HEAVY METALS IN REFINERY WASTEWATER: ASSESSMENT AND TREATMENT USING DIATOMACEOUS EARTH

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Abstract

In refining crude oil, freshwater is applied in distillation, hydration, desalination, system cooling, firefighting and other cleaning operations. The Kenya Petroleum Refineries Limited consumes huge quantities of freshwater daily for various applications leading to generation of contaminated effluents. The effluents contain a cocktail of contaminants such as aliphatic hydrocarbons, polycyclic aromatic compounds, dissolved gases such as Hydrogen Sulphide like algae, fungi, and heavy metals. Except for heavy metals, the refinery wastewater treatment plant is able to remove most of the other contaminants from the wastewater through a combination of processes including filtration, coagulation, sedimentation, softening, de-aeration, chlorination, desulfurization, bioremediation, and ion-exchange. However, these techniques are expensive, generate huge amounts of sludge, and are also not effective for removal of trace levels of heavy metals. Using inductively coupled plasma coupled with optical emission spectroscopy (ICP-OES), the effluents were found to contain significant levels of Iron, Cadmium, Chromium, Manganese, Nickel, Lead, Vanadium and Zinc. Although the installed wastewater treatment could reduce heavy metals load to trace, effluents storage in the tank farm prior to disposal leads to accumulation of heavy metals over time. Diatomaceous earth (DE) was applied to treat the heavy metals from the tank farm to within allowable limits as recommended by the World Health Organisation. Hence DE should be applied to effluents exiting the wastewater treatment plant prior to storage in the tank farm.

Keywords: *Adsorption, Diatomaceous Earth, Heavy Metals, ICP-OES, Refinery Wastewater*

Introduction

Crude oil refining consumes huge amounts of freshwater in various unit operations and unit processes such as desalting, distillation and thermal and catalytic cracking. For every volume of crude oil processed, the amount of wastewater produced is 0.4-1.6 (Ishak et al., 2012) times as much. Untreated petroleum refining wastewater (PRW) contains a cocktail of contaminants including hydrocarbons (benzene, toluene, ethyl benzene, xylenes, and polycyclic aromatic hydrocarbons), phenols, dissolved minerals and heavy metals. Most of these contaminants are toxic and possible carcinogens (Zarooni and Elshorbagy, 2006; El-Naas et al., 2014). Therefore, before discharge into the environment or municipal sewerage system (MSS), PRW needs to be treated to reduce contaminant load to acceptable levels. The Kenya Petroleum Refinery Limited (KPRL) located in Mombasa-Kenya is responsible for processing and storage of petroleum products. It serves Kenya and the wider East African region. Freshwater at KPRL is supplied by the Mombasa Water and Sewerage Company Limited (MWSC). In addition to petroleum processing operations, freshwater at KPRL is also used in firefighting and general cleaning operations. In order to comply with set environmental regulations, the PRW is first treated before discharge into MSS for further treatment at the Kipevu Sewage Treatment Plant (KSTP), Mombasa. The KPRL wastewater treatment plant employs a combination of physical and chemical processes including filtration, coagulation, sedimentation, softening, de-aeration, chlorination, desulfurization, bioremediation, and ion-exchange. These processes are expensive and require specialized skills for operation. Notably, low concentrations of heavy metals are not easily removed by most of these processes.

Adsorption of contaminants onto activated carbons, zeolites, resins, polymers and natural biomass is a cost-effective and easy to operate process. Adsorption process involves transfer of contaminants from the bulk aqueous phase to the adsorbent surface or into the adsorbent pores. Adsorption is essential in water treatment since it transfers a contaminant from a dilute solution to a small concentrated volume which can be subjected to further chemical treatment.

Although activated carbon is a widely used adsorbent in water treatment applications due to its high porosity and surface area (> 1000 m^2/g), it is expensive and its regeneration results in significant loss (20-30%). Therefore, cheaper adsorbents derived from locally available materials are preferred alternatives especially in low and middle income countries such as Kenya.

Diatomaceous earth (DE) is a natural adsorbent that has been applied in wastewater treatment applications. Fine DE is amorphous mineral clay with high porosity and permeability, low thermal conductivity and density and moderate surface area (10-30 m^2/g). DE mined from Kariandusi, Kenya contains mainly Silicon dioxide (SiO_2 (> 70%) and 10% Aluminum Oxide (Al_2O_3 (9-11%) (Jemutai-Kimosop et al. 2020). DE is cheap and readily available and has its Natural and modified forms been extensively used as adsorbent for water treatment in removal of fluoride (Simiyu et al. 2023). Equally, carbamazepine (Jemutai-Kimosop et al. 2020) and E. coli and rotavirus (Simiyu et al. 2023) have been used. In the current work, DE will be evaluated for heavy metals removal in PRW obtained at the KPRL.

