Malaysian Journal of Chemical Engineering & Technology 3 (2) (2020) 60–66

Malaysian Journal of Chemical Engineering & Technology

Journal Homepage: http://myjms.mohe.gov.my/index.php/mjcet

Removal of cadmium ion from aqueous solution using plant-based anionic surfactant impregnated activated carbon

Noor Era Fazirah Jundam, Normadyzah Ahmad*, Siti Wahidah Puasa

Faculty of Chemical Engineering, Universiti Teknologi MARA, Selangor, Malaysia

*Corresponding email: normadyzah@uitm.edu.my

Abstract

Activated carbon was modified by impregnating it with sodium lauryl sulfoacetate (SLSA), a plant-based anionic surfactant and tested to determine whether the surfactant will increase the effectiveness of cadmium ion removal from aqueous solution of cadmium chloride ($CdCl_2$) by activated carbon. The activated carbon used was industrial grade granular type tested without grinding or sieving. The surfactant preparation and the impregnation were done at 600 °C. The heavy metal removal test conducted at 300 °C to mimic normal weather temperature of Malaysia. The granular activated carbon was characterized using BET (Brunauer-Emmet-Teller) while the surfactant chemical properties analysed using FTIR. The aqueous solutions before and after the test were analysed using AAS (atomic absorption spectroscopy). The result obtained has shown that SIAC at 125 ppm has the highest cadmium removal averaging 37.87%. The lowest removal shown by SIAC at 10 ppm with an average of 7.70%.

Article Info

https://doi.org/10.24191/mjcet.v3i2.xxxx

Article history:

Received date: 15 November 2020
Accepted date: 21 December 2020

Keywords:

Impregnation
Plant-based surfactant
Activated Carbon
Cadmium
Adsorption

1.0 Introduction

Activated carbon has always been successful in removing contaminants in wastewater to a certain degree, but there are still some contaminants left that sometimes it requires second treatment (Matthis, 2017) and this increases the operating cost of the treatment plant. The adsorptive properties of activated carbon can be enhanced by impregnating it with a surfactant in which it improves the affinity of the organic or inorganic material towards the activated carbon by protruding the interface and providing more bonding sites for the impurities. Surfactant increases the number of functional groups in activated carbon, allowing it to adsorb metal ion optimally (Mahmoud, El-Deen, & Soliman, 2014) by electrostatic attraction towards its surface (Chen, et al., 2014).

Cadmium is a harmful element that can cause various types of illnesses if consumed by living things. As a naturally occurring element, like lead, mercury and zinc, cadmium is also present in small deposits in soils and rocks. According to OSHA (occupational safety and health administration), up to 300,000 industrial workers exposed in the US alone, mostly are from the metal refining, smelting, battery and paint production, basically any industry that utilize zinc ore in its processes. The same can be said in Malaysia where the smelting industry is considered an important economic drivers as more and more smelting factories and company is built to cater for the demand. These industrial activities produce unwanted side products that eventually become waste and cadmium is one of the major components of the effluents. These effluents may also contaminate the source of drinking waters that enters the environment from dumping sites, smelting, metal-plating and even refining operations (Brooks et al., 2010). Even at small amount, cadmium could cause severe poisoning to adult and children. If cadmium enters the body through inhalation, the symptoms include pleuritic chest pain (sudden stabbing pain on the chest when breathing), dyspnea (shortness of breath), cyanosis (blueish discoloration on the hand and feet), tachycardia (rapid heart rate), fever and nauseous feeling. Acute poisoning could lead to pulmonary related diseases, lung cancer, osteomalacia (bone softening), prostate cancer and proteinuria. It is accumulated within the human body system due to the inability of the kidney and the liver to remove it.

Sodium lauryl sulfoacetate (SLSA) is a chemical or commonly known as the surface-active agent, usually used as an alternative to sodium lauryl sulphate(SLS) (Fig. 1). It is manufactured from the combination of both palm oil and coconut. It is yet to be used as an agent to be impregnated onto activated carbon or applied in any wastewater/water treatment industry. SLSA is a type of anionic surfactant known to remove oily material, dirt and even clay. Any surfactant only works after ionization, in which anionic surfactant is ionized when added to water and will exhibit a negative charge. This negatively charged surfactant will bind to a positively charged particle or ion. In this study, the positively charged substance is cadmium ion.

