EFFECT OF SOME PARAMETERS ON THE ADSORPTION OF HEAVY METALS USING QUININE FUNCTIONALIZED SILICA-COATED MAGNETIC GRAPHENE OXIDE (MgO@SiO₂-Q)

T. Abubakar* and B. K. Ibrahim

Science Laboratory Technology, Chemistry Unit,
Federal Polytechnic Kaura, Namoda, Zamfara State, Nigeria.

*Corresponding Author's Email: teejeekaura@gmail.com

ABSTRACT: *Heavy metal ions are demonstrated to have adverse effects on human health and animals which cause physical discomfort, life-threatening illness and irreversible damage to the vital body systems even at low concentrations. The conventional methods of treatment of heavy metal contamination include chemical precipitation, chemical oxidation, ion exchange etc. These methods are costly, energy-intensive and often associated with the generation of toxic byproducts. Thus, Adsorbent has been investigated as a cost-effective method for the removal of heavy metals from wastewater. In this study, $MGO@SiO_2Q$ nanocomposites functionalized with Quinine Q, was applied to remove Pb(II) and Ni(II)metal ions from contaminated water. For this purpose, the modified Hummers method was used for the synthesis of GO. The synthesized GO was magnetized and coated with 3-chloropropyltrimethoxysilane (CPTS) finally functionalized with Quinine. The results confirmed that GO synthesis processes, magnetization and functionalization were successfully performed. The result of $MGO@SiO_2$-Q adsorption performance revealed that the adsorbent increases as both pH and contact time increase for both Pb(II) and Ni(II) respectively. The results in this study indicate that $MGO@SiO_2$-Q can be considered a practical and effective adsorbent for heavy metal removal in contaminated water.*

KEYWORDS: Adsorbent, Graphene Oxide, heavy metals.

INTRODUCTION

Heavy metal ions are demonstrated to have adverse effects on human health and animals which cause physical discomfort, life-threatening illness and irreversible damage to the vital body systems (Madadrang *et al*., 2012) even at low concentrations. The metal ions bioaccumulate in the aquatic environment and tend to be biomagnified along the food chain. There are 20 metals which are persistent and cannot be degraded or destroyed, those metals include; Mercury (Hg), Lead (Pb), Cadmium (Cd), Chromium Cr (VI), Zinc (Zn), Arsenic (As), Nickel (Ni), etc., which are toxic from ecotoxicological. For instance, exposure to lead could have toxicological effects on the central nervous system, hematopoietic, renal, gastrointestinal, cardiovascular, and reproductive systems (Gupta *et al.,* 2011). Cadmium has been demonstrated to have detrimental effects on the kidneys, lungs, bones, heart and liver (Xi *et al.,* 2015). Furthermore, chronic ingestion of arsenic, mercury, chromium and nickel is linked to dermatological, cardiorenal, gastrointestinal, nervous, DNA and respiratory problems (Chen *et al.,* 2014; Cortés-Arriagada and Toro-labbé, 2016). Removal of heavy metals from wastewater has become an important environmental issue to be solved. At present time, several technologies have been established for the treatment of heavy metals in wastewater including chemical precipitation (Espinoza *et al.,* 2012), extraction, electrochemical treatment, membrane separation (Rajkumar and Palanivelu, 2004), bio-removal and catalytic reduction method (Fu and Wang, 2011; Wu *et al.,* 2010; Nanseu-Njiki*et al.,* 2009; Lertlapwasin*et al.,* 2010; Cai *et al.,* 2017). Adsorption is considered to be superior to other techniques due to its good selectivity, high capacity and efficiency, high surface area of adsorbent and low cost (Chen *et al.,* 2018; Demiral and Güngör, 2016). Graphene Oxide (GO) as a graphene derivative displays excellent physical-chemical adsorption ability due to the existence of a great quantity of hydroxyl, epoxy, carboxyl and oxygen polar groups on both sides of plane and edges (Lian *et al.,* 2010). Magnetic graphene oxide (MGO) is graphene oxide attached to magnetic iron oxide nanoparticles (MNPS) which have been attracted due to their super-paramagnetism, high field irreversibility and high saturation field (Kodama, 1999). Recently, the combination of GO with nanoparticles, forming a graphene-nanoparticle hybrid structure, has been shown to offer many additional unique physiochemical properties that are markedly advantageous for wastewater treatment. Magnetic iron oxide nanoparticle decorated GO has been synthesized by several groups for removing hazardous materials (Zhang *et al.,* 2013).

