ARTICLE IN PRESS

Ain Shams Engineering Journal xxx (xxxx) xxx

Contents lists available at ScienceDirect

Ain Shams Engineering Journal

journal homepage: www.sciencedirect.com

Civil Engineering

Degradation of Cd, Cu, Fe, Mn, Pb and Zn by *Moringa-oleifera*, zeolite, ferric-chloride, chitosan and alum in an industrial effluent

A.H. Jagaba [a,b], S.R.M. Kutty [a], G. Hayder [c,*], L. Baloo [a], A.A.S. Ghaleb [a], I.M. Lawal [b,d], S. Abubakar [b], B.N.S. Al-dhawi [a], N.M.Y. Almahbashi [a], I. Umaru [b]

[a] *Department of Civil and Environmental Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia*
[b] *Department of Civil Engineering, Abubakar Tafawa Balewa University Bauchi, Nigeria*
[c] *Institute of Energy Infrastructure (IEI), Universiti Tenaga Nasional (UNITEN), 43000 Kajang, Selangor Darul Ehsan, Malaysia*
[d] *Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow, UK*

ARTICLE INFO

Article history:
Received 14 March 2020
Revised 6 May 2020
Accepted 4 June 2020
Available online xxxx

Keywords:
Coagulation
Flocculation
Sedimentation
Palm Oil Mill Effluent
Heavy Metals
Jar Test

ABSTRACT

Coagulation-flocculation constitute the backbone process in most water and wastewater treatment plants. This study focused on determining the optimum coagulant dose for *moringa oleifera* seed extract, zeolite, ferric chloride, chitosan and aluminium sulphate coagulants through the coagulation, flocculation and sedimentation process. It also ascertain which coagulant has the potential for higher removal of Cd, Cu, Fe, Mn, Pb and Zn. The test was conducted with initial pH, settling time, coagulant aid dose, rapid mixing speed & time, slow mixing speed & time as constant parameters. The determination of heavy metals concentration in POME was carried out using an Inductively Coupled Plasma (ICP) and an Atomic Absorption Spectrometer (AAS). The process efficiency was assessed in terms of percentage removals for the heavy metals examined. The results proved that chitosan, $FeCl_3$, alum, zeolite and *moringa oleifera* had the concentrations of 400, 2000, 1000, 1000, and 4000 mg/L as the optimum dosage respectively.

1. Introduction

Oil palm development in Malaysia has been remarkable. Starting off as ornamental, the crop has developed into a multibillion ringgit industry [1]. Palm oil is an palatable vegetable oil naturally reddish in colour extracted from the mesocarp of the fruit of an oil palm species called Elaeis guineensis [2]. Palm mesocarp oil is 41% saturated and is one of the few highly saturated vegetable fats. It is a mostly used for cooking in tropical belt of Africa, Southeast Asia and parts of Brazil. It is also used as a raw material for both food and non-food industries [3,4]. As a result of the dramatically rise in world oils and fats market, there is significant growth and expansion in palm oil industries. South East Asia is known as the major production of palm oil. The total oil palm planted areas in Malaysia have been increased to 4.0 million hectares in year 2005 [5]. Growth of palm oil industry in Malaysia has been phenomenally increasing from 400 ha planted in 1920 to 54,000 ha in 1960 [6]. Palm oil is extracted from fresh fruit bunches (FFB) by mechanical process. The modern palm oil mill of today is predominantly based on concepts developed in the early 50 s. An average size FFB weighs about 20–30 kg with about 1,500–2,000 fruits. FFBs are harvested according to harvesting cycles and delivered to the mills on the same day. Crude palm oil quality is dependent on the care taken after harvesting, most especially on the handling of the FFBs. A palm oil mill produces crude palm oil and kernels as primary products and biomass as a secondary product. The capacity of mills varies between 60 and 100 tons FFB/h [7].

