Adsorption Behavior of Heavy Metal Ions (Cr^{3+}, Pb^{2+} and Cu^{2+}) Into Magnetite-Graphite Oxide-Diatomite

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ABSTRACT

In this recent work, magnetite-graphite oxide-diatomite (Mag-GO-diatomite) composite was synthesized using a facile method. GO-diatomite, with and without Magnetite, was used for the adsorption of Cu^{2+}, Pb^{2+} and Cr^{3+}. Langmuir and Freundlich adsorption isotherm models were tested to validate which of these two fits the empirical data. Results showed that the adsorption of Cr^{3+} and Cu^{2+} were best described by Langmuir isotherm and Pb^{2+} was well fitted with the Freundlich isotherm. From the isotherm data, adsorption of Cr^{3+} into GO-diatomite showed the highest adsorption capacity while Pb^{2+} revealed to have the largest adsorption for Mag-GO-diatomite.

Introduction

Worldwide, water contamination by hazardous metal ions is of great concern. Studies have been conducted to eliminate organic and inorganic pollutants. Techniques such as chemical precipitation by controlling pH (Ito, Umita, Aizawa, Takachi, & Morinaga, 2000), chemical oxidation, chemical reduction, ion exchange (Mier, Callejas, Gehr, Cisneros, & Alvarez, 2001), membrane filtration using coagulants, electrochemical treatment, evaporation, constructed wetland, adsorption (Tchobanoglous, Burton, & Stensel, 2003; Mouflih, Aklil, & Sebtib, 2005) are some of the commonly used techniques for reducing level of contamination. Among these techniques, the use of novel adsorbents has been widely studied because of its excellent rate of adsorption, enormous adsorption capacity, and large selectivity to adsorb hazardous metal ions. Activated carbon (Sekar, Sakthi, & Rengaraj, 2004), synthetic resin (Demirbas, Pehlivan, Gode, Altun, & Arslan, 2005), mesoporous silica (Feng, 1997), carbon nanotubes (Li, 2005; Wang, Zhou, Peng, Yu, & Chen, 2007), natural and synthetic zeolite (Wang, Terdkiatburana, and Tadé, 2008; Wingenfelder, Hansen, Furrer, and Schulin, 2005), clay minerals (Sari, Tuzen, Citak, and Soylak, 2007), natural and modified diatomite (Osmanlioglu, 2007; Zhang & Hou, 2008) and biomass (Khraisheh, Al-degs, & Mcminn, 2004) are the types of adsorbents studied having the potential applications in removing waste water's hazardous metal ions.

Graphene has been recently explored as a novel adsorbent material. It is a new member of the carbon family with excellent and fascinating properties. However, researches revealed that graphene oxide (GO), the oxidized form of graphene, is a more promising adsorbent material due to its extraordinary mechanical strength and large specific surface area. GO consists of several functional groups such as hydroxyl, carboxyl, and epoxy groups which are the routes for modification and functionalization of GO. It is also hydrophilic with a highly negative charge density due to the presence of its functional groups (Fan, Lou, Sun, Li, Lu & Qiu, 2012).

There are various works on graphene oxide composites. Previous studies were on graphene oxide/magnetite or graphene oxide/diatomite. A study was made by Li *et al.* (n.d.) on calcined graphene oxide/diatomite and the application of the composite is not as an adsorbent but as a building material. The composite that they prepared has a high electrical conductivity and compressive strength (Li, Gao, Zhang, Zheng, Zhao & Meng, 2015). Dalagan *et al*. (2013) prepared graphene oxide/diatomite composite which was known to attract cationic biomolecules due to the negative surface charge developed on GO-silica. This composite could be possibly be used as a cationic biosensor (Dalagan, Enriquez & Li, 2013). A composite of thiol-functionalized graphene oxide/magnetite was prepared by for the removal of Hg^{2+}. (Bao, Fu & Bao, 2013). Another study was done by Meral and Metin (2014) on graphene oxide-magnetite composite as an adsorbent for methylene blue in aqueous solution. Liu *et al.* synthesized graphene oxide/magnetite for cobalt (II) removal (Liu, Chen, Hu, Wu, and Wang, 2011).

