Biological Forum – An International Journal 11(1): 264-270(2019)

ISSN No. (Print): 0975-1130
ISSN No. (Online): 2249-3239

Study of Langmuir and Freundlich Adsorption Isotherms for Heavy Metal Removal from Soil using New Bidentate Schiff base

Nelofer Jamil[1], Noureen Khan[2], Rukhsana Jabeen[3] and Ziviqar Sheikh[4]
[1]Chemistry Department/Department of Environmental Sciences, SBKWU, Quetta.
[2]Department of Chemistry, SBKWU, Quetta, Pakistan.
[3]Department of Botany, SBKWU, Quetta, Pakistan.
[4]Department of Environmental Sciences, SBKWU, Quetta, Pakistan.

(Corresponding author: Nelofer Jamil, Noureen Khan; neloferirfan@hotmail.com, noureenhej@gmail.com)
(Received 08 February 2019, Accepted 18 April, 2019)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: Soil contamination by heavy metals is one of the most important environmental problem. The restoration and suitable protection of the soil contaminated by heavy metals is consequently required. There are many common techniques which had been used by researchers since long. In the present study newly synthesized Schiff base was used as a adsorbent for physicochemical treatment of soil. Schiff base ligand (SBL) was synthesized from aldehyde and dimer of o-toulidin and then characterized by spectroscopic techniques (UV-Vis, IR spectra and NMR spectroscopy). Results showed the Schiff base was active in adsorbing heavy metals in the sequence as Co>Cu>Zn from the soil. It had been observed that as Greater the concentration greater is the adsorption percentage and same trend was followed by isotherms models (Langmuir and Freundlich) that fits the obtained results as R^2 ranges between 95 to 100%.

Keywords: Soil, heavy metals, adsorption, isotherm models.

How to cite this article: Jamil, N., Khan, N., Jabeen, R. and Sheikh, Z. (2019). Study of Langmuir and Freundlich Adsorption Isotherms for Heavy Metal Removal from Soil using New Bidentate Schiff base. *Biological Forum – An International Journal*, **11**(1): 264-270.

INTRODUCTION

Globally, the most important environmental problem is contamination of heavy metals in soil (Nouri *et al.*, 2006; Doumett *et al.*, 2008). Heavy metal becomes part of the living system due to its ability of accumulation and causes toxicity. The biological systems with heavy metal toxicity may include plants, humans, animals and microorganisms (Nouri, 1980; D'amore *et al.*, 2005). As heavy metals are non-biodegradable and remains in the soil environment for a longer period, so they are referred as chemical toxins by researchers and scientists. In soils the availability of heavy metal considerably changes depending on their chemical structure. The restoration and suitable protection of the soil contaminated by heavy metals is consequently required (Nouri *et al.*, 2008; Nwachukwu *et al.*, 2010). Techniques which are usually used for remediation are dilution methods, excavation (ex-situ), onsite (in-situ) washing /flushing /leaching, chemical stabilization/ immobilization, electro-migration (electro-kinetics) and phytoremediation (GOC, 2003; Fawzy, 2008; Nouri *et al.*, 2009; Wuana *et al.*, 2010; Kord *et al.*, 2010). Adsorption is a physicochemical treatment and considered as highly efficient method to remove pollutants from the system. It is inexpensive and can easily be adapted (Bhattacharya *et al.*, 2006; Shahmohammadi-Kalalagh, 2011). In the last decadeadsorbent derived from biological, chemical and biological substrates can be used as the alternative medium to remediate and manage predictable heavy metal. Chelating resins which are regenerated from metal ions are one of the most promising methods in sorption processes which is different from ion exchange resins and activated carbon (Wan *et al.*, 2002; Varma *et al.*, 2004; Donia *et al.*, 2008). Magnetic resins are efficient in the removal of some metals from aqueous solutions (Atia *et al.*, 2005). Schiff bases have the ability to bind oxygen reversibly, transfer amino acid, can act as catalyst in the hydrogenation of olefins, have the ability to adsorb heavy metal, have good antimicrobial activity and photo chromic properties (Hassan *et al*, 2013). Schiff bases are an important class of ligands which are derived from an amino and carbonyl compound that coordinate to metal ions by means of azomethine nitrogen (Raman *et al.*, 2001).

The C=N linkage is vital for biological activity such as antibacterial, antifungal, anticancer, and diuretic activities (Hassan *et al.*, 2013) and also plays important and wide range of applications in industry, analytical chemistry and agriculture as agrochemicals (Gemi *et al.*, 2000; Gaur, 2003).

