

## **Sorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> from Aqueous Solution Using a Blended Membrane of Immobilized Karkashi (Sesame Leaves) and Sodium Alginate**

**Ibrahim Maradona<sup>1</sup>, J. H. Kanus<sup>2\*</sup> and M. Suleman Stephen<sup>2</sup>**

<sup>1</sup>Department of Basic Sciences, College of Agriculture, Jalingo, Taraba State, Nigeria.

<sup>2</sup>Department of Chemistry, Nigerian Army University Biu, Borno State, Nigeria.

### **Authors' contributions**

*This work was carried out in collaboration among all authors. Author IM, JHK and MSS designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author IM, JHK and MSS managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.*

### **Article Information**

DOI: 10.9734/CSJI/2020/v29i130155

#### Editor(s):

(1) Dr. Akmal S. Gaballa, Professor, Faculty of Specific Education, Zagazig University, Zagazig, Egypt.

#### Reviewers:

(1) V. Madhavi, BVRIT Hyderabad College of Engineering for Women, India.

(2) Jayath P. Kirthisinghe, University of Peradeniya, Sri Lanka.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/54939>

**Original Research Article**

**Received 10 December 2019**

**Accepted 16 February 2020**

**Published 21 February 2020**

### **ABSTRACT**

Sorption techniques are widely used to remove heavy metal ions from large volume of aqueous solutions, this plays a vital role in controlling environmental pollution. Herein, the sorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> with blended membrane of sodium alginate (Na-Alg) and immobilized *karkashi* leaves (IKAL) from aqueous solution was investigated at optimum conditions for effectiveness. Sorption capacities of the membrane for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> were found to be 86.80, 40.60 and 39.55% respectively. The sorption behavior with respect to initial pH, ionic strength, temperature, contact time and initial metal ion concentration was investigated for optimum sorption conditions. Maximum sorption was found to occur at pH 3.0 for all the metal ions studied. Results showed that metallic ion uptake by the blended membrane declined with increase in ionic strength. This trend was also observed at an increased temperature of 50°C for Pb<sup>2+</sup>, Cu<sup>2+</sup> and 40°C for Zn<sup>2+</sup>. Increase in initial metal ion concentration led to increase in metal ion uptake. At the end of the chemical remediation, the blended membrane was found to be effective to some extent, with the reaction being exothermic.

\*Corresponding author: E-mail: [kanusjames@gmail.com](mailto:kanusjames@gmail.com);

**Keywords:** Karkashi; metallic ions; immobilized; sorption; blended membrane; remediation.

## 1. INTRODUCTION

Heavy metal pollution is an environmental problem that has harmful effect on both aquatic and terrestrial environment. This may be traceable to industrial activities such as mining, electroplating and manufacturing of paper and pesticides in form of mine tailings or effluents [1]. They have ability to complex with minerals to form inorganic ligands with variable solubility and acid–base potentials, thus, making their remediation from contaminated body a major concern [2,3].

Pollution arising from heavy metals poses serious health problems to both human beings and animals [4]. Toxicity generally results when an excessive concentration is presented to an organism over a prolonged period of time and when the metal is presented in an unusual biochemical form [5].

Recently, widespread concern over the cumulative toxicity and environmental impact of heavy metals such as  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$  and  $Zn^{2+}$  has led to extensive research into developing alternative technologies for the removal of these potential disease causing substances from contaminated water [1,5]. Various treatment techniques and processes have been developed and used to remove the pollutants from contaminated water. Among all the approaches proposed, sorption is one of the most popular methods and is currently considered as an effective, efficient and economic method for wastewater purification [6].

Combining the oxidation and reduction effect in sorption processes, some redox composite adsorbents have also been developed and applied in water purification recently [7,8].

The conventional methods developed for the removal of heavy metals from aqueous solutions are way too expensive to acquire. This poses great limitation for remediation of heavy metals contaminated water. Hence, there is a need for developing a cheaper method for effluent and waste water treatment [9]. Synthesizing effective and low cost adsorbent that can be recycled for removal of metallic contaminants from aqueous environment will be of high interest [10]. This is the reason why this work intends utilizing a blended membrane of immobilized *karkashi* leaves and sodium alginate to remove metallic

ions from waste water. Immobilization of plant cells facilitates continuous process and physical separation between the cell and reaction medium and also allows reuse of the cells [11].