Materials and methods

Sample preparation

The DE was obtained from African Diatom Industries Limited (ADIL) based at Kariandusi, Kenya. It was cleaned, dried at 120 °C for 24 h and ball milled to fine powder of < 300 µm mesh size. 200 g of the powder was dispersed in 500 mL distilled water. In order to remove dissolved ions, the pH of the suspension was adjusted to 11 using 0.1 NaOH and agitated on an orbital shaker at 300 rpm for 1 h. The mixture was then centrifuged at 5000 rpm to obtain the solid residue which was dried at 120 °C for 24 h. The dry solid was suspended in 500 mL aqueous solution acidified with 0.1 M H_2SO_4 at pH 1. The solid was recovered by centrifugation and washed with distilled water until the supernatant pH was 6.5. The clean DE was dried at 120 °C for 24 h and stored in an air-tight container for further use.

Characterization of the adsorbent

To determine pH, 5 g DE in 50 mL of 1 M KCl was agitated on an orbital shaker at 180 rpm for 24 h. 10 mL of the extract was used for pH measurement using a pH meter S400 (Mettler-Toledo). The point-of-zero charge (pHpzc) of DE was determined by alkalimetric method (Hosseinzadeh and Mohammadi, 2015).

Heavy metals analysis from KPRL wastewater

Sampling glass bottles (1 L) were washed with detergent in running tap water, rinsed with distilled to eliminate any traces of contaminants. Further cleaning of the sampling bottles was done using aqua regia (mixture of concentrated HCl and concentrated HNO_3 in 3:1 volume to volume) and rinsed with double distilled water. Composite sampling of 1 L of PRW was obtained from 7 interceptors over a period of three months (June to August, 2014) namely the main interceptor, blending area interceptor, tank farm interceptor, input tank age interceptor, interceptor 2, DAF 2781 interceptor of the wastewater treatment plant and raw water (municipal freshwater supplied by MWSC) interceptor. Immediately after collection, 2 mL of concentrated HNO_3 (65%) was added to preserve the metals in their metallic form and minimize their precipitation.

For sample dissolution and digestion, 100 mL of water sample was mixed with 10 mL of aqua regia, 1 mL of perchloric acid and incubated at 80 °C in a water bath. After acid-digestion, the sample was mixed with 50 mL double distilled water. Heavy metal content was analyzed using inductively-coupled plasma-optical emission spectrometry (ICP-OES).

Continuous adsorption experiments

All experiments were carried out in triplicate under identical conditions. Composite sampling was performed to collect wastewater for filtration by DE. A 1 m column with internal diameter of 3.5 cm was filled with 400 mg DE to a bed height of about 75 cm. The composited PRW samples were filled to the 1 m mark of the column and allowed to flow through the DE bed filter under gravity. Eluates from the column were collected periodically and subjected

to ICP-OES for heavy metal analysis. Sorption capacity at bed breakthrough point was calculated using equation 1:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad ($$

Where q_e refers to sorption capacity at breakthrough (mg/kg), C_0 and C_e are the initial and equilibrium metal concentrations (mg/L), V is the volume of PRW (L) and m is the mass of adsorbent (kg).

Analytical techniques

Multi-element standards of analytical grade were applied for preparation of a series of standard solutions. Using ICP-OES (PerkinElmer Optima 8000), emission readings of heavy metals in standard samples were determined and calibration curves prepared. The readings were determined at emission wavelengths of 226.5 nm, 220.4 nm, 213.9 nm, 267.7 nm, 239.6 nm, 267.6 nm, 231.6 nm and 292.4 nm for cadmium (Cd), lead (Pb), zinc (Zn), chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), and vanadium (V), respectively. For determination of heavy metals in refinery wastewater, 25 mL of the PRW sample was mixed with 2% HNO_3 in distilled water and 4 mL aliquot applied for ICP-OES measurement. Control samples were prepared by mixing only 25 mL distilled water and 2% HNO_3.

