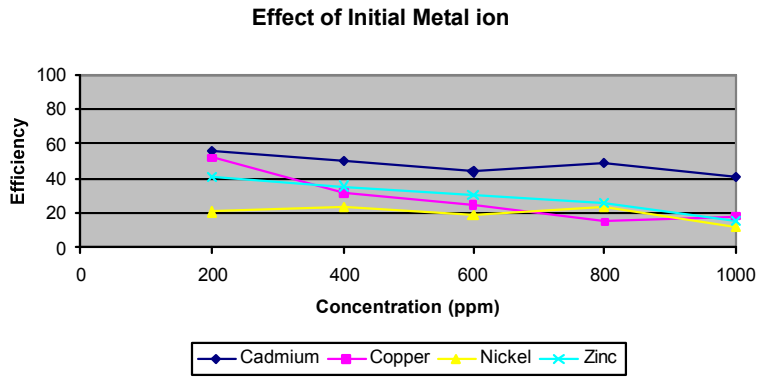


Fig. 4: Effect of initial metal ion concentration on the adsorption of heavy metal ions onto activated sludge at Temperature= 20°C, pH=4, Mixing speed=600 rpm, Solution volume=250 ml, Adsorbent mass = 1g, Contact time=4h

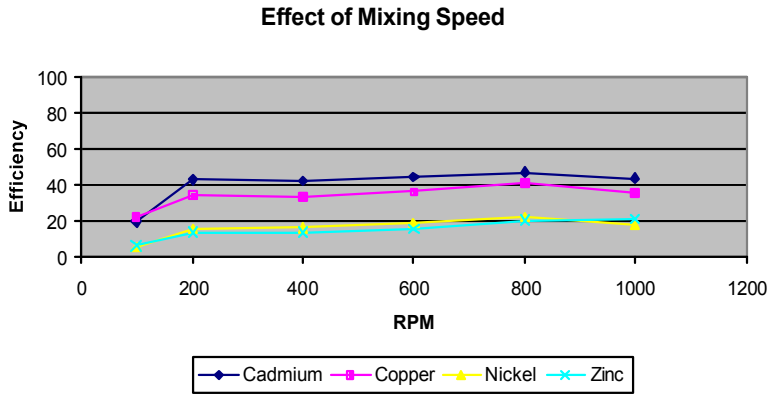


Fig. 5: Effect of mixing speed on the adsorption of heavy metal ions onto activated sludge at Temperature= 20°C, pH=4, Solution volume=250 ml, Adsorbent mass = 1g, Contact time=4h

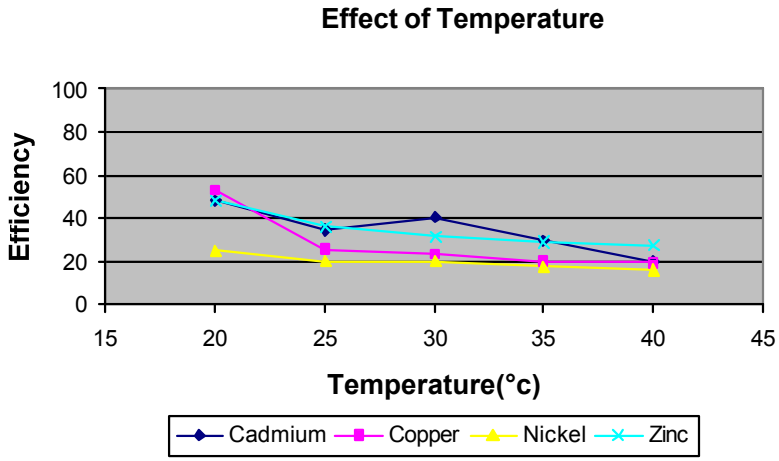
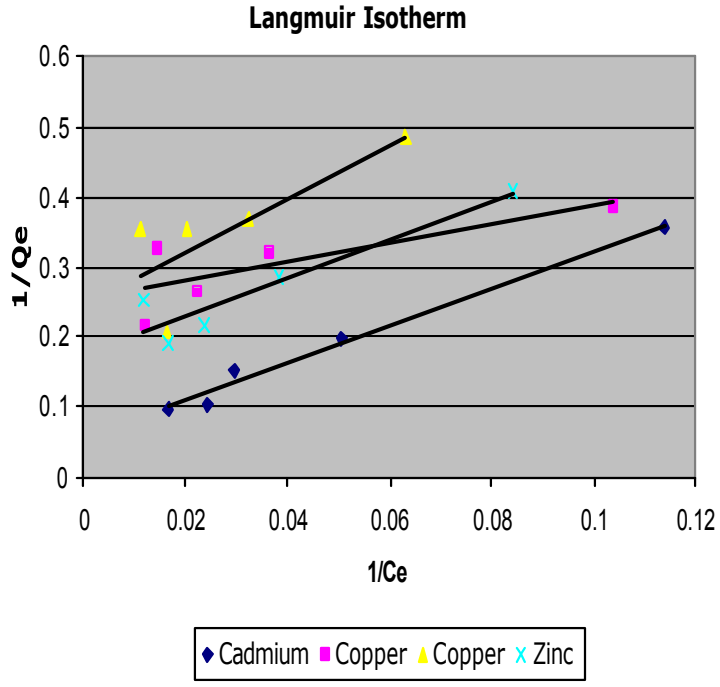
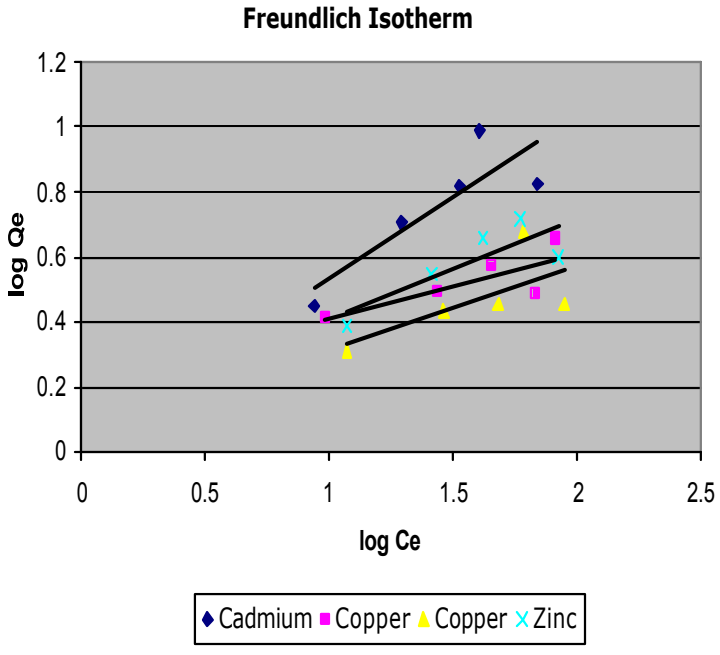


