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Removal of heavy metals from wastewater by using dimethylglyoxime ligand

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Abstract: Oximes constituted an important ligand group of coordination chemistry, have amphoteric property and compose of azomethine (>C=N-) and (-OH) groups. The complexes of transition metals with oxime ligands have been extensively studied in recent years. In this study we investigate the removal of Pb^{2+}, Fe^{3+} and Zn^{2+} from wastewater using dimethylglyoxime (oxime) ligand. In these studies, dimethylglyoxime ligand formed complexes by reaction with high concentrations of iron, lead and zinc ions at physiological pH and room temperature. The obtained complexes are a water-soluble even in high concentration. The resulting complexes were analyzed by Fourier-transform infrared spectroscopy (FT-IR) and elemental analysis. The remaining metals were determined by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). According to ICP-MS results, concentrations of metals were dropped to 5 ppm for Pb, 4 ppm for Hg and 2.5 ppm for Fe from 50 ppm. The FT-IR spectrum showed that the peaks of ligand shifted and new peaks of metal-ligand formed after complexation. These results showed that Pb^{2+}, Fe^{3+} and Zn^{2+} ions in certain concentration known in waste water and formed a complexes with dimethylglyoxime ligand.

Keywords: Wastewater, Dimethylglyoxime, Ligand, Oxime.

Introduction

The oxime group (>C=N–OH), which may be considered to be derived from oxyimine, is amphoteric with slightly basic nitrogen and mildly acidic hydroxyl groups (Bradley et al., 2001). Oximes are easily obtainable compounds with the ability to form intermolecular hydrogen bonds, giving rise to very stable macrocyclic species and oximes group contain two possible coordination sites, the imine nitrogen and the hydroxyl oxygen atom (Arauju et al., 2015; Toma et al., 2013). Oximes have often been used as chelating ligands in the field of coordination chemistry and their metal complexes have been of great interest for many years. The biological importance of oximes and their complexes is very well known (Ponomareva et al., 1996; Kufelnicki et al., 2007). The complexes of transition metals with oxime ligands have been extensively studied in recent years (Karaböcek et al., 1999). Different oximes and their metal complexes have shown notable bioactivity as chelating therapeutics, as drugs, as inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxides (Singh et al., 2007; Trendafilova et al., 2005). Transition metal complexes with ligands containing oxime group have attracted much attention as they exhibit excellent coordination ability. Knowledge of their coordination towards metal atom, especially when more than one oxime group is present, will lead to better understanding of the structure, reactivity and stability of chelates (Hierso et al., 2001; Chang et al., 2010).

The dimethylglyoxime derivatives have received considerable attention from both of the chemical and biological scientists. Moreover, the dioximes are capable of coordinating through N, N or N, O sites of the oxime groups (Shaker, 2010). The aim of this work was to study the coordination of metal ions with dimethylglyoxime (oxime group) ligand which could give stable chelate complexes that may be used in wastewater applications. Because heavy metal pollution has become one of the

Table 1. The physical properties of the complex and ligand (M.P is melting point).

Compound	Colour	M.P.°C	%C		%H		%N	
			Calc.	Found	Calc.	Found	Calc.	Found
DMG	White	241	-	-	-	-	-	-
Complex 1	Brown	>300	37.25	37.12	6.56	6.29	14.46	14.22
Complex 2	Black	>300	35.75	34.93	4.91	5.13	20.52	21.05
Complex 3	White	>300	22.22	21.56	3.03	3.42	47.91	46.72

most serious environmental problems today (Fu et al., 2011). In recent times concerns have been raised about the contamination of the environment with heavy metals. The discharges of industrial wastes that contain heavy metals present a potential hazard to an aquatic environment (Gautam et al., 2014; Tang et al., 2014). Removing heavy metals is necessary because they are toxic substances with carcinogenic nature that should not to be discharged directly into the environment (Hunsom et al., 2005; Adhoum et al., 2004). Previously, dimethylgloxime ligand was used in many studies for different purposes in the complexation of metals, but in this study we investigate the remove the Pb^{2+}, Fe^{3+} and Zn^{2+} from wastewater by using dimethylglyoxime ligand for the first time.