Impregnating granular activated carbon with SLSA is based on the principle of surface adsorption. Adsorption is a process where ions, molecules or atoms of fluid or dissolved solid are adhered to a surface, creating a layer of adsorbate at the surface of the adsorbent. SLSA as dissolved solid will adhere to the surface of granular activated carbon through physisorption instead of chemisorption since there are only physical interaction from weak Van Der Waals and electrostatic forces. There is a chemical interaction (covalent bonding), but the existence does not dominate like physical interactions.

Increment in cadmium concentration in both water and wastewater demanded a better removal solution or alternative to the current technique. A lot of other surfactant have been impregnated onto activated carbon and its cadmium removal capacity was tested like magnesium (Yanagisawa et al., 2010), iron (iii) chloride (Rashad et al.,2017), sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulfonate (SDBS) (Ahn et al., 2009), but not sodium lauryl sulfoacetate (SLSA).

Since sodium lauryl sulfoacetate is a much cheaper anionic plant-based surfactant with a lot of potential to be discovered, it is imperative that the experiment to be conducted to keep the pace of cadmium removal ahead of its demand. With the study on the ratio of impregnation of sodium lauryl sulfoacetate and its effect on the removal of cadmium from aqueous solution, an optimum amount of Sodium lauryl sulfoacetate to be used for the removal of the contaminant can be determined.

SLSA mainly comprises of straight chain of alkane, hydroxyl group, carbonyl group and sulfonate group just as shown in Fig. 1. Straight alkane chain is one of the reasons for SLSA need to be used as impregnation agent since it lacks the benzene ring that usually present in other surfactants such as SDBS (Ahn et al., 2009). In this study, it is hypothesized that sulfonate group will attract cadmium ion from aqueous solution.

2.0 Methodology

2.1 Materials

Solid cadmium chloride ($CdCl_2$) of 99% purity and sodium lauryl sulfoacetate (SLSA) of 98% purity was obtained from Sigma-Aldrich, while granular activated carbon (GAC/AC) was obtained from Soon-Ngai Engineering. An aqueous solution of Cadmium chloride was prepared by diluting 0.25 g of Cadmium chloride with distilled water. Different concentration of sodium lauryl sulfoacetate solution was prepared by diluting SLSA in 200 m L of distilled water.

2.2 Impregnation of SLSA onto AC

The SLSA solution was prepared by incubating it at 60 °C and shaken at 130 rpm inside incubator shaker for 4 hours. The concentration of SLSA prepared was 10, 25, 50, 75, 100, 125, 150, and 175 mg/L. After incubation, the solution was allowed to cool before adding 2 mg of granular activated carbon. The flask containing activated carbon and SLSA was wrapped with aluminium foil before the impregnation process. This is to avoid any interaction between (surfactant-impregnated activated carbon) SIAC and light that may affect the reaction. The wrapped flasks incubated at 60 °C overnight at 130 rpm. A schematic representation of laboratory work is shown on Fig. 2.

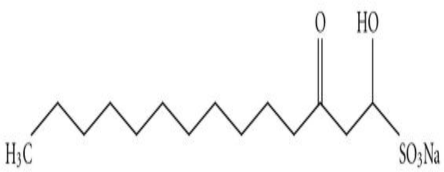

Fig. 1: Structure of SLSA.

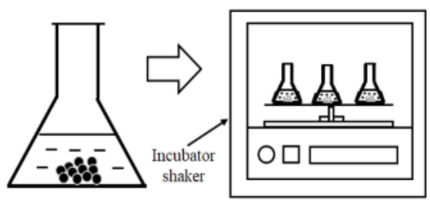

Fig. 2: Schematic diagram of experimental work.