One (1) tonne of crude palm oil production requires 5–7.5 tonnes of water, leading to the generation of large quantity of wastewater, commonly referred to as palm oil mill effluent (POME) which amount to over 50% of the initial fresh water supplied. Based on a report of palm oil production in 2005 (14.8 million tonnes), an average of about 53 million/m^3 POME is being produced each year in Malaysia [8]. Solid waste materials and by-products generated from the palm oil extraction process are empty fruit bunches (EFB) – 23% of FFB, potash – 0.5% of FFB, palm kernel – 6% of FFB, fibre – 13.5%; and shell – 5.5% of FFB [9].

* Corresponding author.
E-mail addresses: ahjagaba@gmail.com (A.H. Jagaba), gasim@uniten.edu.my (G. Hayder).

Peer review under responsibility of Ain Shams University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.asej.2020.06.016
2090-4479/

Please cite this article as: A.H. Jagaba, S.R.M. Kutty, G. Hayder et al., Degradation of Cd, Cu, Fe, Mn, Pb and Zn by *Moringa-oleifera*, zeolite, ferric-chloride, chitosan and alum in an industrial effluentMoringa-oleifera, zeolite, ferric-chloride, chitosan and alum –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.06.016

The waste materials emanating from oil palm processing also consist of oil palm trunks (OPT), oil palm fronds (OPF), POME, empty fruit bunches (EFB), palm press fibre (PPF), shell palm oil mill sludge (POMS), and palm kernel cake (PKC). Fibre, shell, decanter cake and EFB accounts for 30, 6, 3, and 28.3% of FFB respectively [10].

POME is generated mainly from oil extraction, washing and cleaning processes in the mills and consists of water soluble components of palm fruits as well as suspended cellulosic materials such as fat, palm fibre, grease and oil residues [11,12]. It is a known fact that palm oil industry produces POME resulting from palm fruit bunches as shown in Fig. 1.

POME is a thick brownish colour liquid mostly discharged at temperature of between 80 and 90° C containing high concentration of organic matter with COD ranging from 45,000–65,000 mg/L, 5-day BOD 18,000 to 48,000 mg/L and oil & grease > 2,000 mg/L. The COD: N: P ratio is around 750:7.3:1. It represents the highest by-products generated by palm oil mills, which is about 21% [13]. POME comprises combination of the wastewater principally generated and discharged from different major processing operations. POME quantity produced is about 60% for every tonne of fresh fruit bunches (FFB) processed [14].

The POME industry have been classified as a major source of water pollution in Malaysia, generating effluent that contains harmful bacteria, organic waste, inorganic waste and toxic substances (heavy metals) [15]. Among all the contaminants present in POME, heavy metals requires the most attention because of its negative environmental impacts and the prevailing health challenges [16]. Common heavy metals present in POME are cadmium, chromium, copper, iron, manganese and zinc have been causing severe environmental problems because they are carcinogenic and non-biodegradable [17]. Thus, industries are required to comply with standard regulations and ensure that effluents generated are within permissible limits before discharging into the environment. This is to reduce the negative impacts on the environment. To achieve this, appropriate disposal methods are required [18]. As a critical source of water pollution when discharged into waterways without treatment, POME has to be thoroughly treated.

Malaysia, with over 300 palm oil mills, large volumes of effluent generated could give significant impact to the environment since the characteristics of POME are extremely polluting. This leads to certain areas having more stringent requirements (BOD < 20 mg/L). Anaerobic digestions in ponding systems or aerobic systems have been the main practice of treating POME. However, the emission of greenhouse gases (GHG) (CH_4 and CO_2) to the atmosphere from these systems has been recently reported as a source of air pollution from the palm oil mills [19]. The systems are only able to bring the BOD levels to < 100 mg/L [13]. Therefore, tertiary technologies have been developed as new systems towards achieving the discharge standards required by regulatory bodies in a sustainable manner [12].