Batch technique had been used for the removal of heavy metals concentration under varied condition such as contact time, pH and temperature and experimental results were analyzed using four adsorption isotherm models; Freundlich, Langmuir, Temkin and Redlich-Peterson (Shahmohammadi-Kalalagh, 2011).

The adsorption of heavy metals (Cu, Ni, and Zn) were studied in numerous soils by using batch and column method. To find out the effect of temperature, contact time and adsorption isotherm on adsorption the batch method was used. The adsorption isotherm was elucidated by two models: Freundlich and Langmuir. The adsorption was investigated when wastewater was released into soil, the leaching effects of rain, and the repetitive adsorption rates after rainfall (Tsaneva *et al.*, 2017). There are no reports in the literature about the application of the Schiff base for pollution removal of soil, therefore this study aims to assess the adsorption capacity of the Schiff base to remediate soil containing metals and efficiency towards bacterial and fungal strains were also studied.

MATERIALS AND METHODS

A. Schiff Base Synthesis

Schiff's base was prepared by addition of o-tolidine (0.47mmole) and ethanol (25 ml) in 100 ml round bottom flask equipped with a stirrer bar. Stirring at room temperature about 20 min or until all the solid has dissolved. Solution of 2-nitrobenzaldehyde (15 mmole) in ethanol (25 ml) was added with continued stirring of the solution by adding few drops of acetic acid and refluxed for 5 hours. A light yellow coloured compound was isolated in a quantitative yield after filtration it through wattmann filter paper.

B. Soil

The investigated soil in the present study was sampled from 0-1.5m below the ground surface of dasht, suburb area of Balochistan. The red earth soil sample was uncontaminated with toxic heavy metals. Sample of soil was air dried and large particles and stones were removed by screening it through sieve number 02.To ensure uniformity, soil was thoroughly mixed and then stored in a plastic bag 20-30 ˚C (room temperature) for further experimental work (Bilgin & Tulun, 2016).

C. Soil Contamination

Three soil samples (each of 0.5kg) from the prepared soil were taken and were spiked with solutions containing $ZnCl_2$, $CuCl_2$ and $CoCl_2$ separately. The contaminated soil prepared in the laboratory had the good homogeneity with consistent heavy metal concentration and speciation, contamination process, soil composition, and contamination period. Hence the ambiguity in the extraction results from sample heterogeneity would minimize in this way. Soil samples were equilibrated for two weeks and then dried for two months in oven. The wet aging stage of two weeks helps each soil particle to get exposed to contamination. The soils were considered as homogenized and stored in a cooler at four degrees Celsius until they were tested.

The parameters which were determined erstwhile to the extraction experiments includes pH (solid: de-ironed water = 1: 2.5 W/V); water content; total zinc, copper and cobalt contents (after acid digestion). Soil samples were digested for determination of total concentration of Cu, Co and Zn before and after remediation. Soil digestion was carried out with 3:1 ratio of HCl and HNO_3 and digests were tested for Atomic absorption spectrometry (AAA-1400 Thermo). Chemical and physical tests on homogenized bulk soils were performed in triplicates to characterize the three spiked bulk soils and non-spiked soil (control). The pH was recorded with an aqueous soil suspension 1:2 (m/v) by using pH meter (Jenway 3510, Germany). Soil texture was measured in terms of percentage of silt, sand and clay (Tan, 2005). Total organic matter was measured by following walkey-black method (Bahadori and Tofighi, 2017).

D. Batch Adsorption Experiments

Batch experiments were conducted to remove heavy metals from contaminated soil by considering the effect of contact time and weight under constant temperature and pH. In the batch experiments, suspensions were prepared by taking 1 gram of air dried soil in beaker containing 25 ml of water and 0.1g of Schiff base and agitated on rotary shaker at 200±5rpm to prevent any sedimentation and room temperature was kept as (25 ± 2°C). Various concentrations of metal solutions (Zn, Cu and Co) were selected as 1, 10, 100, and 500 mgL^{-1} of distilled water. After agitation at 1-120 hours suspension were filtered for the determination of metal concentrations. Aliquots were then centrifuged at 6000 rpm for 10 minutes. The final metal concentration in the supernatant (or liquid phase) was measured on an AAS. The total initial metal concentration minus the metal concentration in the supernatant was taken as the metal adsorbed by Schiff base. The amount of Zn(II), Cu(II) and Co(II) adsorbed by Schiff base was determined by using a mass balance equation proposed by Shahmohammadi-Kalalagh (2011).