2.3 Cadmium removal from aqueous solution

The resulting activated carbon called SIAC then was dried using oven at 60 °C overnight. The same step was also repeated with virgin activated carbon. Freshly dried activated carbon was added onto 100 mL of cadmium chloride solution. The mixture was then shaken at 130 rpm at 30 °C for 6 hours.

2.4 Analysis of sample

The activated carbon (impregnated and virgin) surface area was analyzed using BET (Micromeritics), while the component of SLSA was analyzed using FTIR (SDTS851, Perkin Elmer). After the incubation, 1 mL of the resulting cadmium chloride solution was analysed using atomic absorption spectrometry (AAS) (Z2000, Hitachi).

2.5 Determination of cadmium removal percentage and adsorption capacity

The removal percentage (%R) was calculated using the following formula:

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where C_i is initial concentration of cadmium ion in the solution (mg/L), C_o is the final concentration of cadmium ion (mg/L).

The adsorption capacity (q_t) of granular activated carbon is calculated using the following formula:

$$q_t = \frac{(C_i - C_t) \times V}{m} \qquad (2)$$

where C_t is concentration of cadmium ion at equilibrium, V is the volume of aqueous solution added onto the AC and *m* is the mass of AC.

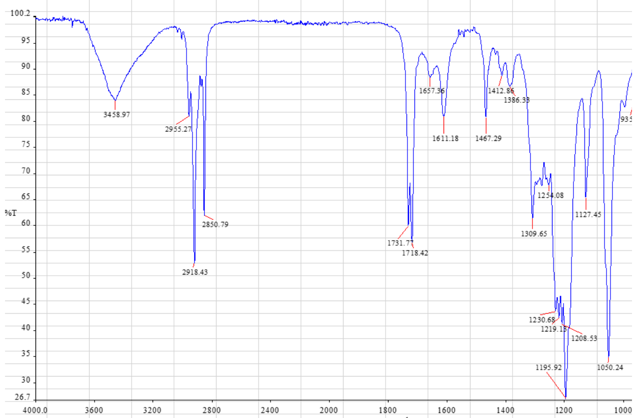

Fig. 3: IR spectra of SLSA.

3.0 Results and discussion

3.1 Characterization of SLSA as a surfactant

As can be seen from Fig. 3, the IR spectra of SLSA has shown that it is a type of anionic surfactant with sulphate functional group (S=O) can be seen at 1412.86 cm^{-1} and 1386.33 cm^{-1}. Sulphate functional group can act as attracting agent for cadmium ion through electrostatic attraction since it is negatively charged head.

The O−H stretch implying the availability of hydroxyl group, which could also help in increasing the affinity of cadmium towards activated carbon by preventing moisture molecules or water from being adsorbed onto the surface of the activated carbon through forming hydrogen bond with water molecules (Deliyanni et al., 2015).

Among the functional group from the spectra includes are tabulated in Table 1:

Table 1: Functional group in SLSA

Functional group	Adsorption (cm^{-1})
Sulphate (S=O)	1412.86, 1386.33
Alkane (C−H)	2918.43
Carboxylic acid (C=O)	1718.42
Phenol (O−H)	1309.65

3.2 BET analysis of granular activated carbon (GAC)

BET analysis was performed to determine the area of total pore surface area. Determining the value of total pore surface area is important in order to make correlation between mesopores and the heavy metal removal capacity of AC. It is hypothesised that larger pore surface area will result in better removal due to the availability of adsorption area (Ching, 2011). It is expected that the surface area of a virgin GAC is larger than surfactant impregnated GAC. Impregnation of SLSA onto GAC will take adsorption region of the AC, reducing the overall surface area but increases its affinity towards cationic heavy metal ion like cadmium.

Table 2: Volume and surface area of GAC.