According to the literature, quite a number of these tertiary treatment technologies involving both physical, chemical and biological processes have been employed [58] for the removal of heavy metals from POME. They are: reverse osmosis, facultative pond system, electrochemical techniques, ultrafiltration, bioreactors, advanced oxidation, sequence batch reactors (SBR), anaerobic digestion adsorption, coagulation etc [20,21]. However, most of these technologies are surrounded by various limitations such as toxic sludge generation, high cost, low removal efficiency, long duration for treatment process and high-energy consumption [22].

Among the treatment methods highlighted above [59], coagulation, flocculation and sedimentation is the most widely used for the removal of heavy metals from POME because the method is cost effective, extremely efficient, and flexible. It has less land area requirement, great enrichment ratio, and natural affinity to metal ions. Coagulation-flocculation constitute the backbone process in most water and wastewater treatment plants with the purpose of improving the separation of particulate species in downstream processes such as sedimentation and filtration [23]. The process is a pre-treatment method capable of reducing total pollution strength of industrial effluents by analytical techniques [16,20].

The necessity for the improvement of the coagulation system has led to the development of various natural and chemical coagulants. Several studies have demonstrated the advantages and disadvantages of these coagulants in POME treatment. Findings revealed that most natural coagulants are biodegradable, abundant in the environment, multi-functional and have low toxicity [24]. these natural coagulants to include; plant fibers of the date palm (PFDP) [25], algal biomass (ulva sp.), nipa palm nut, rice husk, bamboo, bone char, eggshell, palmyra palm nut, java plum seed, peat, water chestnut shell, oil palm, bagasse, corncob, tea waste, pomegranate peel, neem leaf [11,16], palm oil fuel ash and eggshell powder [26], paan masala, naswar, nicotine [27].

To prove the capability of various coagulants towards efficient heavy metal degradation, this study focused on comparing chitosan, *moringa oleifera* and zeolite (natural coagulants) with aluminium sulphate and ferric chloride (chemical coagulants) for the removal of Cd, Cu, Fe, Mn, Pb and Zn from POME through coagulation, flocculation and sedimentation process. Thus, the objectives of the study are to characterize the POME, treat the POME, evaluate the removal efficiencies and finally compare the performance of the natural and chemical coagulants.

(a) (b)

Fig. 1. (a) Fresh fruit bunches on an oil palm tree and (b) Pam oil seeds waiting for processing at palm oil mill.

2. Materials and methods

2.1. POME sample collection

Wastewater used for this study was POME obtained from an Oil Palm Mill located in Malaysia. The POME samples were transported on ice bags to the laboratory for storage and subsequent characterization [28]. Samples cooled for preservation at approximately 4 °C to avoid biodegradation due to microbial action. Sufficient quantity was withdrawn from the preserved sample after it is allowed to reach room temperature (27–30 °C), analysed for their characteristics and chemical properties before the start of the experiments. 500 mL of fresh POME were characterized and then used in the jar tests [29]. Fig. 2 below describes the study outline.

2.2. Materials

Characterization and analysis of samples before, during and after treatment require several apparatus and reagents. The following apparatus were used in this study; GAST DOA-P404-BN filtration Apparatus, DAIKI Sciences SHAKER, Separator funnel, Filter paper, A stirring machine with six paddles or magnetic stirrer, 100 push–pull syringe pump. Others are digital reactor block (DRB 200), HQ440d HACH pH Meteraluminum weighing dishes, Test tubes, Drying Oven, Thermal resistant plastic container, scale for weighing chemicals particle size analyzer brand CILAS, pipets, HACH DR6000 Spectrophotometer, analytical balance, Stopwatch, desiccator and flocculator [53–56].

Reagents used in this study were; sulphuric acid, sodium hydroxide, petroleum ether, acetic acid, potassium dichromate, n-Hexane, mercury powder and distilled water. Coagulant used are aluminium sulphate, ferric chloride, zeolite, chitosan powder, *moringa oleifera* seeds. Pictorial views for alum, chitosan and zeolite in powder and structure form are shown in Figs. 3–5 below.