RESULTS AND DISCUSSION

A. Synthesis and characterization

After following the standard procedure a light yellow coloured compound was isolated in a good quantitative yield as 86%.

UV-VIS Spectral studies: Four bands were showed in DMSO medium. Band A and B at 242 nm and at 296nm wavelength respectively due to transition in aromatic ring ($\pi \rightarrow \pi^*$). Band C appeared at 370nm wavelength due to transition in between n- π^* orbital localization on central azomethine (-CH=N-) bond (Sinthuja *et al.*, 2018). Absorbance of NO_2 appeared as 450nm wavelength which is due to transition in between n- π^* orbital (Alves and Valderrama, 2019).

FTIR Studies: The ν (C=N) absorption band were observed at 1623.83 cm^{-1}(Sharma and Revanasiddappa, 2019). The stretching frequency observed at 1515.33 cm^{-1} and 1348 cm^{-1} shows the presence of N-O bond.

^{1}H NMR Studies: ^{1}H NMR (AV-400 MHz; DMSO): 8.82 (s, N=CH, 2H), 2.48 (s, Ar-CH_3, 6H), 7.63 (d, J = 1.6 Hz, ArAH, 2H), 7.59 (dd, ArAH, J = 8.4; J = 1.6 Hz, 2H), 7.18 7.63 (d, J = 8.4 Hz, ArAH, 2H), 8.08 7.63 (dd, ArBH, J = 8.0; J = 0.4 Hz, 2H), 7.79 (d, ArBH, J = 8.0 Hz, 2H), 8.21 (dd, ArBH, J = 7.6; J = 0.4 Hz, 2H), 7.75 (dd, ArAH, J = 7.6; J = 0.4 Hz, 2H).

FAB-MS (-ve) : [M-1] at *m/z* = 477.2

B. Soil batch experiment

Effect of Contact Time and Initial Metal Ion Concentration. The soil was light brown in appearance with 6.45 pH value, 7.9% moisture content and Organic carbon 1.39%. Contact time is a parameter of great importance as adsorption kinetics of adsorbate can be determined at initial concentration of adsorbate. Contact time effect on the adsorption of heavy metal ions by Schiff base was investigated for 120 hours. The kinetic were also studied for different initial concentrations 1, 10, 100, and 500mg/L for Zn(II), Co(II) and Cu(II) ions on Schiff base at roomtemperature and pH of 6 (Figs. 1, 2 and 3).

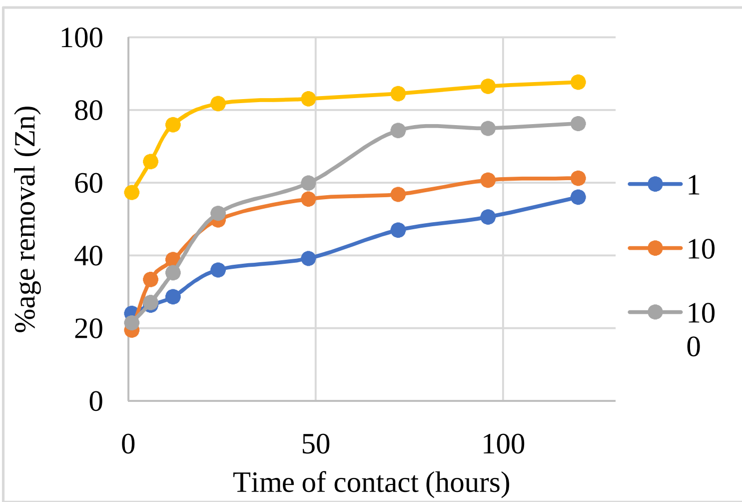


Fig. 1. Percentage removal of Zn(II) versus initial concentration and contact time.