Graphene oxide-diatomite as adsorbent has some adsorption limitations due to the stacking of the graphite sheets. Thus, this recent study aims to prepare a material which could improve the adsorption capacity of graphene oxide/diatomite. The use of magnetite as graphite sheets spacer has been investigated in this study to possibly enhance its ability to adsorb and to open its surface to adhere more molecules or ions. Adsorption behavior of metals unto the magnetite-GO-diatomite composite is also worth investigating by using adsorption isotherm models such as Langmuir and Freundlich. These are helpful tools in determining adsorption capacities of a material for specific metal ions. To date, there are no reported works yet on graphene oxide-diatomite decorated with magnetite.

Methodology

The experimental part of the research was divided into two parts. The first part was on the synthesis of the adsorbent and the second part was on the heavy metal removal using the synthesized adsorbent.

A. Synthesis of the adsorbent

Synthesis of Magnetite (coprecipitation method) supported on GO-diatomite composite (Mag-GO-diatomite). The synthesis was previously reported by Dalagan and Ibale (2015). In brief, an aqueous solution of $FeCl_3.6H_2O$ was prepared by dissolving about 1.5 g in 50 mL of DI water. The solution was added slowly to GO solution at room temperature (RT). NH_4OH (15 M) was added to make the solution pH equal to 10. The temperature was raised to 90°C and was continuously stirred for 4 hours. It was allowed to cool down to room temperature after heating. The black colored solution was subjected to filtration, added with enough water and dried at room temperature.

B. Adsorption Studies

Adsorption of Cr, Pb and Cu on Mag-GO-diatomite and on GO-diatomite. Ten (10) mL of Cr solutions of varying concentrations (2 ppm, 6 ppm and 10 ppm) and about 15 mg of the Mag-GO-diatomite adsorbent were equilibrated by shaking using a mechanical shaker at 180 rpm for 24 hrs. A Whatman #2 filter paper was used for filtration and the filtrate was subjected to Atomic Absorption Spectroscopy (AAS) analysis to determine the metal content. Two other metals, Pb and Cu, were also subjected to the same procedure as above. For comparison purposes, GO-diatomite was also used as adsorbent for the three metals. To investigate the effect on the adsorption of a heavy metal in the presence of other metals, 10 mL of 10 ppm mixture of Cu, Pb, and Cr, 10 ppm of Cr and Pb, 10 ppm of Cr and Cu, 10 ppm of Pb and Cu were equilibrated with a known amount of Mag-GO-diatomite. The same procedure as above was followed to calculate the concentration of the metal ions.

Results and Discussion

Adsorption of Heavy Metals on GO-diatomite and Mag-GO-diatomite. Metals were equilibrated on GO-diatomite (without magnetite) for reason of comparison. Results showed that for all the metal samples used, higher amounts were adsorbed on Mag-GO-diatomite.

Figure 1 shows comparison of the amount of metals adsorbed on the Mag-GO-diatomite and GO-diatomite (without the magnetite). Higher amount of metals are generally observed with Mag-GO-diatomite. Possible explanation for this is the difference in electrostatic attraction between the heavy metals and the adsorbent and the different tendencies of the metals to complex with the adsorbent (Giraldo, Erto, & Moreno-Piraján, 2013). Both GO-diatomite and Mag-GO-diatomite have a negative surface charge at a higher pH so they can adsorb heavy metals through electrostatic interaction. However, GO-diatomite has a tendency to restack into GO sheets thus reducing exposure of the adsorption sites. It is possible that magnetite functions as a "spacer" as shown in Figure 2 thus preventing restacking of GO-diatomite sheets. This increases the distance between sheets and enhances accessibility of the possible sites for adsorption (Wang *et al.*, 2014).

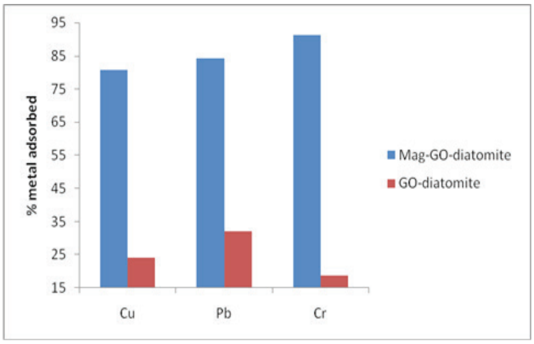


Figure 1. Percentage of metals adsorb by Mag-GO-diatomite and GO-diatomite

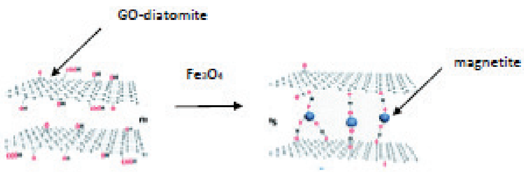
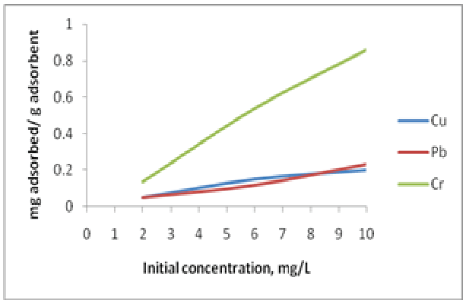