Materials and Methods

In this study, Pb^{2+}, Fe^{3+} and Zn^{2+} complex of dimethylgloxime was synthesized. Dimethylglyoxime ligand formed complexes by reaction with high concentrations of iron, lead and zinc ions at physiological pH at room temperature. The obtained complexes were a water-soluble even in high concentration. The complexes were characterized by elemental analyses, Fourier-transform infrared spectroscopy (FT-IR) spectra and magnetic susceptibility. The remaining metals were determined by Inductively Coupled Plasma- Mass Spectrometer (ICP-MS). All chemicals were purchased from Merck. The infrared spectra of the ligand and complexes were recorded on a Thermo FT-IR spectrophotometer; Smart FITR diamond attenuated total reflection (ATR; 4000-400cm^{-1}) using KBr pellets. Elemental analyses (C, H, N and S) was carried out by Thermo Scientific Flash 2000. Magnetic susceptibility values were measured at room temperature by Guoy's method.

Synthesis of bis(dimethylglyoximato)zinc(II) Complex 1: An methanolic (5 ml) solution of dimethylglyoxime (0.116g, 1.0 mmol) was added to an aqueous solution(5 ml) of Zinc acetate dihydrate (0.219 g, 1.0 mmol), orange-red precipitate was formed. After constant stirring at room temperature for 30 min, the solution was filtered off, white precipitate was formed and the colorless solution is left for slow evaporation in the beaker and brown crystals were formed within 4 days.

Synthesis of bis(dimethylglyoximato) iron(III) Complex 2: An methanolic (5ml) solution of dimethylglyoxime (0. 712 g, 1.0 mmol) was added to an $FeCl_3.6H_2O$ (0.6760 g, 2.50 mmol), black-red precipitate was formed. After constant stirring at room temperature for 30 min, the solution was filtered off, black precipitate was formed.

Synthesis of bis(dimethylglyoximato) lead(II) Complex 3: An methanolic (5ml) solution of dimethylglyoxime (0. 815 g, 1.0 mmol) was added to an lead acetate trihydrate (9.48 g, 25 mmol) (0.9760 g, 2.50 mmol), black-red precipitate was formed. After constant stirring at room temperature for 30 min, the solution was filtered off, white precipitate was formed.

Results and Discussion

Synthesis complex was characterized by the techniques like CHN analysis and FT-IR. The remaining metals were determined by ICP-MS. According to ICP-MS results, concentrations of metals were dropped to 5 ppm for Pb, 4 ppm for Hg and 2.5 ppm for Fe from 50 ppm. The results from the C,H,N elemental analyses are in excellent agreement with the expected chemical formula (Table 1).

The infrared spectum of the complex recorded the band characteristics of the coordinated ligand. The assignment of some of the most characteristic FT-IR band of the complexes are shown in Table 2 and figures (Figures 1-4). All these frequencies confirmed the formation of complex. All these frequencies confirmed the formation of complex.

For many years, researchers have used different methods for removing heavy metals from different wastewaters that can be classified as electrochemical treatments (electrocoagulation, elector-floatation, and electrodeposition), physicochemical processes (chemical

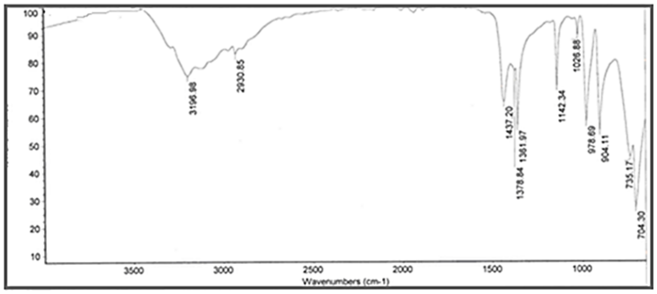

Figure 1. FT-IR spectra of the DMG ligand.

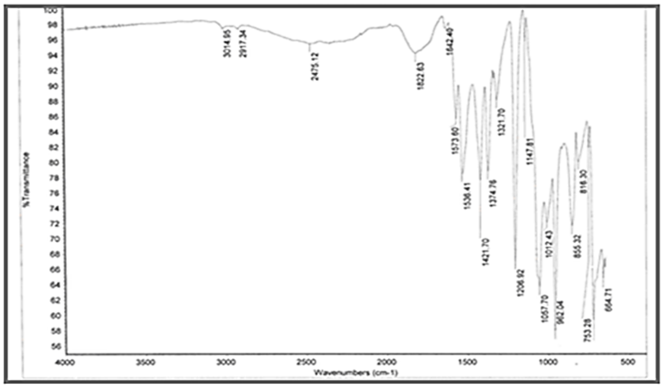

Figure 2. FT-IR spectra of the complex 1.

precipitation, Ion exchange), adsorption (activated carbon, carbon nanotubes, and wood sawdust adsorbents), or current methods (membrane filtration processes, photocatalysis processes, and nanotechnology) (Azami et al., 2017). Among these methods, adsorption is the most efficient as the other techniques have inherent limitations such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions and costly disposal (Fu et al., 2011) Membrane separation has been increasingly used recently for the treatment of inorganic effluent due to its convenient operation. There are different types of membrane filtration such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Kurniawan et al., 2006). Electrochemical treatments of wastewaters have not received great attention so far because of the need of large capital investments and expensive electricity supply.