To this end, this paper is aimed at synthesizing and discovering new novel method of using low cost adsorbent for the removal of metallic ions in aqueous solution as a means for treating a waste water.

## 2. MATERIALS AND METHODS

All reagents used are of analar grade, the equipment used were washed and dried at appropriate temperature.

### 2.1 Sampling Area and Sample Collection

Karkashi (Sesame leaves) which is the main material needed for making the sorbent, was randomly sampled across four farms in different locations at Mayo-Ranewo, a village situated in Ardo-Kola Local Government Area, Taraba state, Nigeria, with geographical coordinates of 8°49'0" North, 10°54'0" East.

Sodium Alginate, Sodium Chloride, Calcium Chloride, NaOH and HCl were obtained from chemical stores.

### 2.2 Sample Preparations

#### 2.2.1 Preparation of sodium alginate and calcium chloride

A solution of sodium alginate was prepared by weighing and dissolving 4.0 g of the chemical in 100 ml volumetric flask with distilled water. This was left overnight for complete dissolution to give 4% w/v. 0.12 M Calcium Chloride was also prepared with a distilled water [12].

#### 2.2.2 Preparation of *Karkashi* (Sesame) leaves

The *Karkashi* leaves were completely dried at ambient temperature. The dried leaves then pounded with a mortar and sieved with a 125 mm-20  $\mu$ m test sieve to produce a fine powder. This was transferred into a polythene bag for further use.

A solution of the powdered sample was made in two places; 4.0 g of the powder was placed in two different beakers labeled A and B.

100 ml of distilled water was added to each and stirred for 20 minutes.

The mixtures (A and B) were transferred into two different separating funnels and left for 12 hours for possible separation.

### 2.2.3 Immobilization of *Karkashi* leaves

25 ml of the viscous layer obtained above, was mixed with 25 ml of 4% sodium alginate and stirred vigorously in a 250 ml beaker. The mixture was then poured into another beaker containing 30 ml of 0.12 M calcium chloride solution. This was given retention time of 1 hour for complete precipitation.

The precipitate was filtered, allowed to dry at room temperature and transferred into a polythene bag.

The above process was repeated by mixing 4% solution of the sodium alginate and viscous layer at different ratio. The precipitates obtained were filtered, dried and kept in different polythene bags for further use [5,12]. Fig. 7 shows how the blended membrane looks.

## 2.3 Determination of Metal Ions in Solutions

The metal ions chosen for this study were  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ . 200 mg/L concentration of each of the metal ions was prepared from their salts using distilled water to represent a waste water sample.

50 ml each of the solutions prepared above, was transferred into 250 ml Erlenmeyer flask and 0.2 gm of the dried precipitate (a blend of immobilized *karkashi* and Na-Alg) was added and shaken vigorously for 2 hours with a mechanical shaker.

The mixture was filtered and residual metal ion concentration was determined using atomic absorption spectrophotometer (Model VGP-210) [13].

## 2.4 Optimization

### 2.4.1 Sorption capacity of immobilized *Karkashi*

For this study, 0.2 g of the sorbent was shaken with 50 ml of 200 mg/L metal ion solution at room temperature for 24 hours as reported by

Osemeahon, et al. [14]. The simulated waste water sample containing the blended membrane was filtered and the filtrate was analyzed for residual metal ion concentration using AAS model VGP-210.

### 2.4.2 Effect of pH on sorption capacity

The sorption characteristic of the blended membrane at different pH values (1 - 6) was investigated at 30°C [12,14]. 2.0M HCl and 2.0M NaOH were used to adjust the pH of the solutions to the required value. The residual metal ion concentrations were measured using AAS (Model VGP-210).

### 2.4.3 Effect of ionic strength on sorption capacity

Useful information regarding salts effect was obtained by measuring sorption capacity of the blended membrane in various concentrations of NaCl solutions. Different concentrations (0.00 - 0.34M) of NaCl were prepared and added to adjust the ionic strength of metal ion solutions and the equilibrium concentration of the residual metal ion was determined.

### 2.4.4 Effect of temperature on sorption capacity

The effect of temperature on the absorption capacity of the blended membrane was investigated. 0.2 g of the blend was shaken with 50 ml of the metal ion solution at different temperature ranging from 30° to 90°C. The mixture was filtered and analyzed for residual metal ion concentration.