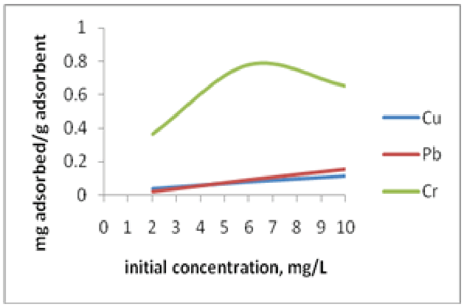
Figure 2. Magnetite acting as "spacer" to GO-diatomite

Adsorption Isotherm of Metals into Mag-GO-diatomite. Adsorption isotherm of metal ions into the GO-diatomite (A) and Mag-GO-diatomite (B) is shown in Figure 3. Adsorption isotherm using Mag-GO-diatomite showed a linear plot for both Cu and Pb which implies that the adsorption did not reach saturation point. On the other hand, Cr showed a near-plateau plot, which could mean that the adsorbent has probably reached a saturation point where it could no longer accommodate adsorbing ions. The adsorption isotherm for GO-diatomite without magnetite support illustrated a similar adsorption behavior with Mag-GO-diatomite in which a linear plot was obtained (Al-Degs *et al.*, 2001).

Known amounts of Pb, Cu, and Cr (2 ppm, 6 ppm and 10 ppm) were equilibrated with the adsorbent for 24 hrs at a basic pH. At this pH, the surface of the adsorbent, Mag-GO-diatomite is more negatively charged. This leads to the adsorption of metal ions into the Mag-GO-diatomite. Figure 3B adsorption isotherm with linear plot for both Cu and Pb implying unsaturated condition could be due to the abundance of free binding sites on the surface of Mag-GO-diatomites so that the adsorbent can adsorb more Cu^{2+} and Pb^{2+}. Previous work of Zhao, Hu, and Ye (2013) reported a similar linear plot for Cu and Pb with graphene-ZnO composite as adsorbent. On the other hand, Cr showed a near-plateau plot which could mean that the adsorbent has probably reached a saturation point where it could no longer accommodate adsorbing ions. Cu and Pb showed similar behavior due to their similarities in physicochemical properties such as electronegativity, ionic radius and ionic charge. On the other hand, Cr being trivalent differs from the divalent Cu and Pb in terms of their physicochemical properties (Kang, Lee, Moon & Kim, 2004). This scheme is also consistent with the work of Yuan *et al.* (2010) on Cr adsorbed on diatomite-magnetite particles. The adsorption isotherm for GO-diatomite shown in Figure 3A demonstrates a similar adsorption behavior with Mag-GO-diatomite.



A



B

Figure 3. Adsorption isotherm of Cu, Pb and Cr in (A) GO-diatomite and (B) Mag-GO-diatomite

Isotherm models were used to analyze the isotherm data. Langmuir and Freundlich isotherm models were used for the purpose of this study. This was to evaluate the experimental results of the adsorption study of the three species involved. It is vital to consider that the mechanism of adsorption cannot be fully assessed from both models. However, these models provide a general assessment of the adsorption behavior. The following are the linear forms of the two adsorption isotherm models (Erena *et al.*, 2009; Shawabkeha, & Tutunji, 2003):

$$\log qe = \log KF + \left(\frac{1}{n}\right) \log Ce \quad (1)$$

Freundlich isotherm

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{Qb}\frac{1}{C_e} \quad (2)$$

Langmuir isotherm

$$R_L = 1 / (1 + bCo) \quad (3)$$

where qe is the total quantity of absorbed metals in every adsorbent unit weight (mg/g), Ce is the metals' equilibrium amount (mg/L), b is a free energy of adsorption correlated constant (L/mg), and where Q is the theoretical maximum adsorption capacity (mg/g). Kf or Freundlich constant is related to the adsorbent's relative adsorption capacity (mg/g), and where (1/n) is indicative of the adsorption strength. The 3rd equation (3) can also be utilized to evaluate the adsorption behavior of the heavy metals where R_L is a dimensionless constant separation factor or equilibrium parameter with b as Langmuir constant and with Co as the metals' initial concentration. R_L signifies the kind of isotherm: unfavorable if $R_L>1$, linear if $R_L = 1$, and favorable if $0<R_L<1$ or irreversible if $R_L = 0$ (Wang, Wang, and Ma, 2010).