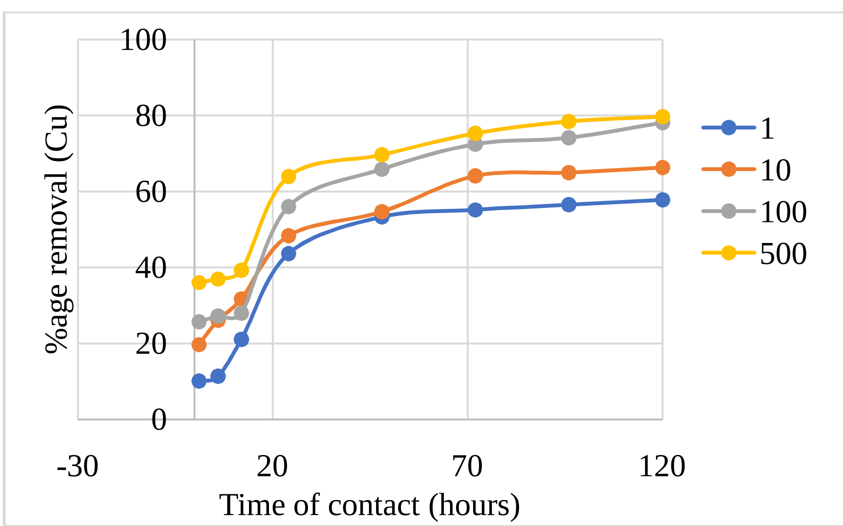


Fig. 2. Percentage removal of Cu(II) versus initial concentration and contact time.

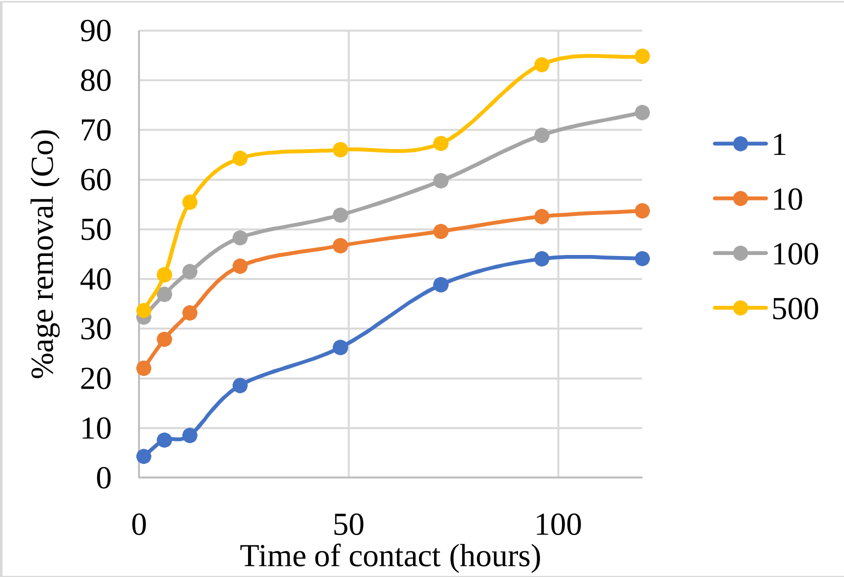
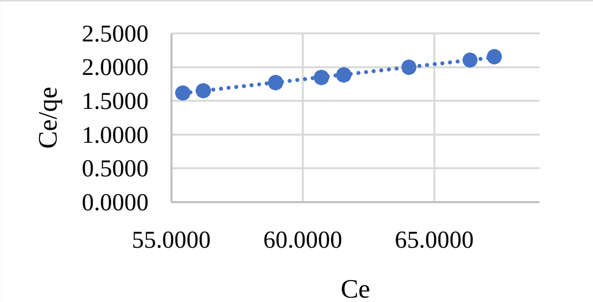


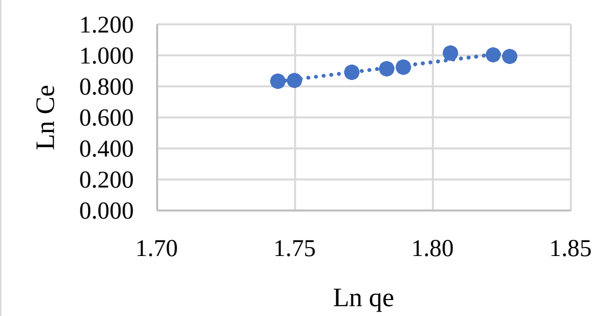
Fig. 3. Percentage removal of Co(II) versus initial concentration and contact time.