Fig. 6: Effect of temperature on the adsorption of heavy metal ions onto activated sludge at pH=4, Mixing speed=600 rpm, Solution volume=250 ml, Adsorbent mass = 1g, Contact time= 4h



(a)



(b)

Fig. 7(a): Isotherms for biosorption of heavy metals (Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) with activated sludge at 20°C. (a) Langmuir (b) Freundlcih

Table 1: Linear regression data for both Langmuir and Freundlich isotherms for the biosorption of the four metal ions

	Langmuir Isotherm			Freundlich Isotherm		
Metal ion	Q_{max}	B*(100)	R^2	K	N	R^2
Cadmium	18.08	2.06	0.98	1.07	1.98	0.73
Copper	3.94	19.24	0.62	1.63	5.03	0.62
Nickel	4.06	6.58	0.63	1.13	3.94	0.43
Zinc	5.71	6.42	0.88	1.22	3.15	0.69

intercept and slope of the plots. A larger value for 1/n indicates a larger change in effectiveness over different equilibrium concentrations. Also, when 1/n >1.0, the change in adsorbed concentration is greater than the change in the solute concentration [26].

The Freundlich equation is empirical equation with no basis in theory, which assumes an exponential variation in site energies and also assumed that surface adsorption is not the rate-limiting step [26]. Figure 7 (b) Shows plots of Freundlich isotherms for the bio adsorption of Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} respectively. The linear plot of $logQ_e$ against $logC_e$ shows that the adsorption of the four metal ions by activated sludge fits well to Freundlich model.

The constant values of all the four metal ions in addition to R^2 values for both isotherms are shown in Table 1.

CONCLUSIONS

A wide range of low-cost adsorbents have been studied worldwide for heavy metal removal and it is evident from this work, that inexpensive and locally available materials could be used. Based upon the experimental results carried out in this work, the following conclusions can be drawn:

- Activated sludge can easily be applied as a cheap adsorbent for heavy metal removal such as Cd^{2+}, Cu^{2+}, $Ni^{2+}$and Zn^{2+}.
- The adsorption capacity of the sludge was improved by treating the sludge with alkaline solutions like NaOH solution when compared to untreated sludge.
- pH had a clear influence on the sorption capacity of activated sludge for removal of heavy metals and it was found that the optimum value is equal to 4 at which the adsorption capacity of the sludge was found to be higher.
- Adsorbent concentration was a main variable in the biosorption process with activated sludge and in this case equilibrium reaches at 2.5g.
- Adsorption of metal ions from activated sludge is very rapid in the first 45 min and the equilibrium time is 180 min.
- Adsorption of metal ions from activated sludge is more efficient in the range of 200-600ppm.
- Mixing speed improves the adsorption capacity of the process and the optimised value is shown as 600 rpm.
- The maximum adsorption capacity of the sludge was found to decrease as temperature increases due to the fact that adsorption is an exothermic process.
- The data pertaining to the sorption dependence upon metal ion concentration fitted both Langmuir and Freundlich isotherms. The Langmuir isotherm is found to be in good agreement with experimental data.