Pore volume (cm^3/g)	0.2331
Total area in pores (m^2/g)	72.58
Max pore volume at P/P_0 (cm^2/g)	0.4039
Micropores surface area (Dubinin-Radushkevich) (m^2/g)	975.56
Micropores surface area (Dubinin-Astakov) (m^2/g)	1030.57

The BET result shows that the total area of pores is rather small in comparison to other adsorbent usually used in the industry. Adsorbent such as zeolites and silica constantly used in wastewater treatment practice have rather high total pore surface area. The average zeolites pores surface area is 723 m^2/g while silica is lower at 262 m^2/g however still higher than GAC at 72.582 m^2/g (Kim et al. 2014). GAC is still a cheaper and simpler alternative in comparison to zeolites and silica despite has lower surface area that might translate to less efficient adsorption. Therefore, impregnating GAC with surfactant that can increases its affinity towards a certain pollutant is used to counter this problem.

3.3 Carbon-water attraction effect on cadmium ion removal

As can be seen from Table 3, virgin activated carbon showed a modest percentage of cadmium ion removal from the cadmium chloride solution, with average of 21.90% difference from the initial concentration of the solution. This could be attributed either to the good pore distribution with the carbon or it could be due to the removal of moisture (drying) increases the amount of available micropores that previously occupied by water molecules. According to Kose (2010), clusters of water usually found inside the pores of activated carbon, and these water clusters affect the ability of the surface forces to attract heavy metal molecules. Water is a polar component, allowing itself to attract or to be attracted by another polar or non-polar component (Pego et al., 2017). Despite the carbon has been dried, it was introduced back to moisture through the synthetic cadmium chloride solution where the water molecule once again clogged up the micropores which are the primary sites of adsorption (Karanfil & Dastgheib, 2004). This interaction of water and carbon has led to reduction of cadmium ion affinity and accessibility to the inner pores.

Table 3: Average removal percentage of cadmium ion.

Activated carbon	Average removal (%)
Virgin	21.90
SIAC at 10 ppm	7.70
SIAC at 25 ppm	25.85
SIAC at 50 ppm	29.25
SIAC at 75 ppm	32.54
SIAC at 100 ppm	32.51
SIAC at 125 ppm	37.87
SIAC at 150 ppm	37.66
SIAC at 175 ppm	37.34

Higher concentration of SLSA impregnated onto activated carbon increases the ability of the carbon to remove heavy metal as shown in Fig. 4. However, at 10 ppm SLSA impregnation, the cadmium removal is reduced significantly. Theoretically, the SLSA was unable to attract the cadmium ion since the Van der Waals forces is too weak due to its low concentration. The impregnated SLSA occupied the micropores of the activated carbon, leaving cadmium ion no space to be adsorbed. It can also be said that water molecule used to dilute the cadmium chloride takes up the adsorption surface of the carbon via bridging (Brennan et al., 2001). According to Brennan et al. (2001), isolated water molecule tends to bond with a surface site that is rich in oxygen. It increases the bulk phase density, attracting more water molecules and form clusters.

The situation remedied at higher SLSA concentration where the removal increases steadily. The amount of cadmium ion removed slightly decreases from 125 ppm to 175 ppm could be attributed to the difference in the activated carbon's sizes, since the GAC was not sieved before use. Therefore, it can be said that the concentration of SLSA that could improve activated carbon's ability to remove cadmium ion is at equilibrium in between 125 ppm and 175 ppm. Any higher concentration will not change the amount of cadmium removed from the solution of cadmium chloride.

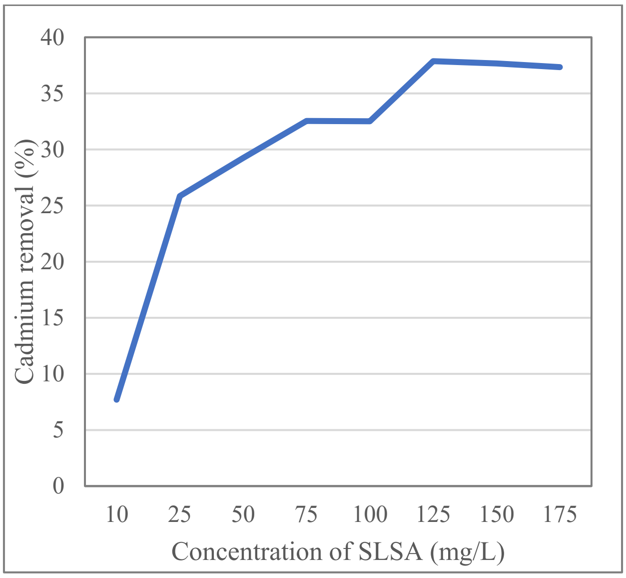

Fig. 4: Percentage of cadmium removal.