A slight difference can be noted in the adsorption trend of three metals. The adsorption in the beginning is zero and increases gradually with respect to contact time due to the large number of vacant sites between the adsorbate surface and adsorbate in suspension. With proceeding time there is reduction in the concentration due to the accumulation of metal concentrations on the vacant sites and hence the gradient of adsorption rate also decreases. The equilibrium time depends on the concentration of the metal present initially. The metal ions adsorbed by adsorbing material were in excess from aqueous solution also reported by Xue (2008) and Radi *et al.*, (2013). The initial concentration is directly proportional to the time interval. At initial concentration of 1 mg/L, the time of reaching equilibrium is about 24, 12 and 24 hours in case of Zn, Cu and Co respectively. While at concentration of 10 mg/L the time of equilibrium was 12, 24 and 24 correspondingly. In case of concentrations of about 100 and 500 mg/L, the time of reaching equilibrium was about 24, 48 and 48 hours for Zn, Cu and Co respectively. Therefore, the recommended running test time for adsorption of Zn, Cu and Co is 48 hours. It was also observed that with unit weight of SBL the initial metal ion adsorption also increased.

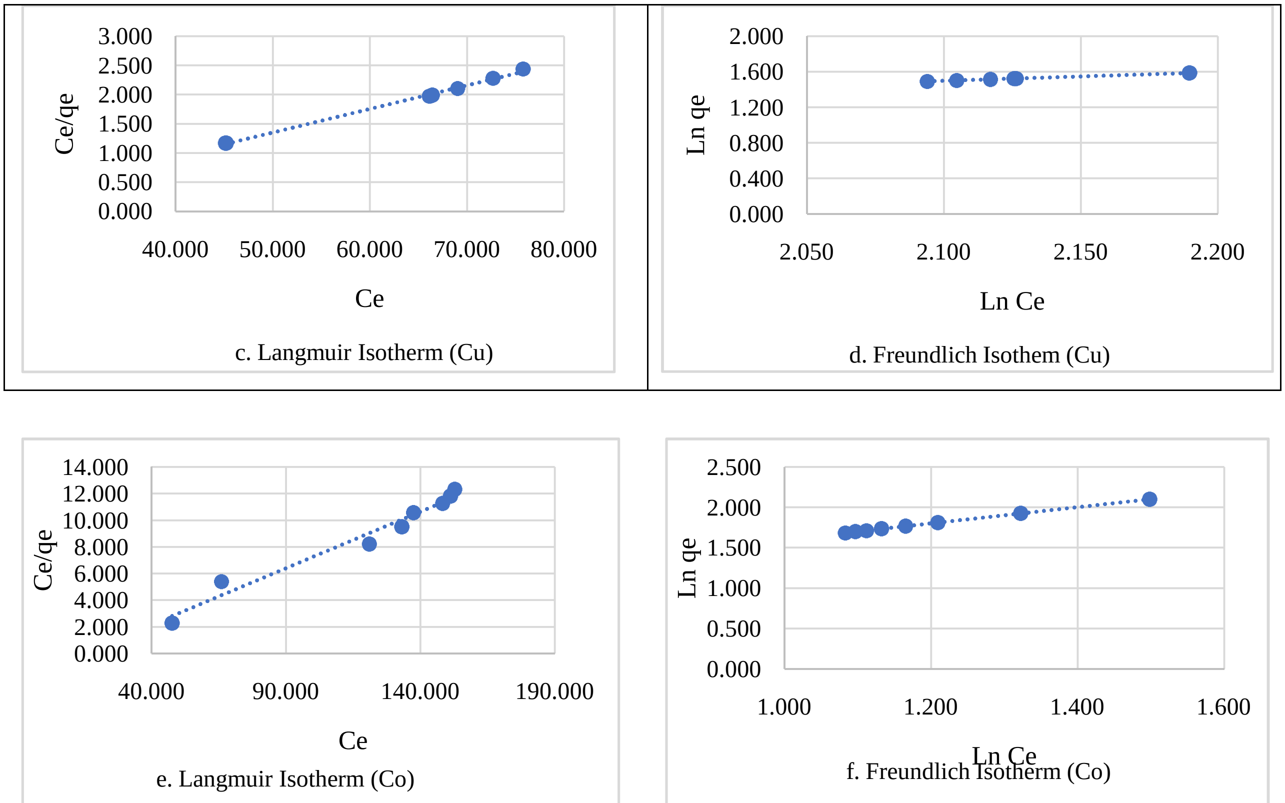
Adsorption Isotherms. The distribution of adsorbate from liquid/suspension to solid phases was described mathematically by models known as isotherms. The coverage type, solid surface heterogeneity/homogeneity and interaction possibility are set of assumptions for these models. Adsorption and desorption studies and drawing patterns haven been reported by many researchers (Ma *et al.* 1993; Barriuso *et al.* 1994; Gan *et al.* 1994; Seybold and Mersie 1996; Ebato and Yonebayashi, 2003). Data were analyzed using Langmuir and Freundlich isotherm expression in the present study.



a. Langmuir Isotherm (Zn)



b. Freundlich Isothem (Zn)



c. Langmuir Isotherm (Cu)

d. Freundlich Isothem (Cu)

e. Langmuir Isotherm (Co)

f. Freundlich Isotherm (Co)

Fig. 4. Langmuir and Freundlich isotherm sorption models of Zn(II), Cu(II) and Co(II) on SBL.