pH plays an important role in heavy metal adsorption as it affects surface charge, metal ion speciation, complexation, and binding sites of the sorbent (Ihsanullah *et al.,* 2016; Zhao *et al.,*2011). pH is considered to be the most important parameter that controls the adsorption of heavy metal ions (Ahmad *et al.,* 2016). Contact time is an important parameter which affects the adsorption of heavy metal ions. Generally, the removal of metal ions increases with an increase in contact time until the equilibrium is achieved. Once the equilibrium is reached, no significant further uptake of metal ions occurs (Zhang *et al.,* 2016).

MATERIAL AND METHODS

Materials

Graphite powder will be obtained from Fluka Chemicals (Shanghai, China). All other chemicals such as $FeCl_3$. $6H_2O$, $FeCl_2$. $4H_2O$, $KMnO_4$, KNO_3 (65%), H_2SO_4 (97%), 5 M HCl, H_2O_2 (30%), sodium acetate (NaAc), conc. HCl, NaOH and ammonia used in this work will be obtained from Shanghai Chemical Reagent Corporation (PR China). All the reagents were analytical grade.

Methods

Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized according to the modified Hummers's method (Hummers and Offeman, 1958). Graphite powdered was prepared with the aid of a pestle and mortar dried at 80 ^{0}C in an oven and then sieved through a 71 μm sieve. Two grams (2g) of the graphite powder was mixed in a solution containing 30 cm^3 of H_2SO_4 (97%) and 20 cm^3 of HNO_3 (65%). The mixture was then stirred for 24 h using a mechanical stirrer. Gradually, 3g of $KMnO_4$ was added in a small portion into the mixture and stirred at 50 ^{0}C for 20 h. The resulting mixture was allowed to cool and the oxidation was quenched by transferring the mixture over ice (300 g), followed by a step-wise addition of 3 cm^3 of H_2O_2 (30%) until the solution turned yellow. The resulting yellow solution was diluted with 800 cm^3 of distilled water and allowed to precipitate overnight at ambient temperature (Pirveysian and Ghiaci, 2018; Hassan *et al.,* 2020).

Synthesis of Magnetic Graphene oxide (MGO)

About 13.32 g $FeCl_3.6H_2O$, 19.88 g $FeCl_2.4H_2O$, 5 cm^3 of 5 M HCl, 40 cm^3milliQ water and 5 cm^3 of ethanol were mixed in a 100 cm^3 flask and refluxed at 40^{0}C until complete dissolution of the salts. Then, 2 g of GO was dispersed in 60 cm^3 of this solution and stirred for 2 h at room temperature. The resulting suspension was then filtered and quickly washed with milliQwater on the filter paper. The filtrate was immediately transferred into 40 cm^3 of 1M ammonia solution. The resulting mixture was stirred for 2 h at room temperature. The prepared MGO was collected by using an external magnet placed on the wall of the beaker thoroughly washed with Milli-Q water and dried under a vacuum (Hassan *et al.*, 2020).

Synthesis of Silica Coated MgO (MgO@SiO₂Cl)

Preparation of MGO@SiO$_2$Cl was achieved by dissolving 10 g of GO in 100 mL toluene. Then 10 mL of 3-chloropropyltrimethoxysilane (CPTS) was added to the mixture, reflux for 3h and conditioned under vacuum to obtain MGO@SiO$_2$Cl (Hassan *et al.,* 2020).

Synthesis of Quinine Functionalized Silica Coated Magnetic Graphene Oxide (MgO@SiO₂-Q)

To prepare MGO@SiO$_2$-Q, 10 g of MGO@SiO$_2$Cl was added to 25 mL quinine and the solution was refluxed for 3h. The product (MGO@SiO$_2$-Q) was separated from the solution with an external magnet, washed with n-hexane and conditioned under vacuum.

