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CHARACTERISATION AND ADSORPTION OF HEAVY METALS IN INDUSTRIAL EFFLUENT FROM PAINT AND COATING INDUSTRIES IN NAIROBI, KENYA

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***Abstract*—A study was conducted to estimate current status of physico-chemical characteristics of effluents emanating from three paint factories within the main industrial area of Nairobi County. The effluents were analysed for temperature, pH, oil and grease, total suspended solids (TSS), chemical oxygen demand (COD), total phosphorus, total nitrogen, total sulphur and heavy metal ions and compared to Kenyan effluent discharge standards. The results were as follows: pH 6.48 - 6.89, temperature 28.07-28.30 °C, COD 916.77-1881.20 mg/L, total phosphorus 145.00-149.32 mg/L, TSS 6382.33-7395.33 mg/L, oil and grease 3525.00-6374.33 mg/L, total sulphur 72.62-73.41 mg/L, total nitrogen 1586.67-4442.67 mg/L. Heavy metal concentrations were 3.03-4.18 mg/L, 2.07-3.04 mg/L and 5.38-17.21mg/L respectively for cadmium, chromium and lead. Adsorbent was made from waste rubber tyres and tested for its suitability in removing three heavy metal ions namely cadmium, lead and chromium from the effluent samples by varying adsorbent dosage, pH and contact time.**

Keywords— **Physico-chemical, Effluents, Adsorbent**

I. INTRODUCTION

Industrial and population growth in developing countries have led to environmental degradation due to discharge of polluted wastewater directly to the environment without any or adequate treatment (Begam et al., 2009). Paint and other coating manufacturing industries are examples of effluents-releasing sources of metal contaminants (Vinod et al., 2012**).**Heavy metals have become a major environmental pollutant of late with even trace concentrations causing toxic impacts when exposed to terrestrial and aquatic ecology (Begam et al., 2009) Albeit acute heavy metals exposure is uncommon through skin or ingestion, small amounts can be detrimental (Appenroth,2010).Paint can be described as a distinctive homogenous formulation of four components namely binder, pigment, solvent and additives that produce a specific end product having a unique properties. When applied to a substrate, it gives an essential characteristic of adhesion, elasticity and durability when the paint dries (Talbert, 2008). The huge effluents discharged from these paint and coating industries play a major role in polluting Ngong and Nairobi rivers with untreated effluents especially loaded with heavy metals (Ogilo et al.,2017), which eventually get into the environment and bioaccumulate in the human system via ingestion or nutritional hierarchy since they are not biodegradable (Fu and Wang,2011).

Many conventional methods employed in the treatment of domestic and industrial effluents include and are not limited to coagulation, ion exchange, electro-coagulation, membrane filtration and reverse osmosis. These methods however are expensive to set up and maintain, produce large volume of wastes which do not meet effluent standards (Akunwa et al., 2014, Fu and Wang, 2011**).** Therefore waste tyres based activated carbon has found its application in up taking of harmful trace contaminants from industrial and domestic effluents (Belgacem et al.,2013)

The objective of this study was therefore to determine the levels of contaminants in wastewater generated by paint manufacturing industries situated in Nairobi's industrial area and the use of waste tyre based adsorbent in metal pollution reduction.

II. METHODS AND MATERIAL

2.1 Study Area

The study site was within the City of Nairobi which is in Nairobi County. The county lies in the geographic coordinates of 01°17′10″S 36°49′02″E and altitude of 1600 to 1860 m above sea level. It is the smallest county covering an area of 696 Km2 besides being the most densely inhabited by approximately 3.9 million people (KNBS, 2015). Three paint manufacturing companies allowed sampling to be done within their premises on condition that their identity was not disclosed. They were labeled A (1º18’00”S 36º50’23”E), B (1º18’29”S, 36º50’50”E) and C (1º15’25”S, 36º52’54”E) respectively. They were situated along Enterprise Road and Outer Ring Road, all within the city. Company A was about 3km from company B and 12.6 km from C. Company B and C were 13 km apart.

2.2 Effluent Sampling

The grab samples were drawn using an auto sampler to a depth of about 50 cm from the waste water receiving tanks. The tanks act as meeting points for each of the companies’ releases from washings prior to discharge into municipal drainage. The samples were transferred into 2.5L clean amber glass bottles assigned codes EMR, ESD and ESP respectively. The samples were then taken to KEPHIS Analytical Chemistry Laboratory (ACL) and stored at 5ºC awaiting analysis.

