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

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A.

Abstract— ***Activated carbon is 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 is industrial grade granular type tested without grinded or sieved. The surfactant preparation and the impregnation were done at 60^0C. The heavy metal removal test conducted at 30^0C to mimic normal weather temperature of Malaysia. The granular activated carbon was characterized using BET (Brunauer-Emmet-Teller) while the surfactant chemical properties analyzed using FTIR. The aqueous solutions before and after the test were analyzed using AAS (atomic absorption spectroscopy). The result obtained has shown that SIAC at 125ppm has the highest cadmium removal averaging 37.87% of cadmium removed. The lowest removal shown by SIAC at 10ppm with an average of 7.70%.***

Keywords— Sodium Lauryl Sulfoacetate, Plant-based anionic surfactant, granular activated carbon, Cadmium Chloride.

II. Introduction

Activated carbon has always been successful in removing contaminants in wastewater to a certain degree, but there is still some contaminant left. Sometimes a second treatment is required (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 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 site 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 also present in small deposits inside soils and rocks. According to OSHA (occupational safety and health administration), up to 300000 industrial workers exposed in the US alone, mostly are from the metal refining, smelting, battery and paint production, basically any industries 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 factory and company is built to cater the demand. These industrial activity produces 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 site, smelting, metal-plating and even refining operations (Brooks et al, 2010). Even at small amount, cadmium could cause severe poisoning symptoms to adults, kids and infants. If cadmium entered 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. That is why in some cases, the symptoms are permanent and sometimes can lead to death.

Sodium Lauryl Sulfoacetate (SLSA) is a chemical or commonly known as the surface-active agent, usually used as an alternative to Sodium Lauryl Sulfate (SLS). It is manufactured from the combination of both palm oil and coconut. It is yet to be used as an agent to be impregnate 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. These negatively charged surfactant will bind a positively charged particle or ion. In this study, the positively charged substance is cadmium ion.

Impregnating the granular activated carbon with SLSA is based on the principle of surface adsorption. Adsorption is a process where ions, molecule 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 demands a better removal solution or a better alternative to the current existing 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.

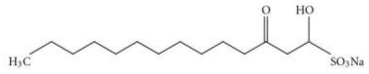

Figure 1: structure of SLSA

SLSA mainly comprises of straight chain of alkane, hydroxyl group, carbonyl group and sulfonate group just as shown in figure 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.

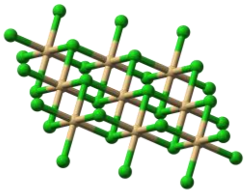
Figure 2: structure of $CdCl_2$

Cadmium chloride ($CdCl_2$) is an ionic compound that form crystal with rhombohedral symmetry (figure 2). It is very soluble in water. Thus, the aqueous solution is easy to prepare.

III. METHODOLOGY

A. 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 0.25g of Cadmium Chloride with distilled water.

Different concentration of Sodium Lauryl Sulfoacetate solution was prepared by diluting SLSA in 200ml of distilled water.

B. Impregnation of SLSA to AC

The SLSA solution was by incubating it at 60^0C and shaken at 130rpm 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 allowed to cool before adding 2mg of granular activated carbon onto it. The flask containing activated carbon and SLSA was wrapped with aluminium foil before the impregnation process started. This is to avoid any interaction between SIAC and light that may cause the reaction to deviate.

The wrapped flasks incubated at 60^0C overnight at 130rpm. A schematic representation of laboratory works is shown on figure 3 below:

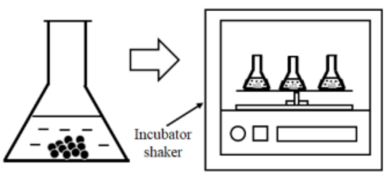

Figure 3: representation of experimental works

C. Cadmium removal from aqueous solution

The resulting activated carbon called SIAC then dried using oven overnight at 60^0C. The steps were repeated with virgin activated carbon. Freshly dried activated carbon then added onto 100ml cadmium chloride solution. The mixture was then shaken at 130rpm at 30^0C for 6 hours.

D. 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.

After the incubation, 1ml of the resulting solution is sampled for AAS (name, supplier) test.

E. Determination of cadmium removal percentage and adsorption capacity

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

$$\%R = [(C_i - C_o)/C_i] \times 100$$

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:

$$q_t = [(C_i - C_t) \times V]/m$$

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.

IV. RESULTS AND DISCUSSION

A. Characterization of SLSA as a surfactant

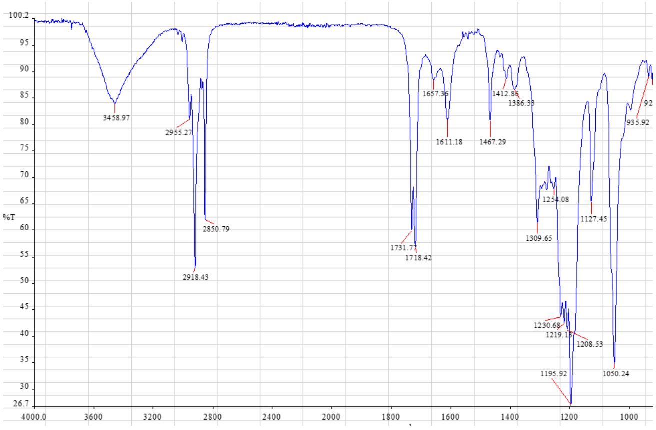

Figure 4: IR spectra of SLSA

As can be seen from figure 4, SLSA IR spectra has shown that it is a type of anionic surfactant with sulfonate functional group (S=O) can be seen at 1412.86 cm^{-1} and 1386.33 cm^{-1}. Sulfonate 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 could also help in increasing the affinity of cadmium towards activated carbon by preventing moisture molecules or water from adsorbed onto the surface of the activated carbon by forming hydrogen bond with water molecules as stated by Deliyanni et al. This can be attributed due to its hydrophilic nature that attract water onto itself.