Instrumentation

The synthesized MGO@SiO$_2$-Q was characterized using Fourier transform infrared spectrometry (FTIR) and field emission-scanning electron microscopy (FESEM). A TM 400 FTIR spectrometer from PerkinElmer (Wal- tham, MA, USA) was used for FT-IR measurements using the KBr pellet technique. All spectra were recorded in transmission mode from 400 cm^{-1} to 4000 cm^{-1}

Optimization of Quinine Functionalized Silica Coated Magnetic Graphene Oxide (MGO@SiO$_2$-Q)

Adsorption experiments of heavy metal ions onto the synthesized MGO@SiO$_2$-Q adsorbent were conducted using the batch method. By varying the pH and contact time of the metal ions. The concentration of heavy metal ions would be determined using AAS. The adsorption capacity of the composite adsorbent would be calculated using Eq. 1

$$qe = \frac{(Co-Ce)V}{w}$$ ……………………………………………………………. (equation 1)

Where;

qe is the adsorption capacity after adsorption in (mg/g), V is the volume of solution (mL), w is the mass of adsorbent (g), Co is the initial concentration of metal ion before adsorption (mg/L) and Ce (mg/L) final concentration of the metal ions after adsorption.

The percentage removal (% R) of the metal ions will be calculated using Eq 2.

$$(\% \ R) = \frac{(Co-Ce)}{Co} x100$$……………………………………………………. (equation 2)

Where;

Co is the initial concentration of the metal ions (mg/L) and Ce is the final concentration of the metal ions (mg/L) (residual concentration in aqueous sample).

The effective parameters such as solution pH, contact time, adsorbent dosage and concentration effect on the adsorption of heavy metals onto MGO@SiO$_2$-Q were studied.

pH

Different studies have shown that pH can play an important role in the removal of heavy metals in aqueous solution. To study the effect of pH, another parameter was kept constant while the pH level was varied from 1-6. The pH of the solution was adjusted carefully by the addition of 0.1ml HCl/NaOH solution using a pH meter until the best pH was established. The concentration of heavy metal ions in solutions at each pH level was measured before and after adsorption using AAS. The percentage removal at each pH was calculated using Eq. (2) (Pirveysian and Ghiaci, 2018; Hassan *et al.,* 2020).

CONTACT TIME

It is clear that the adsorption experiment is time-dependent. Therefore, to study the effect of contact time, another parameter was kept constant while the contact time was varied from 15-35 min. To achieve this a fixed amount of the adsorbent (MGO@SiO$_2$-Q) was placed in several conical flasks containing the same amount of effluent and the mixtures were shaken within the range of 15–35 min contact time. The concentration of metal ions in solutions at different intervals was analysed before and after adsorption using AAS to establish the optimum adsorption time. The percentage removal was calculated using Eq. (2) (Pirveysian and Ghiaci, 2018; Hassan *et al.,* 2020).

RESULT AND DISCUSSION

Characterisation

FTIR spectra were used to confirm the formation of oxidation and grafting functionalized groups on GO. The FTIR spectrum of GO is compared with MGO, MGO@SiO$_2$Cl and MGO@SiO$_2$-Q as shown in Fig 4.1. GO IR peak (**Fig. 1.1a**) appearing at 3300 cm^{-1} assigned to O-H stretching vibrations (Qin *et al.,* 2014). The IR spectra of GO, as the starting material shows similarity with the IR spectra of MGO (**Fig. 1.1b**), but the appearance of IR peak at 601 cm^{-1} assigned to Fe-O bending vibrations indicates magnetic nanoparticles (Fe$_3$O$_4$) on MGO (Cao *et al.,* 2015). However, the appearance of IR peaks at 1100 cm^{-1} (Si-O stretching) in (**Fig. 1.1c**), suggested successful grafting of SiO$_2$Cl onto MGO, thus forming MGOSiO$_2$Cl. Furthermore, other new peaks appeared at 1600 cm^{-1}(N-H, bending vibrations) (Kamboh and Yilmaz, 2013; Ahmad *et al.,* 2017; Gode and Pehlivan, 2007), 2300 cm^{-1} and 2700 cm^{-1}(C=N and O-H) in (**Fig. 1.1d**) after the grafting quinine onto MGOSiO$_2$Cl (Gubbuk, 2011; Radi *et al.,* 2019), which suggested successful synthesis of the adsorbent (MGO@SiO$_2$-Q).
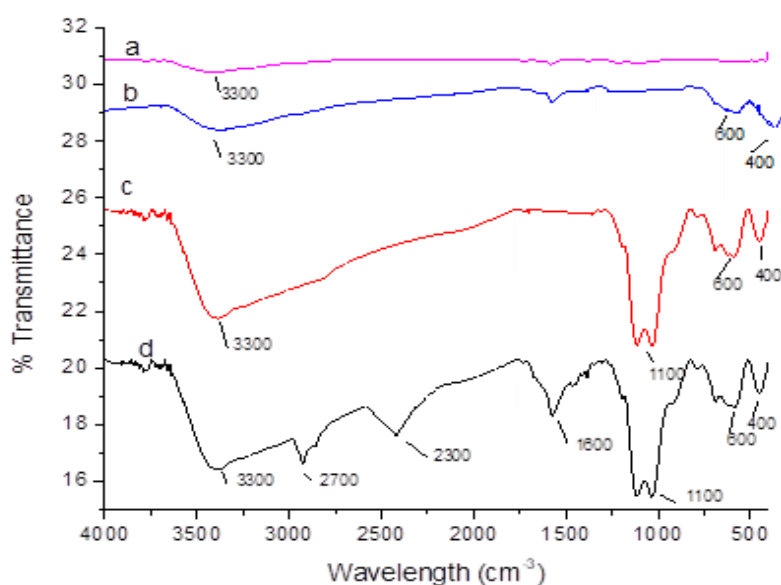