2.3 Waste tyres sampling and preparation

Waste tyre material weighing about 5.0 kg was collected from Kariokor open market of coordinates 1º16’42”S, 36º50’06”E in Nairobi County and packed in a brown manila paper. They were washed with detergent solution and rinsed with 2 litres of distilled water. Washed samples were sun-dried for 3 hours, cut into small pieces about 0.5 to 1.0 cm and analysed as per Bronislaw, (2016).

2.4 Physico-Chemical Analysis

The effluents were analysed for temperature, conductivity, pH, oil and grease, total suspended solids (TSS), chemical oxygen demand (COD), total phosphorus, total nitrogen, total sulphur and heavy metal ions.

Total nitrogen was determined using classical Kjeldahl method. Total sulphur was determined by measuring the turbidity of the samples using UV-Vis spectrophotometer, Perkin-Elmer Lambda 25 model. Phosphorous was analysed as per AOAC 978.01, by complexing using ammonium molybdate-vanadate mixture then measuring using UV-Vis spectrophotometer, Perkin-Elmer Lambda 25 model.

Oil and grease was determined using liquid-liquid extraction method using hexane. Total suspended solid was analysed using gravimetric method. Chemical oxygen demand was digested using Hanna COD Reactor and analysed using Hanna Multiparameter photometer HI 83099 model.

The pH and temperature of effluents was measured at site using Hanna HI1225 EC/pH meter and DT-9 digital thermometer.

The amount of cadmium, chromium and lead was determined by measuring the absorbance of the previously digested samples at their respective wavelengths using AAS, Thermo Electron model.

2.5 Determination of optimum adsorption conditions

The experiment was carried out in batches at different pH, contact time and adsorbent dosage to establish optimum adsorption process conditions. Adsorbent weights ranging between 0.1 and 0.7 g were added into seven 150ml plastic bottles containing 100 ml of wastewater solution, sonicated at room temperature for 1 hour and filtered.5ml of the filtrates were extracted using 10ml and 4ml of concentrated nitric acid and perchloric respectively The cool digests were transferred into 250 ml volumetric flask and the residual metal contaminant using AAS, Thermo Electon model at respective wavelengths.

Waste waters of 100ml were mixed with 0.5 g of adsorbent sonicated at 180rpm for 30, 45 60, 75, 90, 105 and 120 minutes at room temperature and filtered. 5ml of the filtrates were extracted using 10ml and 4ml of concentrated nitric acid and perchloric respectively. The cool digests were transferred into 250 ml volumetric flask and measured for Cd, Pb and Cr using AAS, Thermo Electon model at respective wavelengths.

Waste water pH were adjusted to pH 2, 3, 4, 5, 6, 7, 8 and 9 using 0.1 M HCl and 0.1 M NaOH solutions, sonicated at 180 rpm and filtered.5ml of the resultant filtrate were extracted using 10ml and 4ml of concentrated nitric acid and perchloric respectively The cool digests were transferred into 250 ml volumetric flask and the residual metal contaminant using AAS, Thermo Electon model at respective wavelengths.

III. RESULTS AND DISCUSSION

3.1 Results of wastewater physico-chemical analysis

The results of the physicochemical characterization of wastewater from the selected paint factories are summarized in Table 3.1. The mean values are accompanied by standard deviations of triplicate measurements.

Table 3.1 Summary of physicochemical results.

Parameter	**ESD**	**EUP**	**EMR**	**3RD Schedule Limits**	**5th Schedule Limits**
pH	6.48 ± 0.14	6.89 ± 0.04	6.80±0.03	6.5-8.5	6-9
Temperature (0 C)	28.3 ±	28.13 ±	28.07±0.	Ambient Temp.	20-35

	0.12	0.15	12	±3	
COD (mg/L)	916.77 ±28.15	1881.20±24.82	1163.00 ±17.54	50	1000
Oil &grease (mg/L)	6374.33±23.03	4654.33±46.05	3525.00 ±17.52	nil	10
TSS (mg/L)	7395.33±364.23	6382.33±658.01	7159.00 ±768.56	30	250
Phosphorus (mg/L)	148.69 ±2.50	149.32 ±1.22	145.00±3.61	2.0	30.0
Nitrogen (mg/L)	4442.67±70.47	1586.67±29.14	3042.67 ±21.39	13.5	2.0
Sulphur (mg/L)	73.41±1.71	73.29±3.77	72.62±3.11	0.1	2.0
Lead (mg/L)	12.05±0.41	5.38±1.41	17.21±1.67	0.1	1.0
Cadmium (Cd) (mg/L)	4.18±0.09	3.03±0.83	3.47±1.04	0.1	0.5
Chromium (Cr) (mg/L)	2.07±0.66	2.29±0.24	3.04±0.83	2.0	2.0