Cr, Cu, and Pb shows different adsorption behavior towards Mag-GO-diatomite. Table 1 lists the adsorption constants. Validity of the isotherm models was evaluated using correlation coefficient or R^2. Cu and Cr adsorption data best fit with the Langmuir models with $R_L < 1$. This indicates that the adsorption of Cu and Cr into Mag-GO-diatomite can be considered to be a monolayer adsorption process. In this type of adsorption mechanism, the adsorbed layer is one molecule thick and once the sites are occupied, no adsorption can take place. Zhao *et al.* (2013) also reported similar observation but the adsorbent used in their study was diatomite-supported on magnetite particles. On the other hand, Pb adsorption on Mag-GO-diatomite can be best defined by the Freundlich model with n<1. Same result was observed by Sheng *et al.* (2009) but the adsorbent in their study was activated carbon.

Table1

Langmuir and Freundlich Adsorption Isotherm Parameters for Cu, Pb and Cr on Mag-GO-diatomite

Metal species	*Langmuir isotherm constants*				*Freundlich isotherm constants*		
	Q (mg/g)	*b (L/mg)*	*R_L*	*R^2*	*K_F (mg/g) $(L/mg)^{1/n}$*	*n*	*R^2*
1. Cu	*0.198*	*0.113*	*0.815*	*0.99*	*0.0226*	*1.46*	*0.99*
2. Pb	*-0.186*	*-0.0504*	*1.11*	*0.99*	*113.5*	*0.791*	*0.99*
3.Cr	*1.02*	*0.284*	*0.569*	*0.90*	*0.296*	*2.44*	*0.72*

From the isotherm data, adsorption capacities in mg/g of Mag-GO-diatomite were determined to be 113.5 for Pb^{2+}, 0.296 for Cr^{3+}, and 0.0226 for Cu^{2+}.

Table 2 shows the adsorption constants for GO-diatomite. The R^2 are high for both Langmuir and Freundlich models. The model that best describes the adsorption of Cu^{2+} and Pb^{2+} is Langmuir with RL <1 and Freundlich isotherm model best fit Cr^{3+} with n<1. The three metal ion species, showed different adsorption behavior depending on their interaction with the adsorbent. Divalent ions, Pb^{2+} and Cu^{2+}, have greater ionic radii than the trivalent Cr. Metallic ions with bigger radius tend to form monolayer adsorption due to steric hindrance. The metal ions-adsorbent interaction is maybe restricted to the electrostatic kind. Reasons why Langmuir is the isotherm model that best fits Pb^{2+} and Cu^{2+} (Dronnet, Axelos, Renard & Thibault, 1998). On the other hand, ions with smaller radius such as Cr^{3+} have a tendency to adhere strongly to the different available binding sites with several adsorption energies through complexation reactions. This is how Freundlich adsorption isotherm is being described (Hamza, Hammad & Eltayab, 2013).

Table 2

Langmuir and Freundlich Adsorption Isotherm Parameters for Cu, Pb and Cr on GO-diatomite

Metal species	Langmuir isotherm constants				Freundlich isotherm constants		
	Q (mg/g)	*b (L/mg)*	*R_L*	*R^2*	*K_F (mg/g) $(L/mg)^{1/n}$*	*n*	*R^2*
1. Cu	1.76	0.0142	0.972	0.99	0.0268	1.11	0.99
2.Pb	0.677	0.0410	0.924	0.99	0.0266	1.11	0.98
3.Cr	-1.73	-0.0365	1.08	0.99	0.0622	0.861	0.99

Using the isotherm data, adsorption capacities in mg/g of GO-diatomite obtained were 0.0266 for Pb^{2+}, 0.0622 for Cr^{3+} and 0.0268 for Cu^{2+}.