Fig 1: FTIR spectra of (a) GO (b) MGO (c) MGO@SiO$_2$Cl (d) MGO@SiO$_2$-Q.

FESEM images for the morphologies of GO, MGO, MGO@SiO$_2$Cl and MGO@SiO$_2$-Q are shown in **Fig. 2** Open GO sheet layers were observed in (**Fig. 2a**), while in (**Fig. 2b**), Fe$_3$O$_4$ nanoparticles slightly filled and covered the GO sheets and in between GO layers. In (**Fig. 2c**), the MGO is seen coated with gel-like material; presumably, SiO$_2$Cl, while (**Fig. 2d**) showed a different morphology compared to **Fig. 2c**, with breakage and small deposits of materials presumably quinine on the surface of MGO@SiO$_2$Cl, suggesting successful synthesis of MGO@SiO$_2$-Q
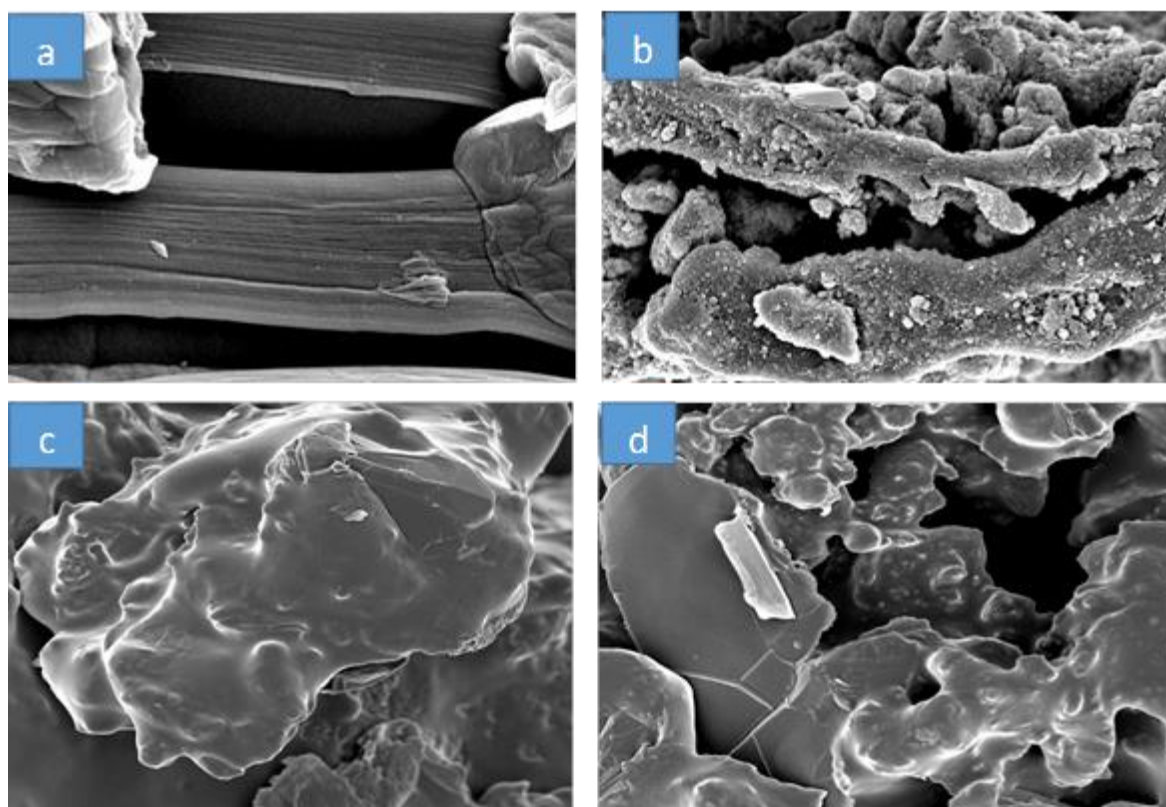