3.4 Adsorption capacity of SIAC

In view of the results from the removal of cadmium, a slight downward trend in the adsorption capacity was observed and illustrated in Fig. 5. This can be attributed to the varying sizes and shapes of the activated carbon used. In a comparative study by Lakdawala (2013) on particle activated carbon (PAC) and granular activated carbon (GAC), it is stated that PAC able to achieve 66.04% COD removal in comparison to GAC's 62.27%. The author emphasized how PAC have smaller sieve size and the irregularities of GAC sizes has contributed to this result. When conducting the experiment, 2 mg activated carbon was used but the sizes was not segregated. Thus, a sample with 2mg activated carbon where the sizes is smaller will have a better removal result in comparison to a sample with 2mg larger activated carbon.

According to a study by Kose (2010), there are 4 types of physical interaction that could lead to adsorption of heavy metal onto a surface of activated carbon, namely the Debye forces, Coulomb forces (dipole-dipole), Keeson energy and London Dispersion. Since Cadmium chloride is a polar molecule, it has a permanent dipole moment. SIAC also a charged molecule, the interaction between cadmium ion and SIAC's sulphate is governed mainly by the Coulomb forces. Coulomb forces are weak; therefore, it requires much of SLSA to be impregnated in the AC for it attract more cadmium ion.

The removal of cadmium ion can be attributed to 2 adsorptions mechanisms, physisorption and chemisorption. Since cadmium chloride is a polar molecule, it has a permanent dipole moment. Thus, the interaction between cadmium ion and SIAC sulphate is governed mainly by the Coulomb forces from physisorption mechanism. Coulomb forces are weak; therefore, it requires much of sulphate to be impregnated in the AC in order for it attract more cadmium ion. Given the probability that not all the pores of the AC filled with SLSA, it will be filled by either cadmium ion or water cluster. If it was filled with water instead of cadmium, thus explained why the removal of cadmium ion is reduced at a certain SIAC concentration.

On the other hand, chemisorption requires a certain degree of affinity from adsorbate to the adsorbent as a result of molecular orbital overlap. After impregnation, the adsorbent become SLSA instead of the activated carbon. The interaction between ionic compound such as cadmium and adsorbent such as SIAC could happen

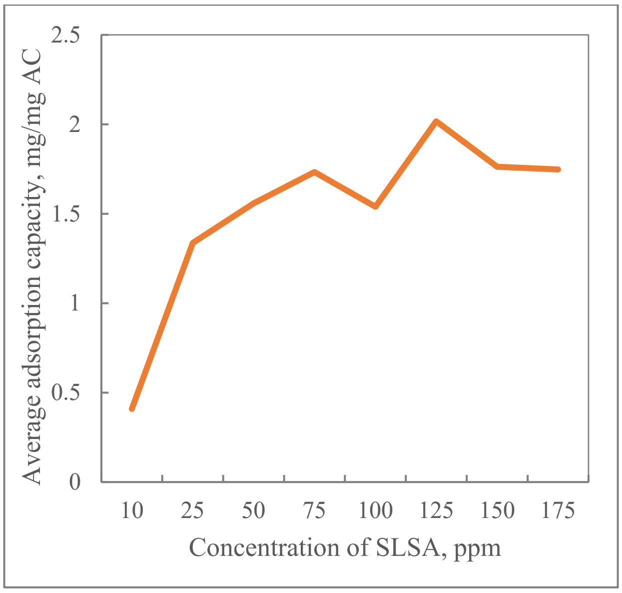

Fig. 5: Adsorption capacity of SIAC.