Conclusion and Recommendations

In this current study, graphene oxide-diatomite was decorated with magnetite and was applied as an adsorbent for heavy metal ions (Cr^{3+}, Pb^{2+} and Cu^{2}). For comparison purposes, GO-diatomite and Mag-GO-diatomite were both used as adsorbents for the three heavy metal ions. Experimental results revealed that with magnetite, the removal of heavy metals was higher than without magnetite. The plausible explanation for this trend is the ability of magnetite to act as a spacer between GO sheets which could imply a more exposed adsorption sites. To describe the adsorption behavior, isotherm models were used. Langmuir was evaluated to be the best isotherm for the adsorption of Cr^{3+} and Cu^{2+} on Mag-GO-diatomite and Freundlich isotherm was for Pb^{2+}.

With these results, the novel adsorbent, Mag-GO-diatomite, could be a useful tool in remediating the water effluents of manufacturing plants in the highly industrial parts of Northern Mindanao. Previous researches showed that the sea water in these areas was found to have heavy metals.

To further improve the adsorbent, future studies could explore different ratios of magnetite to GO-diatomite to be able to investigate the optimum ratio to attain maximum adsorption of heavy metals. Other pollutants such as organic dyes and volatile organic compounds (VOCs) can also be used to adsorb on the Mag-GO-diatomite. The ratio of adsorbent to adsorbate can also be investigated further to obtain the optimum adsorption capacity of Mag-GO-diatomite.

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References

Al-Degs, Y., Khraisheh, M., & Tutunji, M. (2001). Sorption of Lead Ions on Diatomite and Manganese Oxides Modified Diatomite. *Water Research, 35*(15), 3724–3728.

Bao, J., Fu, Y., & Bao, Z., Thiol-functionalized magnetite/graphene oxide hybrid as a reusable adsorbent for Hg2+ removal. *Nanoscale Research Letters, 8*(486).

Dalagan, J. & Ibale, R. (2016). Magnetite-Graphite Oxide Diatomite: An Alternative Adsorbent for Heavy Metal Ions. *Philippine Journal of Science*, *145*(1), 77-86.

Dalagan, J., Enriquez, E., & Li, LJ. (2013). Simultaneous functionalization and reduction of graphene oxide with diatom silica. *Journal of Material Science, 48,* 3415–3421.

Demirbas, A. Pehlivan, E., Gode, F., Altun,T., & Arslan, G. (2005). Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from Aqueous Solution on Amberlite IR-120 Synthetic Resin. *Journal Colloid Interface Science. 282,* 20–25.

Dronnet, V. M., Axelos, M. A. V., Renard, C. M. G. C & Thibault J. F. (1998). Improvement of the binding capacity of metal cations by sugar-beet pulp. 2. Binding of divalent metal cations by modified sugar-beet pulp. *Carbohydrate Polymers*. *35,* 239-241.

Fan L., Luo C., Sun M., Li X., Lu F., Qiu H. (2012), Preparation of novel magnetic chitosan/graphene oxide composite as effective adsorbents toward methylene blue. *Bioresource Technology*. *114,* 703–706.

Feng, X., Fryxell, G. E., Wang, L. Q., Kim, A. Y., Liu, J., & Kemner, K. M. (1997). Functionalized Monolayers on Ordered Mesoporous Supports. *Science*. 276, 923–926.

Giraldo, L., & Erto, A. (2013). Moreno-Piraján, J.C. Magnetite Nanoparticles for Removal of Heavy Metals from Aqueous Solutions: Synthesis and Characterization. *Adsorption*. *19, 465-474.*

Hamza N., Hammad A., & Eltayeb M. (2013). Adsorption of Metals (Fe(II), Cr(III) and Co(II)) from aqueous solution by using Activated carbon prepared from *Mesquite* tree. *Science Journal of Analytical Chemistry*. *1*(2), 12-20.

Ito, A., Umita, T., Aizawa, J., Takachi, T., & Morinaga, K. (2000). Removal of Heavy Metals from Anaerobically Digested Sewage Sludge by a New Chemical Method using Ferric Sulfate. *Water Research. 34*, 751–758.

Kang, S. Y., Lee J., Moon S. H., &Kim K. W. (2004). Competitive adsorption characteristics of Co^{2+}, Ni^{2+}, and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater. *Chemosphere.* 56, 141–147.

Khraisheh, M. A. M., Al-degs, Y. S., & Mcminn, W. A. M. (2004). Remediation of Wastewater Containing Heavy Metals using Raw and Modified Diatomite. Chemical Engineer Journal. 99, 177–184.