Fig. 2**:** FESEM Images of (a) GO (b) MGO (c) MGO@SiO2Cl (d) MGO@SiO2-Q. Mag: 3.00K

Optimization studies

Effect of pH

The effect of pH on the adsorption of Pb (II) and Ni (II)onto MGO@SiO$_2$-Q is presented in **Fig. 3**. In an acidic solution, the amino functional groups on MGO@SiO$_2$-Q are effectively protonated to (NH^{3+}), which repels metal ions. Thus, the removal efficiency of MGO@SiO$_2$-Q for the metal ions decreases significantly at lower pH values. Furthermore, Increasing the pH value reduces the competition between H$^+$ and the metal ions for binding on the oxygenated active sites (COOH and OH) of the adsorbent (Fialova *et al*., 2014). **Fig. 3.** shows an increased removal percentage of Pb (II) and Ni (II) at higher pH values (Xu *et al.,* 2008b) but Pb (II) precipitates in the form of oxide (Pb(OH)$_2$) at pH 7 (Espinoza *et al.,* 2012), while Ni (II) visually forms nickel hydroxide (Ni(OH)$_2$) at pH 9. However, thermodynamically the Ni (OH)$_2$

starts forming at pH 7.6. Therefore, to avoid potential precipitation of the metal ions, pH 6.0 was selected as the optimum pH for Pb (II) and Ni(II) for further studies (Kumar *et al.,* 2014).
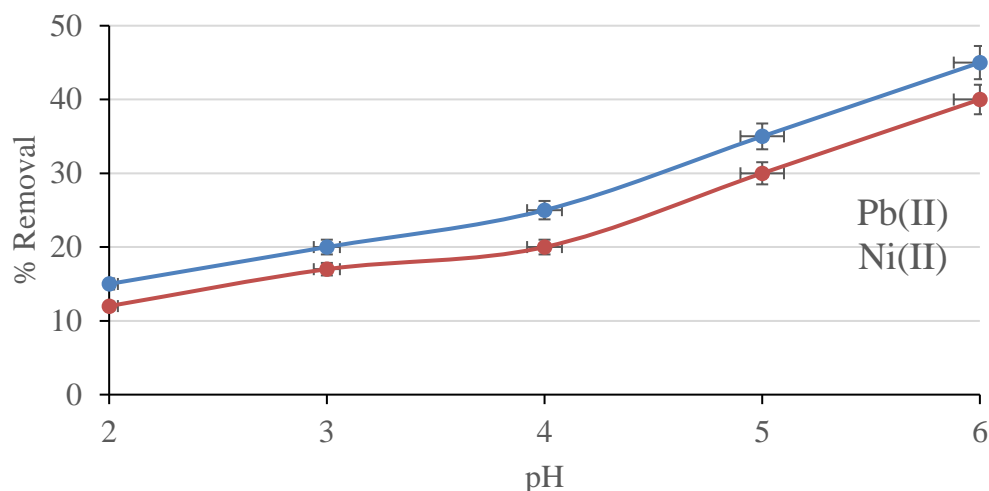

Figure 3: Effect of pH on adsorption of Pb(II) and Ni(II) onto MGO@SiO2-Q. 50 mg/L initial concentrations of Pb(II) and Ni(II) in 50 mL aqueous solution, 20 mg adsorbent. 15 min. contact time at ambient temperature.