The initial characterization of POME focused on the following parameters: pH, Temperature, Cd, Cu, Fe, Mn, Pb and Zn and the result displayed in Table 1.

2.3. Methods

APHA standard methods were strictly adhered to using the analytical methods approved by Department of Environment (DOE) Malaysia, United States Environmental Protection Agency (USEPA) [57,60] and World Health Organization (WHO) [30,31]. Table 2 summarized the equipment, standard and analytical methods adopted for variables to evaluate the performance of the various coagulants after conducting the jar test based on Cd, Cu, Fe, Mn, Pb and Zn removal.

2.4. Preparation of samples

Laboratory grade $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeCl_3$ were obtained after which stock solutions were prepared by following the USEPA procedure for enhanced coagulation [32].

A mining company supplied the zeolite samples utilised. The crushed rock-like form of the original zeolite was ground as fine

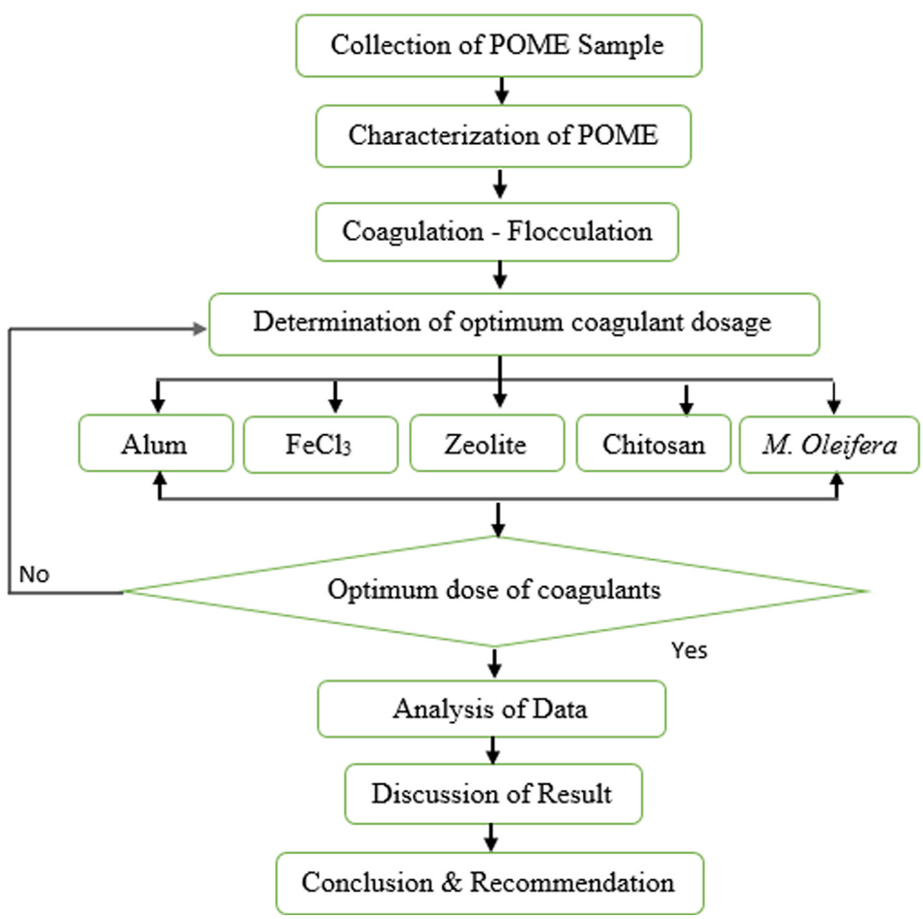
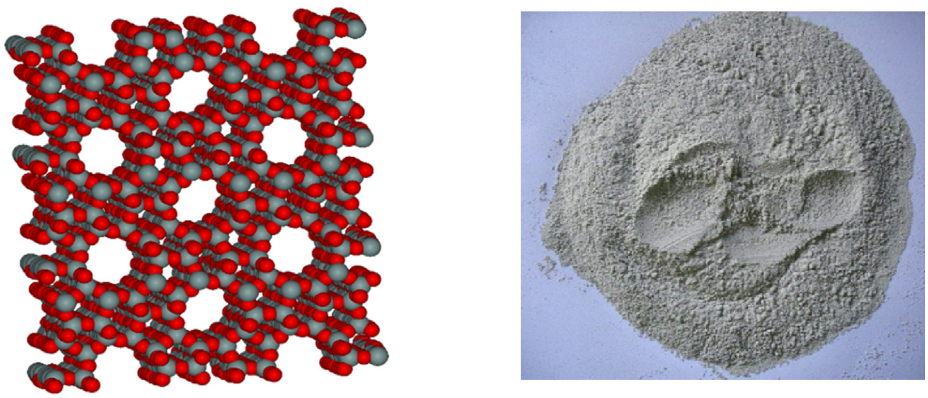