The pH of the effluent ranged between 6.48 and 6.89 across the sampling sites, indicating slight acidity. The values complied with the regulatory body in Kenya of 6.5-8.5 as per as per KS2290:2011. The temperature range was also complaint with the 3rd and 5th schedule limits. Chemical oxygen demand (COD), total suspended substance (TSS), phosphorus (P), nitrogen (N), total sulphur (S) concentrations across the samples were above set limits by the regulatory body for effluent discharge standards into the environment and into public sewers for the parameters under analysis. The levels of lead in the samples ranged between 5.38 mg/L to 17.21 mg/L. Sample EMR had the highest concentration of 17.21 mg/L, ESD 12.05mg/L and EUP 5.38 mg/L. Analytical results for lead in paint industries in Addis Ababa manifested high levels with the highest value being 53.40mg/L. The high concentration of lead was attributed to high employment of inorganic lead pigment during manufacturing (Pravin et al., 2011) and the use of lead driers. The Water Quality Regulation 2006 set limits for lead in the environment and public sewers discharge at 0.1 mg/L and 1.0 mg/L respectively. Therefore, the values obtained were not compliant with set limits. The levels of cadmium in the samples ranged from 3.03 mg/L to 4.18 mg/L with sample ESD having the highest concentration of 4.18 mg/L and EUP having the lowest value of 3.03 mg/L. EMR concentration was 3.47 mg/L. Tesfalem and Abdrie, (2017) in their study of five paint industries effluents in Addis Ababa observed levels of cadmium ranging from 1.58 mg/L to 69.22 mg/L. As reported by Pravin et al, 2011, the high concentration may be attributable to cadmium-containing compounds used as pigments in paint manufacturing. The values obtained were not compliant with 3rd and 5th schedule standards. Chromium concentration in the samples were found to range from 2.07 mg/L to 3.04 mg/L. Sample EMR showed the highest concentration of 3.03 mg/L while ESD was the lowest at 2.07 mg/L. EUP concentration was 2.29 mg/L. These values are comparable with 1.5 to 9.32 mg/L obtained by Tesfalem and Abdrie, (2017) in their analysis of five paint industries effluents in Addis Ababa. Chromium-containing inorganic pigments are used in paint manufacture, hence the presence of chromium in the effluents (Pravin et al., 2011).Values obtained did not comply with effluent discharge limits.

3.2 Results of optimum adsorption conditions

Adsorbent dosage

It was observed from Figures 1-3 that the rate of metal adsorption increased with increase in adsorbent dosage. The increase in adsorption as stated by Dimpe et al., (2017) may have been as a result of increase in exchangeable sites for adsorption in the activated carbon. Saturation point was reached when the available active sites were depleted hence no further significant adsorption could take place (Mousavi et al., 2017). The maximum removal of cadmium was 84.93 % (ESD), 88.78 % (EUP) 62 and 90.49 % (ESD) at the optimum dosage of 0.5 % w/v. The optimum dosage for lead was observed at 0.5%w/v with the maximum removal at 79.92%, 78.81% and 83.96 % for ESD, EUP and EMR respectively. Chromium was desorbed optimally at 0.6 %w/v adsorbent with 68.60 % (ESD), 77.73% (EUP) and 93.42% (ESD).