Freundlich isotherm. The constants of Zn(II), Cu(II) and C0(II) for Freundlich linear isotherm for adsorption SBL are shown in Table 1. The parameter 1/n is the intensity of adsorption of metal ions on the SBL. The Co (II) and Cu (II) showed the higher value of 1/n as 0.997 and 0.992 as compared to Zn(II) which was 0.451 which indicate that better sorption of Cu(II) and Co(II) than Zn(II). The reason may probably be their smaller ionic radius and also proved that SBL can be used to remove even the high concentration of these three metal ions.

Table 1: Parameters for Freundlich isotherm.

Metal ions	**1/n**	**Kf(L/g)**	**R^2**
Zn(II)	0.451	0.3353	0.9233
Cu(II)	0.992	0.5921	0.9995
Co(II)	0.997	0.6021	0.9996

Whereas, KF is the adsorption capacity of the adsorbent which was calculated by using the linear regression equation. The KF value of Co(II) (0.6021 L/g) is greater than that of Cu(II) (0.5921 L/g) and Zn(II) (0.3353 L/g), which confirmed that Co(II) has high adsorption capacity and tendency than two other metals due to hydrated ionic radii. The larger the hydrated radius, the smaller the affinity for adsorption onto the adsorbate.

Langmuir isotherm model. The Langmuir isotherm model was tested to estimate the adsorption capacity with respect to monolayer coverage or target active sites on SBL. The plots (Ce/qe) versus (Ce) for three metals were used to calculate linear isotherm parameters, qm, KL and the R2 values (coefficient of determinations). The qm which is the measure of sorption capacity showed the sorption capacity as Co (0.085mg/g)>Zn 0.0449mg/g)>Cu 0.0405mg/g). The energy of sorption KL was Co (1.2475L/g)>Zn (0.8761L/g)>Cu (0.6732L/g).

Table 2: Parameters for Langmuir isotherm.

Metal ions	**qm (mg/g)**	**KL (L/g)**	**R^2**
Zn(II)	0.0449	0.8761	0.9993
Cu(II)	0.0405	0.6732	0.9968
Co(II)	0.085	1.2475	0.9673

This preferential sorption behavior could be explained in terms of ionic radii of the metal ions. Smaller the ionic radii will occupy the active site more radii than the metals with larger radii.

The most essential part of Langmuir isotherm is the separation factor SF which is also termed as dimensionless constant. The SF value for the Zn(II), Cu(II) and Co(II) on SBL at lowest concentration of 1mg/L was Cu>Zn>Co while at highest concentration of 500 mg/L, it was observed as Co>Cu>Zn (Table 3).

Table 3: Separation factor SF for adsorption of Zn(II), Cu(II) and Co(II) on SBL.

Metal ions	Initial Concentration	
	1mg/L	500mg/L
Zn(II)	0.5330206	0.0019974
Cu(II)	0.5976572	0.0020024
Co(II)	0.4449388	0.0020633

The values of SF are less than unity which indicates the efficiency of SBL towards metals, among three metals Co(II) is better in binding with actives sites than Zn(II) and Cu(II) when higher in concentration. Similar studied were conducted and results reported by Shahmohammadi-Kalalagh (2011).

CONCLUSION

Present study was based on the estimation of feasibility of Schiff base ligand use as a efficient adsorbent for the removal of Zn(II), Cu(II) and Co(II) from soil suspension/solution.

The results were analyzed using two adsorption isotherm models naming as the Freundlich and Langmuir, isotherm models. By using the Langmuir isotherm, the adsorption capacities for Co(II), Zn(II) and Cu(II) are found as 8.5 mg/g, 4.5 mg/g and 4.0 mg/g respectively. The effectiveness of SBL with respect to adsorption of the three metals from soil system was Co(II) > Zn(II) > Cu(II) and this could be explained with reference to ionic radii of the metal ions. The SF (separation parameters) are found to be less than 1 which indicated the SBL is a good adsorbent for Zn, Cu, and Co metal ions. Adsorption studies in batch experiments, there was in increase in the uptake (mg/g) of Zn(II), Cu(II) and Co(II) ions with increase in contact time and concentration. Therefore, study concluded that removal of pollution caused by heavy metal pollution may be removed by using SBL, since it is easy to prepare and used in smaller quantity.