## 2.5 Effect of Sorption Kinetics

To determine the kinetics of sorption, eight different aliquots consisting of 0.2 gm of the dried blend and 50ml of the metal ion solution were agitated and picked off the mechanical shaker, one after the other at a predetermined time interval ranging from 3 minutes-24 hours. The solution were filtered and analyzed for residual metal ion using AAS model VGP-210. [12,15].

## 2.6 Effect of Initial Metal Ion Concentration on Sorption Capacity

To investigate the effect of initial metal ion concentration on sorption capacity, a range of the metal ion concentration from 5 mg/L to 1000 mg/L was prepared. From each of the prepared

concentrations, 50 ml was transferred into a 250 ml Erlenmeyer flask and 0.2 gm of the blended membrane was added, shaken and taken out for filtration and analysis of residual metal ion concentration.

### 3. RESULTS AND DISCUSSION

The results have shown that the blended membrane of *karkashi* and sodium alginate is an efficient sorbent for the removal of heavy metal ions from aqueous solution.

The study has shown that factors such as pH, Ionic Strength, temperature, concentration and reaction time can affect the sorption capacity of the blended membrane. Sorption was found to be more effective at pH value of 3-6. This suggests that the environment to be treated must be slightly acidic [16].

Heavy metal polluted water treated with this method should be post-treated to improve on its portability for domestic, industrial and other uses.

Fig. 1 shows the equilibrium sorption for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  by immobilized *karkashi* leaves. It is clearly observed that this immobilized *karkashi* has the ability to take up significant quantity of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ . The values 86.80%, 40.60% and 39.55% respectively were obtained as sorption capacity from the present study and are comparable with those reported by several authors [17,14,5]. The high affinity for  $Pb^{2+}$  also agrees with earlier reports on similar work for heavy metal adsorption at acidic pH [18,19].

The differences noticed in the sorption capacity for the different metal ions can be explained in terms of differences in hydration free energy, the ability of the metal ion to form covalent bond with ligands, the metal polymeric cat ion with the membrane structure and the nature of the surfaces sites available [20].

The pH of the sorption media reflects the nature of the physiochemical interaction between the ions in solution and the nature of the sorption site [21].

Fig. 2 represents the effect of pH on the sorption of metal ions by the blended membrane. It can be observed that at the range of pH 3.0-6.0, more metal ions were absorbed. Low absorption was observed at pH values of 1-2. The figure shows that  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  have optimal pH values of 3.0 at which they can be extracted by the membrane used for the study.

The pH influences the equilibrium of metal ion uptake in aqueous solution by affecting the speciation of the metal ion(s) in solution, the concentration of the competing hydrogen ions as well as the chemistry of the active binding sites on the sorbent [22]. Increasing pH leads to precipitation as insoluble hydroxides or hydrated oxides, which lowers the availability of metal ions for sorption. On the other hand, a decrease in pH results in an increase in the hydrogen ion concentration and hence possible competition with the metal ions for the available binding site [23]. This is shown in Fig. 2.

The effect of temperature on the sorption capacity for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  by blended membrane is shown in Fig. 3. The sorption of the metal ions decreased with increase in temperature. Temperature of 40°C represents the optima temperature at which the blended membrane could be used for the removal of the metal ions in aqueous solution. This trend of result may be explained by the following factors:

- The sorption process may be physical adsorption. Physical adsorption is normally exothermic. Thus, the extent of adsorption generally increases with decreasing temperature [24].
- Inherent molecular structure which influenced the properties of the blended membrane prepared [25].
- Contraction of the immobilized *karkashi* leaves molecules with increase in temperature to give a more compacted form of blended membrane, which causes the pores to be narrower and some sorption sites to be hidden or inaccessible to the metal ions [21] and
- Dissolution of low molecular weight polymers and non-cross-linked polymers with increasing temperature [26].

The kinetics of sorption for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  on the blended membrane was studied (Fig. 4). Complete saturation was reached after 0.05 hour of contact for  $Pb^{2+}$  and  $Cu^{2+}$  while 1 hour was recorded for  $Zn^{2+}$ . The relative rapid uptake for  $Pb^{2+}$  and  $Cu^{2+}$  by the blended membrane could be explained by the porous structure of the functional groups [18]. This result is a positive development especially in terms of economy. The observed trend after maximum absorption by the blend may be due to inadequate drying of the *karkashi* leaves [13]. This is shown in Fig. 4.