Results and discussion

Composited samples from seven interceptors (sampling points) at KPRL were collected and analyzed for heavy metals. Eight heavy metals namely Cd, Pb, Zn, Cr, Fe, Mn, Ni and V were detected in the samples. The concentration levels of these metals at the different sampling points are presented in Figure 1.

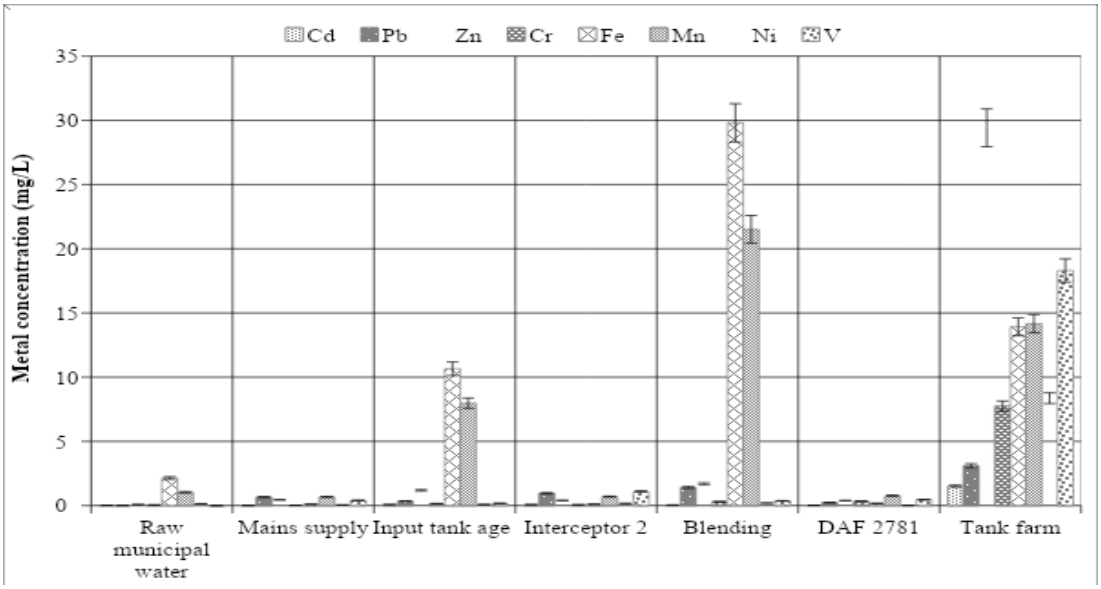

Figure 1: The levels of heavy metals in refinery wastewater at the Kenya Petroleum Refineries Limited (pH = 6.5; volume of composited sample = 1 L; number of replicate experiments = 3)

As can be seen in Figure 1, no significant levels of heavy metals were found in raw municipal water and the storage mains supply. The main source of freshwater at KPRL is supplied by MWSC. The input tank age and interceptor 2 are channels for distributing crude oil from the supplier to the processing zone. No significant levels of heavy metals were found in interceptor 2. The crude storage input tank age had high amounts of Fe and Mn. The blending area showed even a higher amount of Fe and Mn (≈ 28-30 mg/L) with increased levels of other metals. The blending area is where all crude operations are carried out. This observation clearly indicates that heavy metals are derived from refinery operation rather than from freshwater supplied by MWSC. After processing, the effluents are passed through a wastewater treatment plant. The KPRL wastewater treatment plant uses a combination of treatment processes including filtration, coagulation, sedimentation, softening, de-aeration, chlorination, desulfurization, bioremediation, and ion-exchange. The DAF 2781 was selected as the sampling point for effluents exiting the wastewater treatment plant. As can be seen in Figure 1, nearly all the heavy metals are removed by the treatment plant to below 1 mg/L which is within the world health organization (WHO) limits. The tank farm is where all

treated effluents are stored before discharge to KSTP. The storage takes a couple of days or weeks. Although the wastewater treatment plant is able to reduce heavy metal load to recommended WHO limits, it can be seen in Figure 1 that heavy metals load in tank farms is significantly high. This could be due to trace heavy metals accumulation over time. The DAF 2781 shows trace levels of heavy metals. Since the effluents are not immediately released from the tank farm, trace levels of heavy metals leaving the wastewater treatment plant accumulate over time.

In order to treat heavy metals load in refinery wastewater, composited samples from the tank farm were passed through DE in column studies. The wastewater flow through the DE bed filter in the column was done under gravity flow. The results are shown in Figure 2.