ACKNOWLEDGEMENT

The authors gratefully acknowledge HEC, Pakistan, for their financial support under their SRG program.

CONFLICT OF INTEREST

No potential conflict of interest was reported by the authors.

REFERENCES

Atia, A.A., Donia, A.M., & Elwakeel, K.Z. (2005). Selective separation of mercury (II) using a synthetic resin containing amine and mercaptan as chelating groups. *Reactive and Functional Polymers*, **65**(3): 267-275.

Alves, F.C., Coqueiro, A., Março, P.H., & Valderrama, P. (2019). Evaluation of olive oils from the mediterranean region by UV–Vis spectroscopy and independent component analysis. *Food chemistry*, **273**, 124-129.

Barriuso, E., Laird, D. A., Koskinen, W. C., & Dowdy, R. H. (1994). Atrazine desorption from smectites. *Soil Science Society of America Journal*, **58**(6): 1632-1638.

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.

Bilgin, M., & Tulun, S. (2016). Removal of heavy metals (Cu, Cd and Zn) from contaminated soils using EDTA and $FeCl_3$. *Global Nest Journal*, **18**: 98-107.

D'amore, J. J.; Al-abed, S. R.; Scheckel, K. G.; Ryan, J. A., (2005). Methods of speciation of metals in soils. *Journal of Environmental Quality*, **34**(5): 1707-1745.

Donia, A. M., Atia, A. A., & Elwakeel, K. Z. (2008). Selective separation of mercury (II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde. *Journal of hazardous materials*, **151**(2-3): 372-379.

Doumett, S., Lamperi, L., Checchini, L., Azzarello, E., Mugnai, S., Mancuso, S., Petruzzelli, G., Del Bubba, M., (2008). Heavy metal distribution between contaminated soil and Paulownia tomentosa, in a pilot-scale assisted phytoremediation study: Influence of different complexing agents. *Chemosphere*, **72**(10): 1481-1490.

Ebato, M., & Yonebayashi, K. (2003). Relationship between Freundlich isotherm Coefficients, log KF and 1/n for atrazine desorption from soils in Japan. *Soil Science and Plant Nutrition*, **49**(5): 677-683.

Elwakeel, K.Z., & Atia, A.A. (2014). Uptake of U (VI) from aqueous media by magnetic Schiff's base chitosan composite. *Journal of Cleaner Production*, **70**: 292-302.

Fawzy, E.M., (2008). Soil remediation using in-situ immobilization techniques. *Chemistry and Ecology*, **24**(2), 147-156.

Gan, J., Weimer, M. R., Koskinen, W. C., Buhler, D. D., Wyse, D. L., & Becker, R. L. (1994). Sorption and desorption of imazethapyr and 5-hydroxyimazethapyr in Minnesota soils. *Weed Science*, **42**(1), 92-97.

Gaur, S. (2003). Physico-chemical and biological properties of Mn(II), Co(II), Ni(II) and Cu(II) chelates of Schiff bases. *Asian Journal of Chemistry*, **15**(1): 250–254.

Gemi, M.J., Biles, C., Keiser, B.J., et al. (2000). Novel 1,5diphenylpyrazolenon nucleoside HIV-1 reverse transcriptase inhibitors with enhanced activity versus the delavirdine resistant P236L mutant: lead identification and SAR of 3- and 4-substituted derivatives. *Journal of Medicinal Chemistry,* **43**(5): 1034–1040.

GOC, (2003). Site Remediation Technologies: A Reference Manual, Contaminated Sites Working Group, Ontario, Chapter 6.

Hassan, R., Arida, H., Montasser, M., & Abdel Latif, N. (2013). Synthesis of new Schiff base from natural products for remediation of water pollution with heavy metals in industrial areas. *Journal of Chemistry*, **2013**: 1-10. http://dx.doi.org/10.1155/2013/240568.

Khan, Sara Shoaib, Tareen, H., Jabeen, U., Mengal, F., Masood, Z., Ahmed, S., Bibi, S., Riaz, M., Rizwan, S., Mandokhail, F., Irum, U. and Mengal, R. (2015). Quality assessment of drinking water from the different colonies of Quetta city, Pakistan according to WHO Standards. *Biological Forum - An International Journal*, **7**(2): 699-702.