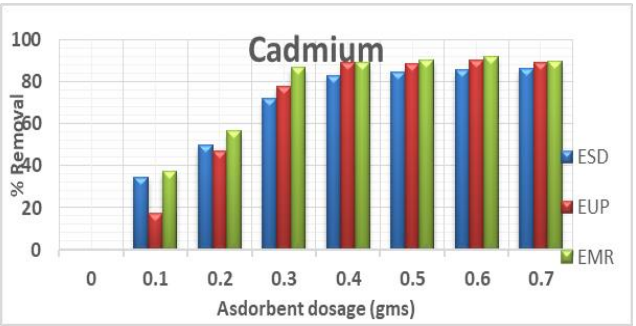

Fig.1: Adsorbent dosage on the adsorption of Cadmium

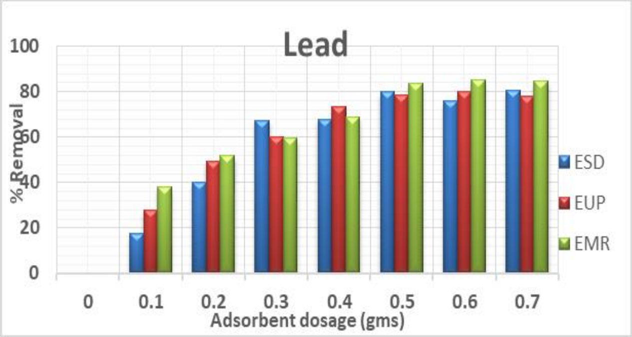

Fig.2: Adsorbent dosage on the adsorption of Lead

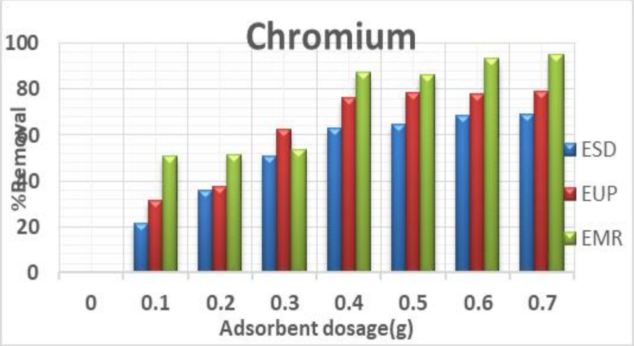

Fig.3: Adsorbent dosage on the adsorption of Chromium

Contact time

It was noted that the contaminants removal increased with increase in contact time (Fig 4-6).

This was necessitated by the availability of adsorption sites and significant mass transfer driving force, although this is slowed down as the process approaches equilibrium due to increase in the clogging of the active sites which slows down the movement of adsorbate (Nurulhuda et al.,2009). The maximum cadmium uptake from the aqueous solution was observed at 81.60% (ESD), 90.10% EUP and 85.88 % EMR at equilibrium. The optimum contact time was observed at 90 minutes with no significant adsorption of the contaminant.

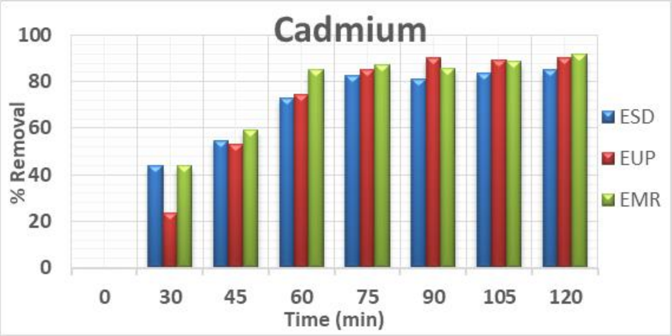

Fig 4: Effect of contact time on the adsorption of Cadmium

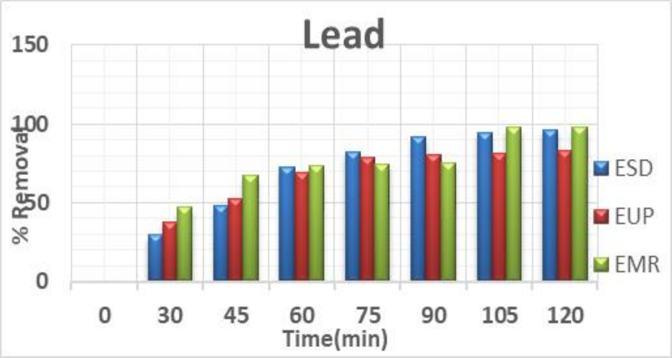

Fig 5: Effect of contact time on the adsorption of Lead

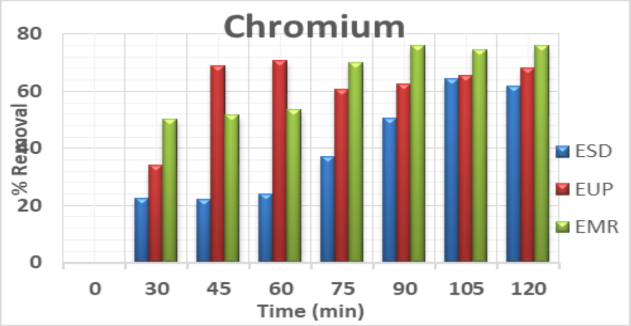

Fig 6: Effect of contact time on the adsorption of Chromium

pH range

The metal ions uptake increased as pH increased as shown indicated in Figures 7-9. This was due to reduction in the net competition between hydronium ion and the metal ion (Onoja and Idoko, 2017). The adsorbent surface is deprotonated and hence negatively charged and this escalates electrostatic attraction of the adsorbate (Lohani et al., 2008). There was remarkable increase in cadmium and lead removal as the solution pH was elevated. However, for chromium, when pH was increased above 6, there was a sudden decline in adsorption. This may have been attributed to the fact that the covalent coordination existing between Cr^{3+} ions and functional groups existing on the surface are weak in basic environment (Attia et al., 2010). The weak bond is due to competition for active sites by both chromate and hydroxyl anions hence reduction in the adsorption (Salam et al., 2011). Maximum cadmium uptake at pH 6 was 84.21% (ESD), 89.77% (EUP) and 90.20 %(EMR).Lead was adsorbed optimally at pH 5 corresponding to 86.64 %(ESD), 79.55% and 80.88% (EMR) while chromium maximum uptake was 73.91 % (ESD), 91.27% (EUP) and 84.87% (EMR) at pH 6.