Effect of Contact Time

The effect of the contact time on the adsorption of Pb (II) and Ni (II)onto MGO@SiO$_2$-Q is presented in **Fig. 4.** The adsorption equilibrium for the metal ions was attained at 30 min. Furthermore, it can be observed that the removal rate of the metal ions was rapid within the first 15 min., reaching up to 45 and 40% Pb(II) and Ni(II) respectively, then increased slowly until equilibrium was attained for the respective metal ions. The initial fast adsorption of the metal ions was due to the higher number of active sites on the surface of the adsorbent available for interaction with the cations. When the contact time was increased further, the available active sites gradually reduced and the attractive force weakened, resulting in the slow adsorption rate (Liu *et al.,* 2015). Wang *et al.,* (2013) and Wu *et al.,* (2013), also reported similar findings of fast adsorption of metal ions within the first few minutes of contact.
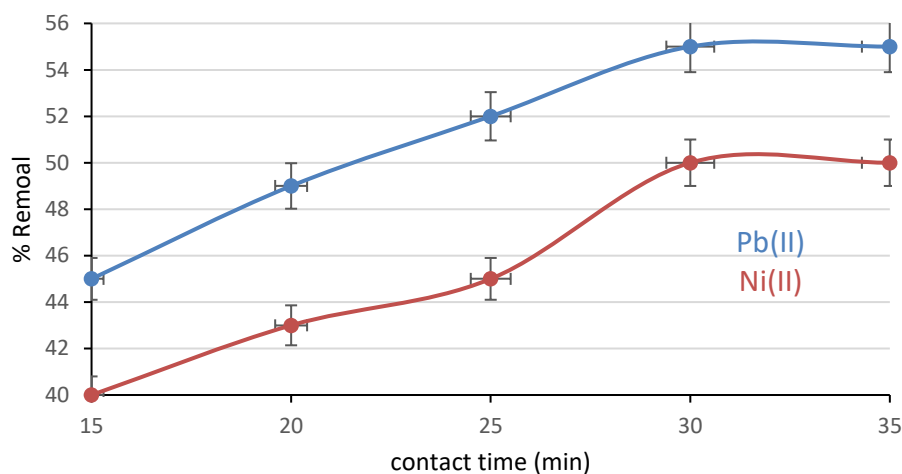
Figure 4. Effect of contact time on adsorption of Pb(II) and Ni(II) onto MGO@SiO2-Q. 50 mg/L initial concentrations of Pb(II) and Ni(II) in 50 mL aqueous solution, pH 6, 20 mg adsorbent at ambient temperature.

CONCLUSION

From the findings of this research it was observed that at optimum conditions, the adsorbent showed excellent adsorption capacity of Pb(II) and Ni (II) in an aqueous environment, also the adsorption process of the metal ions is affected by pH and contact time since the adsorption of the metal ions increases as the pH and contact time increases. The synthesized adsorbent is practical and efficient for the treatment of Pb(II)and Ni(II) contaminated water. Thus, $MGOSiO_2Q$ can serve as a sustainable means of Pb(II) and Ni(II) decontamination in aquatic environments.

REFERENCE

Ahmad, M., Manzoor, K., Venkatachalam, P and Ikram, S (2016). Kinetic and thermodynamic evaluation of adsorption of Cu (II) by thiosemicarbazide chitosan. *Int. J. Biol. Macromol.* 910–919. doi:10.1016/j.ijbiomac.2016.07.075

Ahmad, N. F., Kamboh, M. A., Nodeh, H. R., Abd Halim, S. N. and Mohamad, S. (2017). Synthesis of piperazine functionalized magnetic sporopollenin: A new organic-inorganic hybrid material for the removal of lead (II) and arsenic (III) from aqueous solution, *Environmental Science Pollution Res*earch, 24, 21846 -21858.

Cai, Q., Liu, C., Yin, C., et al., (2017). Biotemplating synthesis of graphitic carbon-coated TiO_2 and its application as efficient visible-light-driven photocatalyst for Cr^{6+} removal. ACS Sustain. *Chem. Eng*. 5, 3938–3944.