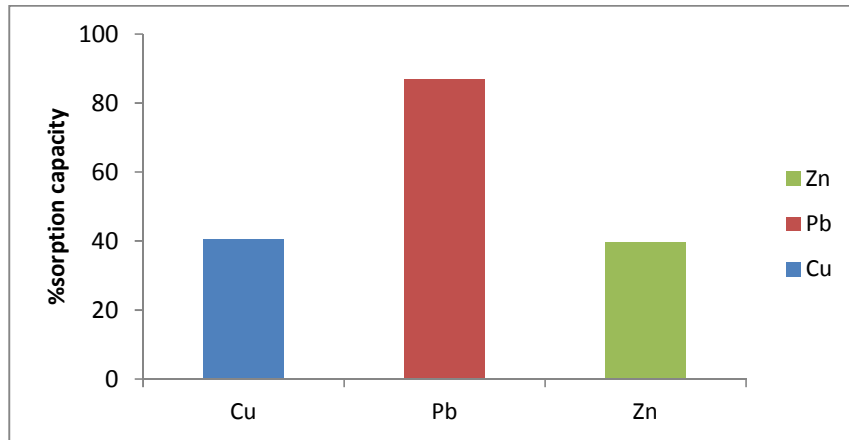


Fig. 1. Sorption capacity of the blended membrane

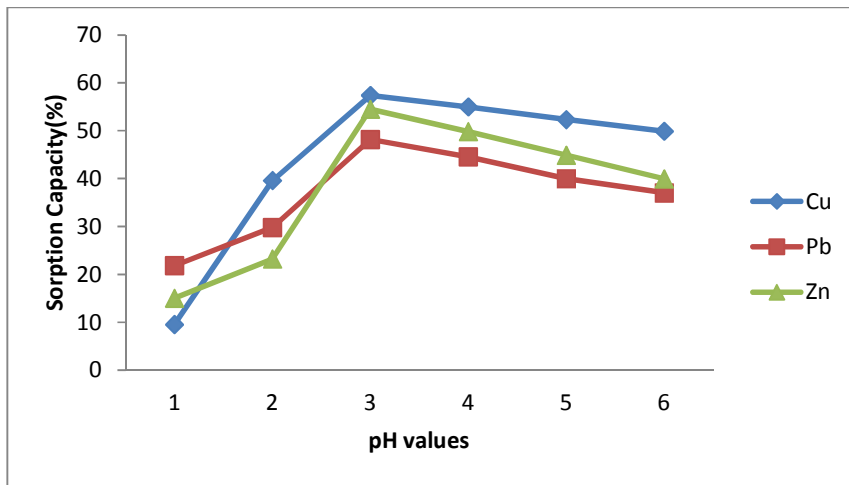


Fig. 2. Effect of pH on sorption capacity

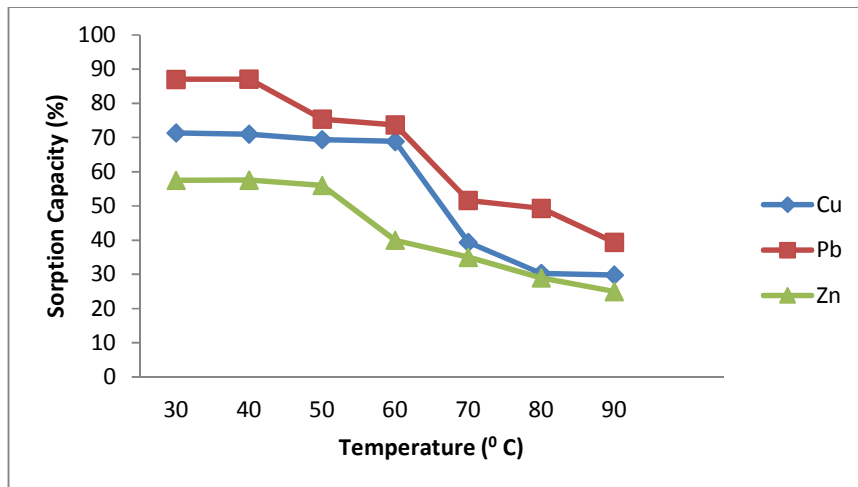


Fig. 3. Effect of temperature on sorption capacity

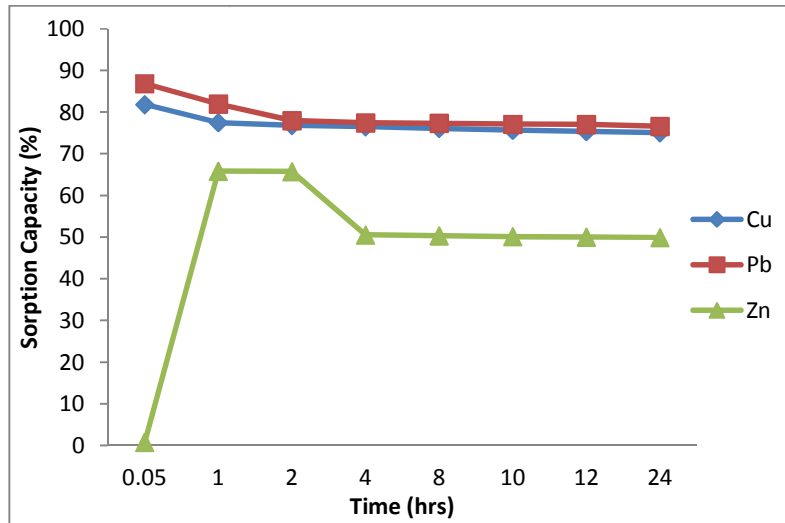


Fig. 4. Effect of kinetics on sorption capacity

Industrial wastewater or natural water often contains ions such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ; hence the influence of ionic strength on the sorption capacity of the blended membrane was investigated. Fig. 4 is a chart showing the effect of ionic strength on the blend performance. It was observed that the sorption capacity decreases with increasing ionic strength of the salt solution [5].

Studies found indifferent literatures suggested that the decrease in sorption capacity with increasing ionic strength is attributed to the reduction of the difference in ionic osmotic

pressure between the blend and the external solution. The difference in ionic osmotic pressure between the blend and the external solution decreases as the ionic strength of the external solution increases. Therefore, the sorption of metal ions decreases when the ionic strength in the solution increases [17]. From this study, the co-existence of metal ions in solution caused an interference with the performance of the *karkashi*/Na-Alg blended membrane [5]. A pretreatment of effluent to remove the interfering ions seems necessary for effective application of the blended membrane. The above discussion is illustrated in Fig. 5.