Fig. 2. Flowchart for the study outline.

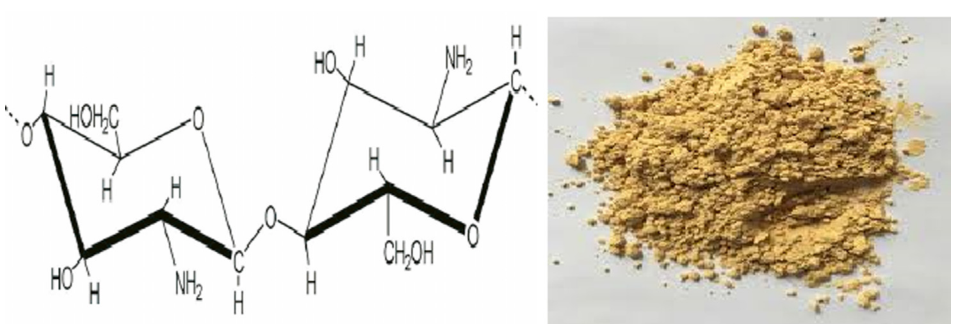
(a) (b)

Fig. 3. (a) Alum crystal and (b) Alum powder.



(a) (b)

Fig. 4. (a) Zeolite structure and (b) Zeolite powder.



(a) **(b)**

Fig. 5. (a) Chitosan structure and (b) Chitosan powder.

Table 1
Initial Characteristics of Raw POME.

Parameter	pH	Temperature °C	Mn (mg/L)	Fe (mg/L)	Cu (mg/L)	Pb (mg/L)	Cd (mg/L)	Zn (mg/L)
Conc.	4.50	49.5	8.216	63.14	0.823	0.026	0.007	3.554

as possible using a crusher and a Ball Mill. It was further pulverised and sieved to obtain particle sizes of 63 µm. The zeolite was then submerged for 24 hrs in 1 M aqueous NaCl to enhance its cation exchange capacity. Material sample washed with distilled water, rinsed and subsequently placed at 105 °C for approximately 24 hrs in an oven to clear it of impurities [33]. Dried for two hours in a desiccator before use, sample characterized by X-ray diffraction (XRD) [34].

Table 2
POME quality parameters, standard Methods, analytical method and equipment.

Variable	Standard	Analytical method	Equipment
pH	APHA 4500H + B	Electrometric Method	Portable pH Meter
Temperature	APHA 2550B	Temperature of Water	Thermometer
Iron	APHA 3500-Fe B	Atomic absorption	Polarized Zeeman
Zinc	APHA 3500-Zn B	spectrophotometry	Atomic Absorption
Lead	APHA 3500-Pb D	(AAS)	Spectrophotometer
Manganese	APHA 3500-Mn B		ZA3000 Series
Copper	APHA 3500-Cu C		
Chromium	APHA 3500-Cr B		

The study used the purchased powdered chitosan for the experimentation purpose. Stock solution was prepared by dissolving 1.5 g of chitosan powder in 150 mL of 0.1 M HCl solution. The solution agitated with a magnetic stirrer at 100 rpm to ensure complete dissolution. Further dilution with 150 mL of distilled water produced a solution comprising 5.0 g/L chitosan per ml of solution [35].