REFERENCES

1. Dobson, R.S. and J.E. Burgess, 2007. Biological treatment of precious metal from refinery wastewater: A review. Minerals Eng., 20(6): 519-532.
2. Karvelas, M., A. Katsoyiannis and C. Samara, 2003. Occurance and fate of heavy metals in the wastewater treatment process. Chemosphere, 53: 1201-1210.
3. Al-Qodah, Z., 2006. Biosorption of heavy metal ions from aqueous solutions by activated sludge. Desalination, 196: 164-176.
4. Jooste, S., 2000. A model to estimate the total ecological risk in the management of water resources subject to multiple stressors. Water SA., 26(2): 159-166.
5. Ajaykumar, A.V., Saleh Al Hashimi and Nidal Hilal, 2008. Investigation of Kinetics and Mechanism Involved in the Biosorption of Heavy metals on Activated sludge. Intl. J. Green Energy (In Press).
6. Gulnaz, O., S. Sayagideger and E. Kusvuran,2005. Study of Cu (II) biosorption by dreid activated sludge: effect of physico-chemical environment and kinetics study. J. Hazazrdous Mat., B120: 193-200.

7. Chang, D., K. Fukushi and S. Ghosh, 1995. Stimulation of activated sludge cultures for enhanced heavy metal removal. Water Environ. Res., 34: 822-827.
8. Volesky, B. and Z.R. Holan, 1995. Biosorption of heavy metals. Biotechnol. Progress, 11: 235-250.
9. Yuncu, B., F.D. Sanin and U. Yetis, 2006. An investigation of heavy metal biosorption in relation to C/N ratio of activated sludge. J. Hazardous Materials, 137(2): 990-997.
10. Guibaud, G., N. Tixier, A. Bouju and M. Baudu, 2003. Relation between extracellular polymers' composition and its ability to complex Cd, Cu and Pb. chemosphere 52.
11. Aksu, Z. and D. Akpinar, 2000. Modelling of simultaneous biosorption of phenol and nickel (II) onto dried aerobic activated sludge. Separation and Purification Technology, 21(1-2): 87-99.
12. Saglam, N., R. Say, A. Denizli, S. Patir and M.Y. Arica, 1999. Biosorption of inorganic mercury and alkylmercury species on to Phanerochaete chrysosporium mycelium. Process Biochem., 34(6-7): 725-730.
13. Hammaini, A., F. González, A. Ballester, M.L. Blázquez and J.A. Muñoz, 2006. Biosorption of heavy metals by activated sludge and their desorption characteristics. J. Environ. Manage., 84(4): 419-426.
14. Kelly, C.J., N. Tumsaroj and C.A. Lajoie, 2004. Assessing wastewater metal toxicity with bacterial bioluminescence in a bench-scale wastewater treatment system. Water Res., 38(2): 423-431.
15. Bux, F. and H.C. Kasan, 1994. Comparison of selected methods for relative assessment of sulfate charge on waste sludge biomass. Water SA., 20: 73-76.
16. Sag, Y., A. Kaya and T. Kutsal, 1998. The simultaneous biosorption of Cu (II) and Zn on Rhizopus arrhizus: application of the adsorption models. Hydrometallurgy, 50: 297.
17. Setatnia, A., A. Madami, M.Z. Bakhti, L. Keryous, Y. Mansouri and R. Yous, 2004. Biosorption of Ni^{2+} from aqueous solution by a NaOH treated bacterial dead Streptomices rimosus biomass. Minerals Eng., 17: 903-911.
18. Beveridge, T.J., 1986. Metal-Refining and fossil Fuel Processing Industries. Biotechnol. Bioeng. Symposium 16, Wily Interscience.
19. David, K. and B. Volesky, 1998. Advances in the biosorption of heavy metals. Trends Biotechnol., 16(7): 291-300.
20. Dorris, K.L., B. Yu, Y. Zhang, A. Shukla and S.S. Shukla, 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption-removal of copper. J. Hazardous Materials, B80: 33-42.
21. Yasemin, B. and Z. Tez, 2007. Adsorption studies on ground shells of hazelnut and almond. J. Hazazrdous Materials, 149(1): 35-41.
22. Sag, Y. and T. Kutsal, 2000. Determination of the biosorption heats of heavy metal ions on Zoogloea and Rhizopus arrhizus. Biochem. Eng. J., 6: 145-151.
23. Rouquerol, F., J. Rouquerol and K. Sing, 1999. Adsorption by powders and porous solids: Principles, Methodology and Applications. New York, Academic Press, Inc.
24. Zeng, L., X. Li and J. Liu, 2004. Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. Water Res., 38: 1318-1326.
25. Freundlich (1928). Colloid and Capillary Chemistry. New York, E.P.Dutton and Co.
26. Mattson, J. and H. Mark, 1971. Activated Carbon. New York.