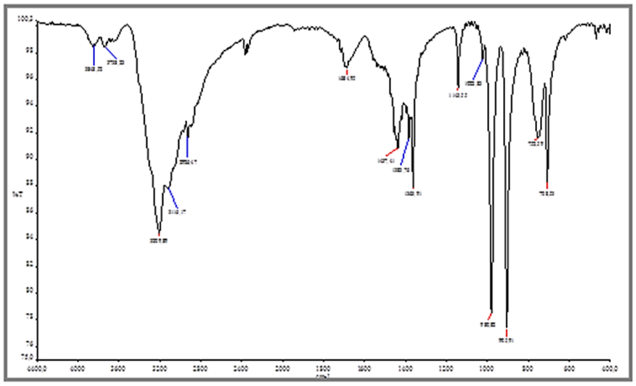

Figure 3. FT-IR spectra of the complex 2.

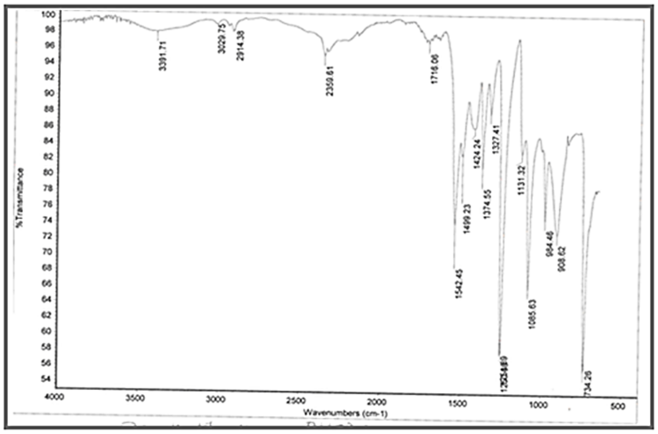

Figure 4. FT-IR spectra of the complex 3.

Electrotreatments such as electrodialysis has also contributed to environmental protection (Holt et al., 2005; Pedersen, 2003). Each method has its own heavy metal removal efficiencies and the specific parameters that affect the removing. In this study we have been studied for the development of cheaper and more effective technical for removal of heavy metals from industrial wastewater.

Conclusion

Wastewaters almost always contain heavy metal coming from any anthropogenic industries. Heavy metal ions are elements from the fourth period of the periodic table, mostly chromium (Cr), cobalt (Co), nickel (Ni), copper

Table 2. FT-IR spectra data of the DMG ligand and its complexes.

Compound	v(OH)	v(C=C)	v(N-O)	v(C=N-O)	v(C-H)	V(Fe-N)
DMG	3204	1490	1145	760	-	-
Complex 1	3210	1445	1138	745	-	-
Complex 2	-	-	1038	-	3210	745
Complex 3	3549	1550	1030	750	-	-

(Cu), zinc (Zn), arsenic (As, lead (Pb), mercury (Hg). Removing heavy metals is necessary because they are toxic substances with carcinogenic nature that should not to be discharged directly into the environment (Hunsom et al., 2005; Adhoum et al., 2004; Brusick, 1993). The contamination of wastewater with heavy metal ions are an environmental toxin problem throughout the whole world. The aim of this study was to investigate the removal of Pb^{2+}, Fe^{3+} and Zn^{2+} from wastewater using dimethylglyoxime ligand. In these studies, dimethylglyoxime ligand formed complexes by reaction with high concentrations of iron, lead and zinc ions at physiological pH at room temperature. The obtained complexes are a water-soluble even in high concentration. The resulting complexes were analyzed by FT-IR, and elemental analysis. The remaining metals were determined by ICP-MS. According to ICP-MS results, concentrations of metals were dropped to 5ppm for Pb, 4 ppm for Hg and 2.5 ppm for Fe from 50 ppm. The FT-IR spectrum showed that the peaks of ligand shifted and new peaks of metal-ligand formed after complexation. These results showed that Pb^{2+}, Fe^{3+} and Zn^{2+} ions in certain concentration known in waste water and formed a complexes with dimethylglyoxime ligand. Therefore, it is thought that dimethylglyoxime is suitable for this purpose in further researches.