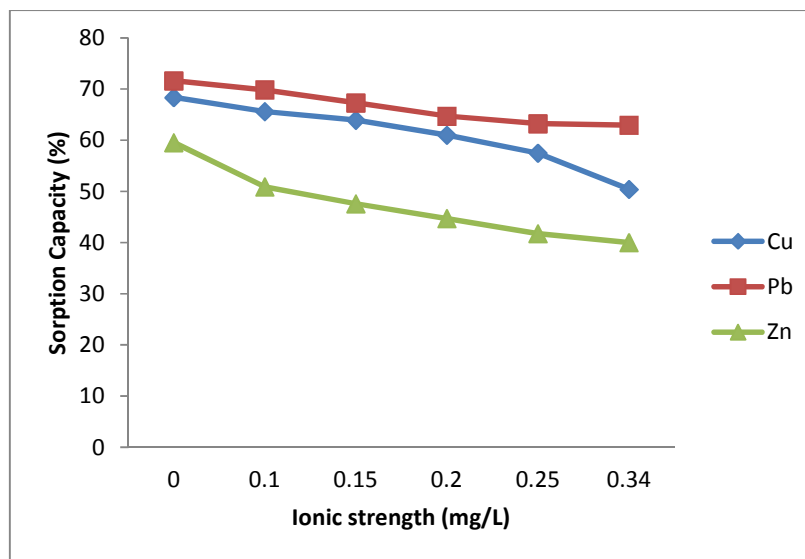


Fig. 5. Effect of ionic strength on sorption capacity

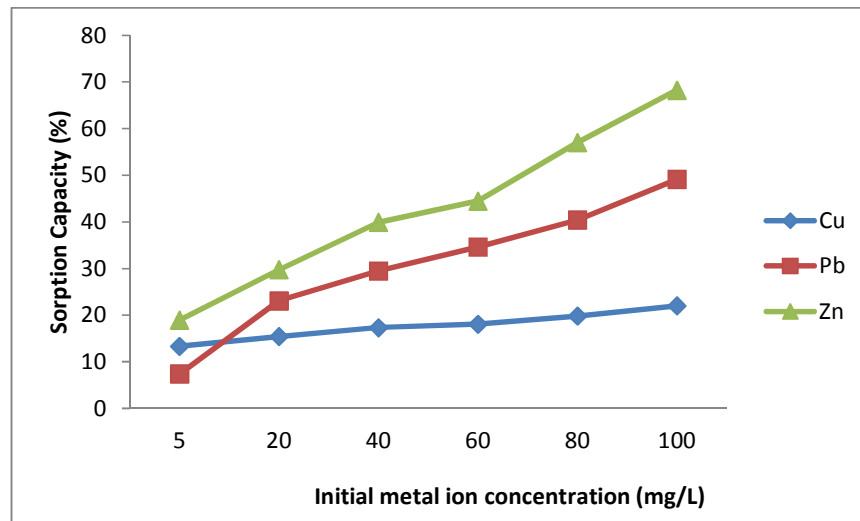


Fig. 6. Effect of metal ion concentration on sorption capacity



Fig. 7. Blended membrane of immobilized *Karkashi* and Sodium alginate

The effect of initial metal ion concentration on sorption capacity of the blended membrane is shown in Fig. 6. It was observed that the sorption of metal ions by the blend increase with increase in the initial metal ion concentration. This behavior can be explained in terms of increase in flux of the metal ion [22]. The flux of a cat ion varies in direct proportion with the metal ion concentration and hence, there should be an increase in flux with increase in metal ion concentration.

#### 4. CONCLUSION

The results obtained showed that *karkashi*/Na-Alg blend is efficient in removing heavy metal ions in aqueous solution. The study further showed that various factors such as pH, concentration, temperature, reaction time and ionic strength can affect the efficiency of the blended membrane.

The blend was found to be more effective in acidic medium than in basic medium, with an optimal pH value of 3.0. This suggest that the environment to be treated must be slightly acidic before treatment. The environment must also not be too acidic as  $H^+$  would compete with metal ions for available binding site.

The respective maximum sorption capacities of the blended membrane were 86.80, 40.60 and 39.55% for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ . The sorption equilibrium studies also showed that metal ion uptake by the blended membrane decreased with increasing ionic strength and after a temperature of 40°C while increases in initial metal ion concentration was found to be in direct proportion with metal ion uptake. The study has shown that the membrane is a potential material for the removal of these ions from wastewater.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