Acquired *Moringa oleifera* dry seeds, was cleaned and ground to a fine powder. It was subsequently screened through 0.8 mm – 2.5 mm mesh. Soxhlet apparatus was used to magnify the extraction of dried *moringa oleifera.* for about 8 h. The stock solution for *moringa oleifera* cake after extracting oil through the dissolution of 5 g of the cake in a 100 mL distilled water was prepared. Extracting the highly active coagulant agents required a blender and the mixture stirred for about 120 s. *Moringa oleifera* seeds pastes were filtered using the Muslin cloth before adding into POME sample [36].

2.5. Jar test

The design used was experimental laboratory research with a jar test with controls the design approach [37]. The standard jar test device displayed in Fig. 6 during the investigation to coagulate fresh POME using various types of coagulants. The POME samples were homogeneously mixed and fractioned into beakers each containing 500 mL of suspension and subsequently measured for Cd, Cu, Fe, Mn, Pb and Zn to represent the initial concentration.

Six different doses of aluminium sulphate coagulant (1000, 2000, 3000, 4000, 5000 and 6000 mg/L) were poured into beakers containing raw POME and rapidly mixed at a speed and time of 250 rpm and 3 min, respectively. Slow mixing speed and time of 30 rpm and 30 min adopted. The suspension was then allowed to settle for 60 min [38]. 5 mL of an anionic polymer was added to each sample during the slow mixing period [39,40]. Samples withdrawn from the top of the supernatant from each beaker to measure Cd, Cu, Fe, Mn, Pb and Zn. The tests were also performed using the original pH values and at ambient temperature [41].

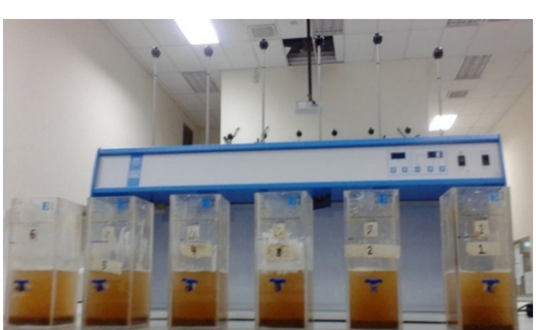


Fig. 6. Jar Test Apparatus for POME Coagulation.

Eqs. (1) & (2) were used to determine the removal of heavy metals as follows:

$$\text{Heavy metal concentration},\ C_e = C_o - C_1 \tag{1}$$

where (C_e) = [initial concentration (C_o)] – [final concentration (C_1) at given tine (hrs) interval].

$$Re = \frac{C_o - C_e}{C_0}\ x\ 100\ \% \tag{2}$$

where,
Re = metal removal efficiency (%)
C_o = initial metal concentration
C_e = residual metal (mg/L) concentrations at equilibrium

Evaluation of the process performance for determination of optimum dose for alum was based on the highest percentage of Cd, Cu, Fe, Mn, Pb and Zn removal from the sample. The coagulation-flocculation procedure was repeated using different doses of ferric chloride, zeolite, chitosan and *moringa oleifera* coagulant.