References

Adhoum N., Monser L., Bellakhal N. 2004. Treatment of electroplating wastewater containing Cu^{2+}, Zn^{2+} and Cr(VI) by electrocoagulation. Journal of Hazardous Materials, 30: 112(3): 207-13.

Araujo C.R.M., Gonsalves AA. 2015. Araujo CRM., Gonsalves AA. 2015. Revista Virtual Quimica. Revista Virtual Quimica, 7(4): 1469-1495.

Azimi A., Azari A., Rezakazemi M., Ansarpour M. 2017. Removal of heavy metals from industrial wastewaters: a review. ChemBioEng Reviews, 4(1): 37-59.

Bradley D.C., Mehrotra R.C., Rothwell I.P., Sing A. 2001. Alkoxo and aryloxo derivatives of metals. Academic Press, London.

Brusick D. 1993. Genotoxicity of phenolic antioxidants. Toxicology and Industrial Health, 9(1-2): 223-30.

Chang E.L., Simmers C., Knight D.A. 2010. Cobalt complexes as antiviral and antibacterial agents. Pharmaceuticals, 3: 1711-1728.

Fu F., Wang Q. 2011. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management, 92(3): 407-418.

Gautam R.K., Mudhoo A., Lofrano G., Chattopadhyaya MC. 2014. Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. Journal of Environmental Chemical Engineering, 2(1): 239-59.

Gautam R.K., Mudhoo A., Lofrano G., Chattopadhyaya MC. 2014. Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. Journal of Environmental Chemical Engineering, 2(1): 239-59.

Hierso J.C., Bouwman E., Ellis D.D., Cabero M .P., Reedijk A., Spek A.L. 2001. Cobalt(II) aldoxime complexes stabilised by halide hydrogen bonding: crystal structures of [Co{HON C(H)(Me)}4X_2] (X=Cl or Br) and [Co{HON C(H)(Pr)}4Cl_2]. Journal of the Chemical Society, Dalton Trans, 197-201.

Holt PK., Barton GW., Mitchell CA. 2005. The future for electrocoagulation as a localised water treatment technology. Chemosphere, 59(3): 355-67.

Hunsom M., Pruksathorn K., Damronglerd S. 2005. Electrochemical treatment of heavy metals (Cu^{2+}, Cr^{6+}, Ni^{2+}) from industrial effluent and modeling of copper reduction. Water Research, 39: 610-616.

Karabocek N., Karabocek S. 1999. Polymeric copper(II) and nickel(II) complexes of a tetraoxime containing a binucleating macrocycle ligand. Transition Metal Chemistry, 24-84-8.

Kufelnicki A., Fritsky I.O., Sliva T.Y., Golovaneva I.F., Lampeka R.D. 2007. Stereoselective synthesis of cobalt(III) anionic complexes with chiral pyruvylaminoacid oximes and metal–ligand interactions in aqueous solution. Polyhedron, 26 (12): 2894-2900.

Kurniawan T.A., Chan G.Y.S., Lo W.H., Babel S. 2006. Physicochemical treatment techniques for wastewater laden with heavy metals. Chemical Engineering, 118: 83-98.

Ponomareva V.V., Dalley N.K., Xiaolan K., Gerasimchuk N.N., Domasevich K.V. 1996. Synthesis, spectra and crystal structures of complexes of ambidentate $C_6H_5C(O)C(NO)CN$. Journal of the Chemical Society, Dalton Trans., 2351-2359.

Shaker SA. 2010. Preparation and Spectral Properties of Mixed-Ligand Complexes of VO(IV), Ni(II), Zn(II), Pd(II), Cd(II) and Pb(II) with Dimethylglyoxime and N-Acetylglycine. E-Journal of Chemistry, 7 (1): 580-586.

Singh B.K., Jetley U.K., Sharma R.K., Garg B.S. 2007. Synthesis, characterization and biological activity of complexes of 2-hydroxy-3, 5-dimethylacetophenoneoxime (HDMAOX) with copper (II), cobalt (II), nickel (II) and palladium (II), Spectrochim Acta, 68: 63-73.

Tang W.W., Zeng G.M., Gong J.L. 2014. Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials: a review. Science of the Total

Environment, 468: 1014-27.

Toma H.E. 2013. Quimica de coordenaçao, organometalica e catalise. Coleçao de Química Conceitual. Editora Blucher, Sao Paulo.

Trendafilova G.N., Santiago L.R., Sodupe M. 2005. Coordination Properties of the Oxime Analogue of Glycine to Cu(II). The Journal of Physical Chemistry A, 109(25): 5668-567.