The extent of metal ion uptake under study was in agreement with the works of Onoja et al, (2017**)**, Mousavi et al, (2017**)** and Dimpe et al,(2017)

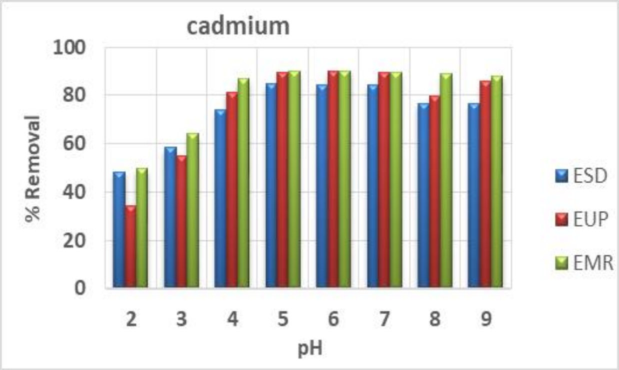

Fig.7: Effect of pH on the adsorption of Cadmium

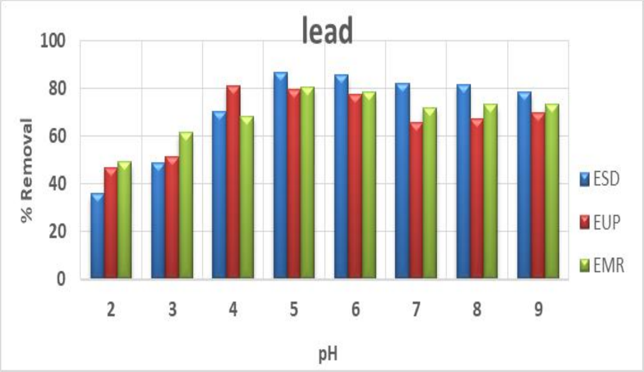

Fig 8: Effect of pH on the adsorption of Lead

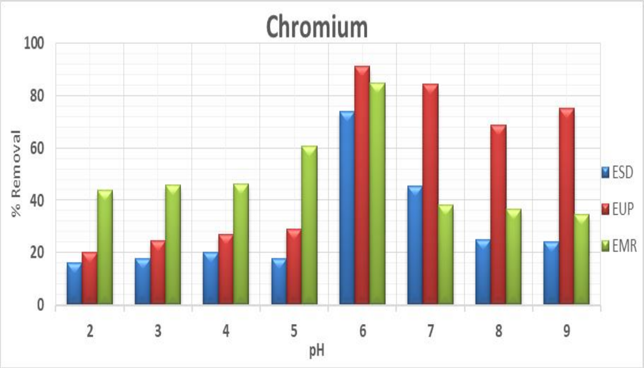

Fig 9: Effect of pH on the adsorption of Chromium

IV. CONCLUSION

From the results of physicochemical analysis, apart from pH and temperature, most of the parameters studied were found to be higher than the maximum limits set by the Environmental Management and Coordination Act of 2006 for discharge into public sewers and the environment. These parameters namely; TSS, COD, Total Nitrogen, Total Phosphorus, oil and grease, Sulphur and heavy metals were above the permissible of limits set by the Act. These high levels of metallic and organic contaminants in the effluents, are likely to raise the respective levels in the public sewers into which the effluents are drained into, consequently degrading the environment and human ecology.

The batch adsorption experiment was dependent on the contact time, pH and adsorbent dosage. The optimum conditions of adsorption of metal ions was found to be pH range of 56, adsorbent dosage of 0.5-0.6 %w/v and contact time of 90-105 minutes across all the metal ions. It was clearly shown that activated carbon made from waste tyres was an effective adsorbent in the removal of chromium, lead and cadmium from paint effluent though not to the level that meets the standard set by the regulatory the body in Kenya. The waste tyres which are readily available can be transformed into a useful water and effluent treatment material hence a low cost way of up taking metal ions from industrial effluents.

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