- Ifeoma Mary Ugwu, Onyedikachi Anthony Igbokwe. Sorption of heavy metals on clay minerals and oxides: A review; 2019. DOI:<http://dx.doi.org/10.5772/intechopen.80989>
- Lee JC, Pandey BD. Bio-processing of solid wastes and secondary resources for metal extraction - A review. Waste Management. 2012;32(1):3-18.
- Peligro FR, Pavlovic I, Rojas R, Barriga C. Removal of heavy metals from simulated wastewater by in situ formation of layered double hydroxides. Chemical Engineering Journal. 2016;306:1035-1040.
- Carolin CF, Kumar PS, Saravanan A, Joshiba GJ, Naushad M. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. Journal of Environmental Chemical Engineering. 2017;5(3):2782-2799.
- Osemeahon SA, Barminas TJ, Aliyu BA, Nkafamiya. Development of sodium alginate and konkoli gum-grafted-polyacrylamide blend membrane: Optimization of grafted conditions. African Journal of Pure and Applied Chemistry. 2008;2(3):032-036. ISSN 1996 - 0840 © 2008 Academic Journals Available:<http://www.academicjournals.org/AJPAC>
- Guixia Zhao, Xilin Wu, Xiaoli Tan, Xiangke Wang. Sorption of heavy metal ions from aqueous solutions: A review. The Open Colloid Science Journal. 2011;4:19-31. DOI: 191876-5300/11.
- Qu J. Research progress of novel adsorption processes in water purification: A review. J. Environ. Sci. 2008;20:1-13.
- Anyanwu EE. Review of solid adsorption solar refrigeration II: An overview of the principles and theory. Energy Convers. Manage. 2004;45:1279-1295.
- Zhao G, Wu X, Tan X, Wang X. Sorption of heavy metal ions from aqueous solutions: A review. The Open Colloid Science Journal. Bentham Open. 2011;4:19-31. DOI: 1876-5300/11
- De Gisi S, Lofrano G, Grassi M, Notarnicola M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. Sustainable Materials and Technologies. 2016;9:10-40.
- Fukushi K. Modelling sorption processes of trace elements by earth surface materials. Journal of Geography- Chigaku Zasshi. 2017;126(3):325-341.
- Osemeahon SA, Barminas JT, Nkafamiya II, Esenowo DI. Immobilization of konkoli (*Maesopsis eminii*) leaves with calcium alginate and study of its swelling behavior. International Research Journal of Plant Science. 2011;2(6):186-190. (ISSN: 2141-5447). Copyright © 2011 International Research Journals Available:<http://www.interestjournals.org/IRJPS>
- Barminas JT, Ajayi JO, Osemeahon SA. Development of sodium alginate and konkoli gum-grafted-polyacrylamine blend membrane. Science Forum J. Pure and Applied Sci. 2005;1:70-79.
- Osemeahon SA, Kolo AM, Opara IJ, Hamma'Adama MA. Bioremediation of wastewater with immobilized dargaza (*Grewia mollis*): Effect of some physical properties. IOSR Journal of Applied Chemistry (IOSR-JAC). 2016;9(10):37-43. e-ISSN: 2278-5736. Available:[www.iosrjournals.org](http://www.iosrjournals.org)
- Medjor WO, Egharevba F, Akpoveta VO, Ize-Iyamu OK, Jatto EO. Remediation of crude-oil contaminated groundwater by fenton-oxidative method. International Journal of Environmental Sciences. 2012;2(3):1398-1407.
- Shinggu DY, Kanus JH, Medjor WO. Remediation of surface water contaminated with domestic purpose kerosene using Fenton's oxidation. Chemical Science International Journal. 2019;28(1):1-9. Article no.CSIJ.50873 ISSN: 2456-706X (Past name: American Chemical Science Journal, Past ISSN: 2249-0205)
- Lee W, Lin G. Supersorbent polymeric materials viii: Swelling behavior of crosslinked poly (Sodium acrylateco-trimethyl methacryloyl oxyethyl ammonium iodide) in aqueous salt solution. J Appl. Polym Sci. 2000;79:1665-1674.
- Godjevargova T, Simeonova A, Dimov A. Absorption of lead and copper on modified



- polysaccharide bead. J Chem Technol. Biotechnol. 2001;79:283-288.
19. Rio S, Delebane A, Hequet V, Cloirec PL, Bundin J. Metallic ion removal from aqueous solution by fly ashes: Multicomponent studies. J. Chem Technol. Biotechnol. 2001;77:382-388.
  20. Cooper C, Jiang JQ, Ouki S. Preliminary evaluation of polymeric Fe and Al-modified clays as absorbents for heavy metal removal in water treatment. J. Chem Tech. Biotechnol. 2002;77:546-551.
  21. Mcox E, Pichugin AA, Appleton Q, application of a carbon sorbent for the removal of Cd and other heavy metal ion from aqueous solution. J. Chem. Technol. Biotechnol. 2002;77:429-436.
  22. Yen-Peng T, Sung G. Use of polyvinyl alcohol as a cell immobilization matrix for copper biosorption by yeast cells. J. Chem. Technol. Biotechnol. 2000;75:541-546.
  23. Toti SU, Mahadevappa Y, Kumaresh K, Soppimath S, Aminabhavi TM. Sorption, diffusion and pervaporation separation of water/acetic acid mixture through the blend membrane of sodium alginate and guar gum-grafted polyacrylamide. J. Appl. Polym. Sci. 2002;83:259-277.
  24. Ozer D, Ozer A, Dursun G Investigation of Zink (II) adsorption on cladophora crispate in a two-staged reactor. J. Chem. Technol. Biotechnol. 2002;75:410-416.
  25. Huang J, Richard CJ, Matsuura T, Roy C. Development of polyimide membrane for the separation of water vapour from organic compounds. J. Appl. Polym. Sci. 2002;85:139-152.
  26. Horike S, Matsuzawa S, Yanaura K. Preparation of crosslinked gels with maleate-denatured poly (Viny alcohol) and its application to drug release. J. Appl. Polym. Sci. 2002;85:139-152.

© 2020 Maradona et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*  
*The peer review history for this paper can be accessed here:*  
<http://www.sdiarticle4.com/review-history/54939>