in form of electron donor-acceptor between carbonyl group (C=O) of a surfactant (Pego et al 2017). In the case of SLSA and $CdCl_2$, Cl replaces O, leaving cadmium to be taken by sulphate. The Na^+ attached to sulfonate group will undergo ionic exchange with cadmium, Cd^{2+} from $CdCl_2$ forming NaCl. This is also supported by Paria et al. (2004) that stated ionic exchange could happens in the reaction between surfactant's hydrophilic head with ion of the same charge.

pH of a solution plays important role on activated carbon's adsorption efficiency (Mahmoud et al. 2014). This is because pH influences the surface charge and the degree of ionization. The surface of activated carbon has a net charge, depending on the solution. Since the SLSA is dissolved in water, it became acidic. At low pH, the surface of carbon will be positively charged, allowing negatively charged anion to electrostatically adsorbed onto the surface. Therefore, the interaction is governed by electrostatic forces instead of dispersion interaction.

4.0 Conclusions

Improving the current industrial grade granular activated carbon capable of removing cationic heavy metal like cadmium to be more effective by impregnating with anionic surfactant was studied in this work. This is also reducing the dependency of the industry from using a chemical-based surfactant, instead using a plant-based one that is safer to use and less dangerous to the environment. The investigations had led us to believe that SLSA as a surfactant is effective in improving the adsorption capacity and the heavy metal removal percentage of GAC. The removal properties mainly attributed to the negatively charged head of SLSA that capable of attracting the positively charged cadmium ion. Therefore, it can be concluded that removing cadmium ion from aqueous solution can be enhanced using plant-based anionic surfactant impregnated activated carbon.

Acknowledgment

The authors would like to thank Universiti Teknologi MARA and the Ministry of Education Malaysia for the financial supports grant number 600-IRMI/5/3/LESTARI(039/2019).

References

A. Al-Alawy (2017). Comparative Study Between Nanofiltration and Reverse Osmosis Membranes for the Removal of Heavy Metals From Electroplating Wastewater. Journal of engineering (23), 25-32.

B. L. Mohammad (2018). Determination of Cadmium, Chromium and Lead from Industrial Wastewater in Kambolcha, Ethiopia using FAAS. Journal of Environmental Analytical Chemistry, 34-52.

E. Deliyanni, G. Kyzas, K. Triantafyllidis, & K. Matis (2015). Activated Carbons for the Removal of Heavy Metalions: A Systematic Review Of Recent Literature Focused On Lead and Arsenic Ions. De Gruyter Open Chem, 699-708.

Environmental Protection Agency. (1999). Choosing an Adsorption System for VOC: Carbon, Zeolites or Polymers. Technical Bulletin, 1-22.

G. Rashad, M. Mahmoud, & R. Sheha, (2017). Impregnated Activated Carbon for Adsorption of Gd(III) Radionuclides from Aqueous Solutions. particulate science and technology, 62-74.

H. Kose (2010). The Effect of Physical Factors on The Adsorption of Synthetic Organic Compounds by Activated Carbon and Activated Carbon Fibres. Clemson University Tigerprints, 133-145.

H. Liu, S. Feng, N. Zhang, & X. Du (2013). Removal of Cu(II) Ions from Aqueous Solution by Activated Carbon Impregnated with Humic Acid. Environmental science engineering, 198-234.

H. Yanagisawa, Y. Matsumoto, & M. Machida (2010). Adsorption of Zn(ii) and Cd(ii) Ions onto Magnesium and Activated Carbon Composite in Aqueous Solution. Applied science surface, 344-356.

I. Isik-Gulsak (2016). Investigation of Impregnated Activated Carbon Properties Used in Hydrogen Sulfine Fine Removal. Brazilian Journal Of Chemical Engineering, vol 33, 1-20.

Innofresh. (2017). Activated Carbon under the Microspcope. Retrieved from www.innofresh.com: https://innofresh.com/activated-charcoal/how-does-activated-charcoal-work/activated-carbon/

J.K. Brennan, K. T. Thomson, & Gubbins, K. E. (2001). Adsorption of Water in Activated Carbon: Effect of Pore Blocking and Connectivity. Langmuir, 5438-5447.