3. Results and discussion

3.1. Effect of alum dose

Several operating factors such as initial pH of POME, effluent concentration, coagulant dose, settling time, slow stirring speed and temperature were observed and studied to optimize the treatment performance via coagulation– flocculation using alum. Fig. 7 shows removal efficiencies at different doses of alum in the removal of Zn, Fe, Pb, Cu, Cd and Mn in the POME sample. Results showed that the increase of alum dose increases the removal efficiency until the optimum dose was reached where the removal efficiency start to decrease with the increase of alum dose. Alum dose of 4000 mg/L provides the highest removal percentages of Pb, Cd and Mn as 91.27%, 95.75% and 92.54% respectively while dose of 3000 mg/L provides highest removal percentage Zn as 80.47%. Dose of 5000 mg/L provides highest removal for Cu at 86.79% with no much difference from 86.05% obtained at 4000 mg/L. However, 89.51% was obtained at dose of 1000 mg/L as the highest removal efficiency and subsequently decreases with increase in alum dose. This implies that higher alum doses results to less Fe removal. From the results obtained for this experiment, it can be concluded that the optimum dose of Alum is 4000 mg/L.

3.2. Effect of ferric chloride dose

Removal efficiencies at different doses of $Fecl_3$ in the removal of Mn, Zn, Cu, Cd and Pb in the experimental sample are being shown in Fig. 8. Results showed that the increase of ferric chloride dose

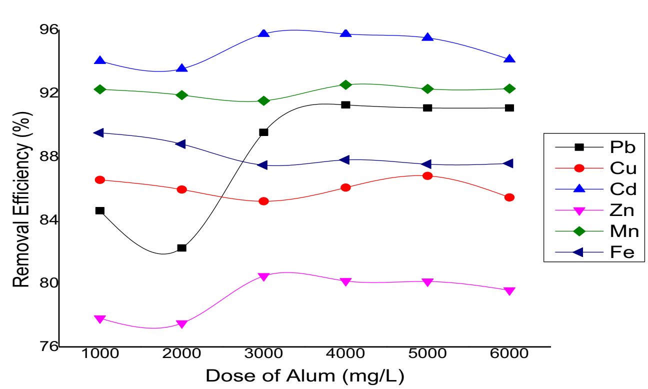


Fig. 7. Contaminants removal efficiencies by Alum.

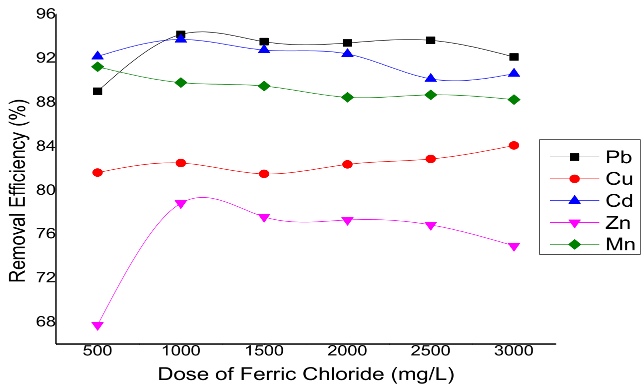


Fig. 8. Contaminants removal efficiencies by Ferric chloride.

increases the removal efficiency until the optimum dose was reached where the removal efficiency start to decrease with the increase of ferric chloride. Ferric chloride dose of 1000 mg/L provides the highest removal percentages of Pb, Cd and Zn as 94.17%, 93.71% and 78.81% respectively. Mn achieved best removal efficiency of 91.23%, at 500 mg/L respectively and subsequently decreases as the $Fecl_3$ dose increases. Highest Cu removal of 84.07% was obtained at the last dose of 3000 mg/L which signifies that Cu requires much higher dose to achieve better removal. From these results, it can be deduced that 1000 mg/L dose of $FeCl_3$ is the optimum due to its best performance in Pb, Cd and Zn removal.

3.3. Effect of chitosan dose

Chitosan like most other coagulants, showed continuous removal efficiency until the optimum dose was reached. Dose of 400 mg/L provides the highest removal percentages of Pb, Cd, Mn and Fe as 89.15%, 94.62%, 91.67% and 90.49% respectively. Best Zn removals of 83.28% was experienced at 350 mg/L as can be seen in Fig. 9 below. 82.96% removal was obtained at 2500 mg/L dose as the highest removal efficiency. It subsequently decreases with increase in chitosan dose which implies that chitosan is not suitable for Cu removal. Obtaining best removal efficiencies at 400 mg/L for most heavy metals examined implies that the dose is the optimum required for the treatment of POME.