Kord, B., Mataji, A., Babaie, S., (2010). Pine (*Pinus eldarica* Medw.) needles as indicator for heavy metals pollution. *International Journal of Environmental Science* and *Technology,* **7**(1): 79-84.

Ma, L., Southwick, L.M., Willis, G.H. and Selim, H.M. (1993). Hysteretic characteristics of atrazine by sharkey soils. *Weed Science,* **41**: 627-633.

Nouri, J., (1980). Heavy metals in sewage sludge, soils amended with sludge and their uptake by plants. Ph.D. dissertation, Westfield College, University of London.

Nouri, J., Mahvi, A.H., Babaei, A., Ahmadpour, E., (2006). Regional pattern distribution of groundwater fluoride in the Shush aquifer of Khuzestan County Iran. *Fluoride,* **39**(4): 321-325.

Nouri, J., Khorasani, N., Lorestani, B., Karami, M., Hassani, A.H., Yousefi, N. (2009). Accumulation of heavy metals in soil and uptake by plant species with phytoremediation potential. *Environmental Earth Sciences,* **59**(2): 315-323.

Nwachukwu, M. A.; Feng, H.; Alinnor, J., (2010). Assessment of heavy metal pollution in soil and their implications within and around mechanic villages. *International Journal of Environmental Science* and *Technology*, **7**(2): 347-358.

Radi, S., Tighadouini, S., Bacquet, M., Degoutin, S., Cazier, F., Zaghrioui, M., & Mabkhot, Y. N. (2013). Organically modified silica with pyrazole-3-carbaldehyde as a new sorbent for solid-liquid extraction of heavy metals. *Molecules*, **19**(1): 247-262.

Raman, N., Raja, Y.P., & Kulandaisamy, A. (2001). Synthesis and characterisation of Cu (II), Ni (II), Mn (II), Zn (II) and VO (II) Schiff base complexes derived fromo-phenylenediamine and acetoacetanilide. *Journal of Chemical Sciences*, **113**(3): 183-189.

Seybold C.A. and Mersie W. (1996). Adsorption and desorption of atrazine, deethylatrazine, deisopropylatrazllle, hydroxyatrazine, and metolachor III two soils from Virginia. T. *Environmental Quality,* **25**: 1185.

Shahmohammadi-Kalalagh, S. (2011). Isotherm and kinetic studies on adsorption of Pb, Zn and Cu by kaolinite. *Caspian Journal of Environmental Sciences*, **9**: 243-255.

Sharma, D., & Revanasiddappa, H. (2019). Synthesis, spectroscopic characterization, crystal structure and Hirshfeld surface analysis of Co (III), Ni (II) and VO (IV) metal complexes with a novel Schiff base ligand and their antimicrobial activities. *Current Chemistry Letters*, **8**: 39-52.

Sherene, T. (2010). Mobility and transport of heavy metals in polluted soil environment. In *Biological Forum—An International Journal*, **2**: 112-121.

Sinthuja, S. A., Shaji, Y. C., & Rose, G. L. (2018). Synthesis, Characterization and Evaluation of Biological Properties of Transition Metal Chelates with Schiff base Ligands Derived from Glutaraldehyde with L-Leucine. *IJSRST*, **4**: 587-582.

Tan, K.H. (2005). *Soil sampling, preparation, and analysis*. CRC press.

Tsaneva, D.K., Nikolova, M.I., Prokopov, T.V., Stoyanova, A.S., &Denev, P.P. (2017). Evaluation of Adsorption Capacity of Chitosan-Citral Schiff Base for Waste water Pre-Treatment in Dairy Industries. *Ecologia Balkanica*, **9**(1): 91-102.

Varma, A. J., Deshpande, S. V., & Kennedy, J. F. (2004). Metal complexation by chitosan and its derivatives: a review. *Carbohydrate Polymers*, **55**: 77-93.

Wan, L., Wang, Y., & Qian, S. (2002). Study on the adsorption properties of novel crown ether crosslinked chitosan for metal ions. *Journal of applied polymer science*, **84**: 29-34.

Wuana, R. A., Okieimen, F. E., & Imborvungu, J. A. (2010). Removal of heavy metals from a contaminated soil using organic chelating acids. *International Journal of Environmental Science & Technology*, **7**, 485-496.

Xue, X., & Li, F. (2008). Removal of Cu (II) from aqueous solution by adsorption onto functionalized SBA-16 mesoporous silica. *Microporous and Mesoporous Materials*, **116**: 116-122.