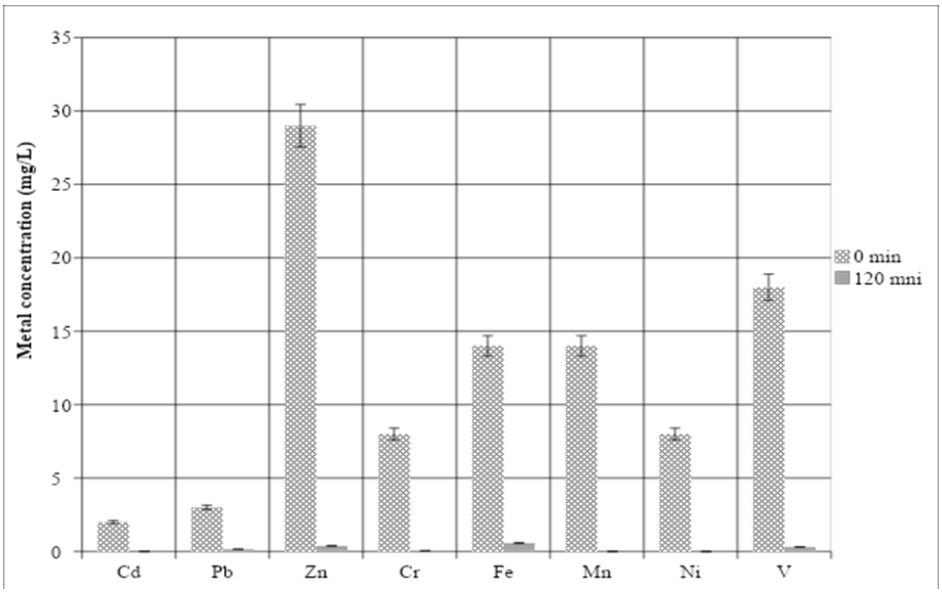

Figure 2: Removal of heavy metals from refinery wastewater by a fixed bed of diatomaceous earth under gravity flow (1 m glass column with 3.5 cm internal diameter; pH = 6.5; DE bed height = 75 cm; DE mass = 400 mg)

Figure 2 shows heavy metal removal by DE bed filter under gravity flow. A contact of time of about 120 min was essential for heavy metals removal by DE under the experimental conditions. This shows that heavy metals could easily be removed by adsorption onto DE. DE is a microporous clay mineral rich in Aluminum and Silicon with moderate surface area

(20-30 m^2/g) (Jemutai-Kimosop et al., 2020). Since the point of zero charge of DE was found to be 3.5, it implies that under the experimental conditions (pH = 6.5), negative charged species are responsible for adsorption of heavy metals. The adsorption process is due to electrostatic forces between the positively charged metal ions and negative charged surface groups on DE.

Conclusions

Eight types of heavy metals namely Cadmium (Cd), Lead (Pb), Zinc (Zn), Chromium (Cr), Iron (Fe), Manganese (Mn), Nickel (Ni) and Vanadium (V) were detected and quantified in refinery wastewater at KPRL. Among all the metals, Fe and Mn had the highest concentrations. The heavy metals were found to have resulted from refinery operations and not from freshwater supplied by the MWSC. The installed wastewater treatment plant at the refinery is able to reduce heavy metals load to within WHO recommended limits. However, storage of treated wastewater at the tank farm in the refinery leads to accumulation of trace metals to higher levels with time. Thus, DE bed filters should be applied to effluents exiting the wastewater treatment plant prior to storage in the tank farm.

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SYSTEMATIC LITERATURE REVIEW ON APPLICATION PROGRAM INTERFACE - BASED ANDROID MALWARE DETECTION

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Abstract.

Over the years, various malware detection approaches have been proposed in a bid to address evolving malware threats landscape in android operating system. Systematic literature reviews to analyze these detection approaches have been carried out, but none have been tailored to identifying challenges with android malware detection based on the use of Android program interface (API) features, hence there is no aggregated information on what work has been done by researchers in this area. This research, therefore, presents a systematic literature review on API feature based android malware detection literatures between 2018 to 2022 collected systematically using PRISMA frameworks. This study seeks to identify the challenges faced in android malware detection over the years, methodologies used to address them and limitations of API based feature detection. These useful insights documented in this research will serve as valuable resources which researchers can leverage on to improve the detection of android malware.

Keywords: *Android Platform, Malware Detection, Application Program Interface, PRISMA Framework*