Li, Y. H., Di, Z. C., Ding, J., Wu, D. H., Luan, Z. K., & Zhu, Y. Q. (2005). Adsorption Thermodynamic, Kinetic and Desorption Studies of Pb2+ on Carbon Nanotubes. *Water Research* 39, 605–609.

Li, M. K., Gao, C. X., Zhang, X., Zheng, W. T., Zhao, Z. D., & Meng F. L. Electrical conductivity of calcined graphene oxide/diatomite composites with a segregated structure. *Materials Letters*, *141*, 125–127126.

Liu M, Chen C, Hu J, Wu X, and Wang X. (2011). Synthesis of Magnetite/ Graphene Oxide Composite and Application for Cobalt(II) Removal, *Journal of Physical Chemistry C.* 115, 25234–25240.

Meral, K. & Metin, O. (2014). Graphene oxide–magnetite nanocomposite as an efficient and magnetically separable adsorbent for methylene blue removal from aqueous solution, *Turkish Journal of Chemistry 38*: 775 – 782.

Mier, M. V., Callejas, R. L., Gehr, R., Cisneros, B. E. J., & Alvarez, P. J. J. (2001). Heavy metal removal with mexicanclinoptilolite: multi-component ionic exchange. *Water Research. 35*, 373–378.

Mouflih, M., Aklil, A. S., & Sebtib, J. (2005). Removal of lead from aqueous solutions by activated phosphate. *Hazard Mater*. *B119*, 183–188.

Sari, A., Tuzen, M., Citak, D., & Soylak, M. (2007). Equilibrium, Kinetic and Thermodynamic Studies of Adsorption of Pb(II) from Aqueous Solution onto Turkish Kaolinite Clay. J. *Hazard. Mater*. *149*, 283–291.

Sekar, M., Sakthi, V., & Rengaraj, S. (2004). Kinetics and Equilibrium Adsorption Study of Lead(II) on Activated Carbon Prepared from Coconut Shell. *Journal Colloid Interface Science. 279*, 307–313.

Shawabkeha, R. A., & Tutunji, M. F. (2003). Experimental Study and Modeling of Basic Dye Sorption by *Diatomaceous Clay. Applied Clay Science*. *24*, 111–120.

Sheng, G., Wang, S., Hu, J., Lu, Y., Li, J., Dong, Y., & Wang, X. (2009). Adsorption of Pb(II) on Diatomite as Affected via Aqueous Solution Chemistry and Temperature. *Colloids and Surfaces A: physicochemical and Engineering Aspect*. *339*, 159-166.

Tchobanoglous, G., Burton, F. L., & Stensel, H. D. (2003). *Wastewater Engineering: Treatment and Reuse*. New York: McGraw-Hill Inc.

Wang, F. Y., Wang, H., & Ma, J. W. (2010). Adsorption of Cadmium (II) Ions from Aqueous Solution by a New Low-Cost adsorbent - Bamboo Charcoal. *Journal of Hazardous Mat. 177*, 1-3.

Wang, S. B., Terdkiatburana, T., & Tadé, M. O. (2008). Adsorption of Cu(II), Pb(II) and Humic Acid on Natural Zeolite Tuff in Single and Binary Systems. *Separation Purification Technology*. *62*, 64–70.

Wang Y., He Q., Qu H., Zhang X., Guo J., Zhu J., Zhao G., Colorado, H. A., Yu, J., Sun L., Bhana, S., Khan M. A., Huang X., Young D. P., Wang H., Wang X., Wei, S., & Guo Z. (2014). Magnetic graphene oxide nanocomposites: nanoparticles growth mechanism and property analysis. *Journal Mater. Chem*. *C, 2*, 9478-9488.

Yuan, P., Liu, D., Fan, M., Yang, D., Zhu, R., Ge, F., Zhu, J., & He, H. (2010). Removal of Hexavalent Chromium [Cr(VI)] from Aqueous Solutions by the Diatomite-Supported/Unsupported Magnetite Nanoparticles. *Journal of Hazardous Materials*. *173*, 614-621.

Zhang, S. Q., & Hou, W. G. (2008). Adsorption Behavior of Pb(II) on Montmorillonite, Colloids Surf. A: Physicochem. *Engineering Aspects. 320*, 92–97.

Zhao, X., Hu, B., Ye, J., & Jia, Q. (2013). Preparation, Characterization, and Application of Graphene Zinc Oxide Composites (G-ZnO) for the Adsorption of Cu(II), Pb(II), and Cr(III). *Journal Chemical Engineering Data*. *58*, 2395-2401.