Chen, X., Yang, L., Zhang, J., Huang, Y., (2014). Exploration of As (III)/As (V) uptake from aqueous solution by synthesized calcium sulfate Whisker. Chinese *J. Chem. Eng*. 22, 1340–1346. doi:10.1016/j.cjche.2014.09.018

Chen, H., Luo, J., Wang, X., Liang, X., Zhao, Y., Yang, C., Baikenov, M.I and Su, X (2018). *Synthesis of Al$_2$O$_3$/carbon composites from wastewater as superior adsorbents for Pb (II) and Cd (II) removal.* Microporous Mesop. Mater. 255, 69–75.

Cortés-arriagada, D., Toro-labbé, A., (2016). Aluminium and iron-doped graphene for adsorption of methylated arsenic pollutants. Appl. Surf. Sci. 386, 84–95. doi:10.1016/j.apsusc.2016.05.154.

Demiral, H and Güngör, C (2016). Adsorption of copper (II) from aqueous solutions on activated carbon prepared from grape bagasse. *J. Cleaner Prod.* 124, 103–113.

Espinoza, E., Escudero, R and Tavera, F. J (2012). Wastewater treatment by precipitating copper, lead and nickel species. Res. *J. Recent Sci.* 1 (10), 1-6.

Fialova, D., Kremplova, M., Melichar, L., Kopel, P., Hynek, D., Adam, V. and Kizek R. (2014).Interaction of heavy metal ions with carbon and iron-based particles, *Materials,* 7, 2242-2256.

Fu, F and Wang, Q (2011). *Removal of heavy metal ions from wastewaters: a review.* Environ. Manage. 92, 407–418.

Gubbuk, I.H (2011). Isotherms and Thermodynamics for the Sorption of Heavy Metal Ions onto Functionalized Sporopollenin. Journal of. Hazardous Materials. 186: 416 – 422.

Gupta, V.K., Gupta, B., Rastogi, A., Agarwal, S., Nayak, A., (2011). Pesticides removal from wastewater by activated carbon prepared from waste rubber tyre. Water Res. 45, 4047–4055. doi:10.1016/j.watres.2011.05.016.

Gode, F. and Pehlivan, E (2007). Sorption of Cr (III) onto chelating b-DAEG–sporopollenin and CEP–sporopollenin resins. *Bioresource Technology*, 98, 904–911

Hassan, A. M., Wan, A. W. I., Mohd, B. B., Mohd, M. S., Zetty, A. S., Hamid, R. N and Mohd, M (2020). New effective 3-aminoproplytrimelhoxysilane functionalized magnetic sporopollenin-based silica coated graphene oxide adsorbent for removal of Pb (II) from aqueous environment. *J. Environmental Management*. 253, 109653.

Hummers W.S. and Offeman R.E., (1958). Preparation of graphitic oxide. J. Am. Chem. Soc. 80, 1339-1339. https://doi.org/10.1021/ja01539a017

Ihsanullah, A.A., Al-amer, A.M., Laoui, T., Al-marri, M.J., Nasser, M.S., Khraisheh, M and Ali, M (2016). Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. Sep. Purif. Technol. 157, 141–161. doi:10.1016/j.seppur.2015.11.039

Kamboh, M. A and Yilmaz, M (2013). Synthesis of N- methylglucamine functionalized calix (4) arene-based magnetic sporopollenin for the removal of boron from aqueous environment Desalination 310, 67-74.

Kumar, S., Nair, R., Pillai, P., Gupta, S., Iyengar, M. and Sood, A. (2014) Graphene oxide-Mn Fe$_3$O$_4$ magnetic nanohybrids for efficient removal of lead and arsenic from water. *ACS Applied Material and Interf*aces, 6 (20), 17426–17436.

Kodama, R.H. (1999). Magnetic nanoparticles. *J. Mang. Mang. Mater*. 200, 359-372 [Google Scholar][CrossRef]

Lertlapwasin, R., Bhawawet, N., Imyim, A and Fuangswasdi, S (2010). Ionic liquid extraction of heavy metal ions by 2-aminothiophenol in 1-butyl-3-methylimidazolium hexafluorophosphate and their association constants. Sep. Purif. Technol. 72, 70–76.