Among the functional groups from the spectra includes:

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

Table 1: Functional group in SLSA determined from the IR spectra

B. 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.

The result of the BET analysis can be seen below:

Pore volume, cm^3/g	0.2331
Total area in pores, m^2/g	72.582
Max pore volume at P/P_0, cm^2/g	0.403963
Micropores surface area, m^2/g (Dubinin-Radushkevich)	975.5684
Micropores surface area, m^2/g (Dubinin-Astakov)	1030.5798

Table 2: Volume and surface area of GAC

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. A study by kim et al in 2014 indicates that 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.

GAC is still a cheaper and simpler alternative in comparison to zeolites and silica despite has lower surface area that might translated to less efficient adsorption. Therefore, impregnating GAC with surfactant that can increases its affinity towards a certain pollutant is used to counter this problem.

C. Carbon-water attraction effect on heavy metal removal

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

Table 3: Average removal percentage of cadmium ion

Virgin activated carbon have 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, 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. This is further supported by Pego et al's statement, saying that water is a polar component, allowing itself to attract or to be attracted by another polar or non-polar component. 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 primary site of adsorption. This interaction of water and carbon has led to reduction of cadmium ion affinity and accessibility to the inner pores.

D. Percentage of Cadmium removal

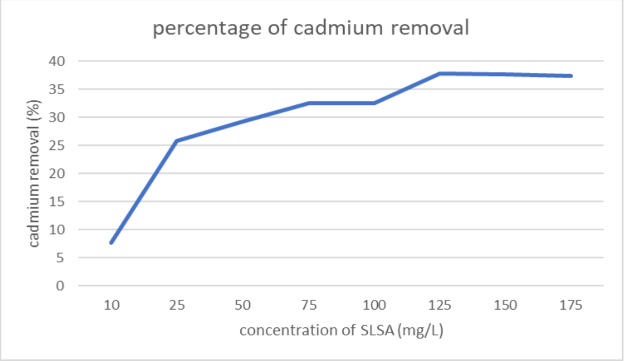

Figure 5: Percentage of cadmium removal

Higher concentration of SLSA impregnated onto activated carbon increases the ability of the carbon to remove heavy metal as shown in figure 5.

However, at 10ppm 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 but not strong enough to enhance the carbon's affinity towards cadmium. It can also be said that water molecule used to dilute the cadmium chloride takes up the adsorption surface of the carbon via bridging. According to Brennan et al in their study of water adsorption on activated carbon in 2001, isolated water molecule tends to bond with a surface site that are 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 125ppm to 175ppm could be attributed to the difference in the activated carbon's sizes, since the GAC was not sieved before used. 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 125ppm and 175ppm. Any higher concentration will not change the amount of cadmium removed from the solution of cadmium chloride.

E. *Adsorption capacity of SIAC*

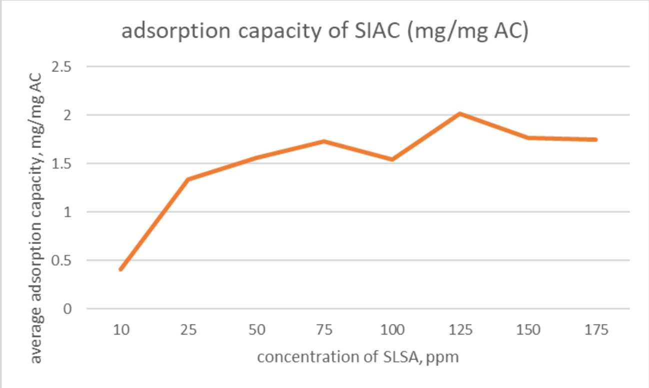

Figure 6: Adsorption capacity of SIAC

From figure 6, a slight downward trend can be observed. This can be attributed to the varying sizes and shapes of the activated carbon used. In a comparative study by Lakdawala et al 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 Hatice Kose, 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 sulfate is governed mainly by the Coulomb forces. Coulomb forces are weak, therefore it requires much of SLSA 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 (Kose, 2010). The AC's surface might be hydrophobic as stated by Mahmoud et al (2014), however it can interact with water molecule via bridging and filled by water clusters. This explains why the removal of cadmium ion is reduced at a certain test

Chemisorption requires a certain degree of affinity from adsorbate to the adsorbent as a result of molecular orbital overlap. After impregnation, the adsorbing properties are governed by SLSA instead of the activated carbon. However, some of the free pores are still available for adsorbing cadmium ion.

In a study by Pego et al in 2017, it was stated that the interaction between ionic compound such as cadmium and adsorbent such as SIAC could happen in form of electron donor-acceptor between carbonyl group (C=O) of a surfactant. In the case of SLSA and $CdCl_2$, Cl replaces O, leaving cadmium to be taken by Sulfate. 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.

According to Mahmoud et al study in 2014, pH of a solution plays important role on activated carbon's adsorption efficiency. 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 it is in. 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.

V. Conclusion

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.

VI. Acknowledgement

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