J. Kim, E. Park, J. Kim, J. Han, T. S. Kwon, Y.K. Park, & J. K. Jeon (2014). Isomerization of Endo-Tetrahydrodicyclopentadiene over y Zeolite Catalysts. Journal of the Korean Industrial and Engineering Chemistry , 66-71.

J. Gamboa-Carbalo, D. Valdes, K. Melchor-Rodriguez, & J. Ulises-Javier (2016). Theoretical Study of Chlordecone and Surface Groups Interaction in an Activated Carbon Model under Acidic and Neutral conditions. Journal of Molecular Graphic & Modelling, 83-93.

J. Matthis (2017). Activated Carbon Option. Retrieved from https://www.watertechonline.com/activated-carbon-options-0517/ May 25, 2017

M. Byambaa, E. Dolgor, K. Shiomori, & Y. Suzuki (2018). Removal and Recovery of Heavy Metals From Industrial Wastewater by Precipitation and Foam Separation Using Lime and Casein. Journal of Environmental Science and Technology, 1-9.

M. Lakdawala, & J. Lakdawala, (2013). Comparative Study of Effect of PAC and GAC on Removal of COD Contributing Component of Sugar Industry Wastewater. Research Journal Of Recent Sciences, 90-97.

M. Mahmoud, G. S. El-Deen, & M. Soliman, (2014). Surfactant-impregnated Activated Carbon for Enhanced Adsorptive Removal of Ce(IV) Radionucleoside from Aqueous Solution. Annals of Nuclear Energy, 134-144.

M. Pego, J. Carvalho, & D. Guedes (2017). Surface Modification of Activated Carbon and Its Impact on Applications. World Scientific, 1-10.

R. A. Bernhoft (2013). Cadmium Toxicity and Treatment. The Scientific World Journal, 97-112.

R. Brooks, M. Bahadory, F. Tovia, & H. Rostami (2010). Removala of Lead from Contaminated Water. International Journal Of Soil, Sediment and Water, 1-12.

S. Malekmohammadi, A. Mirbagheri, & M. Ehteshami (2016). Comparison of Silica, Activated Carbon, And Zeolite Adsorbents in the Removal Of Ammonium, Iron, COD, Turbidity and Phosphate Pollutants, and Investigating The Effect Of Discharge on the Removal of Pollutants. International Journal of Humanities and Cultural Studies, 667-679.

S. Abo-El-Enein, M. Eissa, A. Diafullah, M. Rizk & F. Mohamed (2009). Removal of Some Heavy Metals Ions from Wastewater by Copolymer of Iron and Aluminium Impregnated with Active Silica Derived from Rice Husk Ash. Journal of Hazardous Material, 574-579.

S. Ching, M. Yusoff, H. A. Aziz, & M. Umar (2011). Influence of Impregnation Ratio on Coffee Ground Activated Carbon As Landfill Leachate Adsorbent for Removal of Total Iron and Orthophosphate. Desalination, 225-234.

S. Lin, W. Chen, M. Cheng, M., & Q. Li (2013). Investigation of Factors That Affect Cationic Surfactant Loading on Activated Carbon and Perchlorate Adsorption. Colloids and surfaces: A physicochemical and engineering aspect, 236-242.

S. Paria, & K. C. Khillar (2004). A Review on Experimental Studies of Surfactant Adsorption at the Hydrophilic Solid-Water Interface. Advances in Colloids and Interface Science, 75-95.

T. Osmari, R. Gallon, M. Schwaab, E. Barbosa-Coutinho, J. Severo, & J. Pinto (2013). Statistical Analysis of Linear and Non-Linear Regression for the Estimation of Adsorption Isotherm Parameters. Adsorption Science & Technology, 433-458.

W. Chen, L. Pan, L. Chen, Z. Yu, Q. Wang, & C. Yan (2014). Comparison of EDTA and SDS as Potential Surface Impregnation Agents for Lead Adsorption by Activated Carbon. Applied Surface Science, 1-8.