Lian, P., Zhu, X., Liang, S., Li, Z., Yang, W and Wang, H (2010). Large reversible capacity of high-quality graphene sheets as an anode material for lithium-ion batteries.Electrochim. Acta 55, 3909–3914.

Liu, J., Du, H., Yuan, S., He, W. and Liu, Z. (2015) Synthesis of thiol-functionalized magnetic graphene as adsorbent for Cd(II) removal from aqueous systems. *Journal of Environmental Chemical Engineering,* 3, 617–62.

Madadrang, C. J., Kim, H.Y., Gao, G. H et al., (2012). Adsorption behavior of EDTA-graphene oxide for Pb(II) removal. *ACS* Appl Mater Inter, 4: 1186−1193

Nanseu-Njiki, C.P., Tchamango, S.R., Ngom, P.C., Darchenb, A and Ngamenia, E (2009). Mercury (II) removal from water by electrocoagulation using aluminium and iron electrodes. *J. Hazard. Mater.* 168, 1430–1436.

Pirveysian, M., and Ghiaci, M. (2018). Synthesis and characterization of sulfur functionalized graphene oxide nanosheets as an efficient sorbent for removal of Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions from aqueous solution: A combined thermodynamic and kinetic studies. *Applied Surface Science, 428*, 98–109.

Qin Y L. Juan K. Yong L. Xiazhang T. YongxinLiS. Wang Y (2014). In Situ Growth of Au Nanocrystals on Graphene Oxide Sheets. Nanoscale. 6: 1281.

Radi S. Abiad C. E. Moura N.M.M. Faustino M.A.F. Neves M. G. P.M.S (2019). New Hybrid Adsorbent Based on Porphyrin Functionalized Silica for Heavy Metals Removal: Synthesis, Characterization, Isotherms, Kinetics and Thermodynamics Studies. Journal of Hazardous Material. 370: 80–90.

Rajkumar, D and Palanivelu, K (2004). Electrochemical treatment of industrial wastewater. *J. Hazard Mater.* B113, 123-129.

Wang, H., Yuan, X. Z.., Wu, Y., Huang, H. J., Zeng, G.G., Liu, Y., Wang, X. L, Lin, N. B. and Qi, Y. (2013) Adsorption characteristics and behaviors of graphene oxide for Zn(II) removal from aqueous solution, *Appl. Surf. Sci.* 279: 432–440.

Wu, Y., Luo, H.J., Wang, H., Wang, C., Zhang, J. and Zhang, Z.L. (2013) Adsorption of hexavalent chromium from aqueous solutions by graphene modified with cetyltrimethylammonium bromide, *Journal of Colloid and Interface Sci*ence, 394, 183– 191.

Wu, G., Kang, H., Zhang, X., Shao, H., Chu, L and Ruan, C (2010). A critical review on the bioremoval of hazardous heavy metals from contaminated soils: issues, progress ecoenvironmental concerns and opportunities. *J. Hazard. Mater.* 171, 1–8.

Xi, Y., Luo, Y., Luo, J., Luo, X., (2015). Removal of Cadmium(II) from Wastewater Using Novel Cadmium Ion-Imprinted Polymers. J. Chem. Eng. Data 60, 3253–3261.doi:10.1021/acs.jced.5b00494

Xu, C., Wang, X., Zhu, J., Yang, X.J. and Lu, L.D. (2008) Deposition of Co_3O_4 nanoparticles onto exfoliated graphite oxide sheets. *Journal of Material Chemi*stry, 18, 5625-5629.

Zhang, L., Luo, H., Liu, P., Fang, W and Geng, J (2016). A novel modified graphene oxide/chitosan composite used as an adsorbent for Cr (VI) in aqueous solutions. *Int. J. Biol. Macromol.* 87, 586–596. doi:10.1016/j.ijbiomac.2016.03.027

Zhang, W, Shi, X.; Zhang, Y.; Gu, W.; Li, B.; Xian, Y. (2013). Synthesis of water-soluble magnetic graphene nanocomposites for recyclable removal of heavy metal ions. *J. mater. Chem.* A1, 1745-1753. [Google Scholar][CrossRef]

Zhao, G., Li, J., Ren, X., Chen, C and Wang, X (2011). Few-layered graphene oxide nanosheets as superior sorbents for heavy metals ion pollution management. *Environ. Sci. Technol.* 45, 10454-10462.