3.4. Effect of moringa oleifera dose

Fig. 10 shows removal efficiencies at different doses of *moringa oleifera* in the removal of Zn, Fe, Pb, Cu, Cd and Mn in the POME

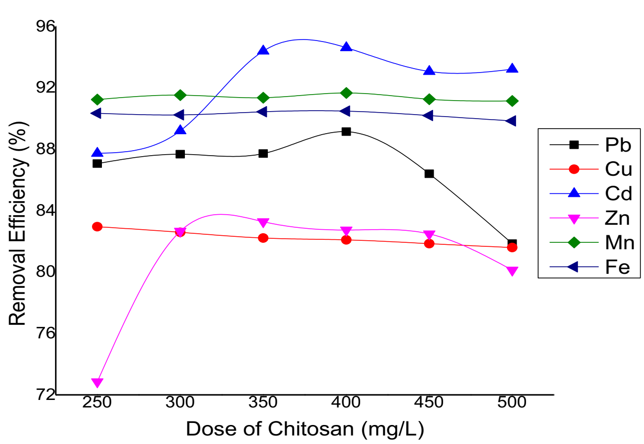


Fig. 9. Contaminants removal efficiencies by Chitosan.

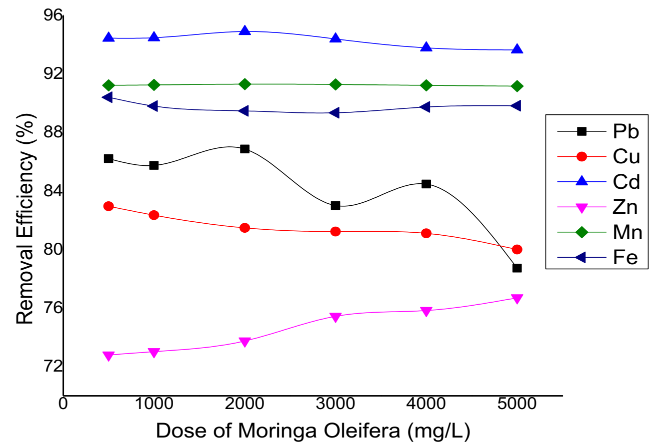


Fig. 10. Contaminants removal efficiencies by *Moringa oleifera.*

sample. Results showed that the increase of *moringa oleifera* dose increases the removal efficiency until the optimum dose was reached where the removal efficiency start to decrease with further dose increment. *Moringa Oleifera* dose of 2000 mg/L provides the highest removal percentages of Pb, Cd and Mn as 86.87%, 94.91% and 91.31% respectively. Zn removal efficiency was increasing continuously as the *moringa oleifera* dose is being increased up to the last dose of 5000 mg/L which obtained 76.70% removal. 82.96% and 90.41% removal were obtained at dose of 500 mg/L as the highest removal efficiencies for Cu and Fe which subsequently decreases with increase of *moringa oleifera* dose. From the results obtained for this experiment, it can be concluded that 2000 mg/L dose of *moringa oleifera* is effective in heavy metals removal.

3.5. Effect of zeolite dose

Zeolite is seen as a potential adsorbent for natural gas due to the ability of the micro porous structure to adsorb molecules selectively, depending upon the size of the pore window. Some of the most common mineral zeolites are heulandite, analcime, stilbite, clinoptilolite, natrolite, chabazite and phillipsite [42]. Acording to [43], (metallic ions sorbent behavior of natural zeolite has been studied by several researchers, and it has been recognized as a promising sorbent for heavy metals. In this study, zeolite showed significant increase in removal efficiencies until the optimum dose was reached. Fig. 11 illustrates that 1000 mg/L of zeolite provides the highest removal percentages for Cd and Fe as 89.87% and 86.34% respectively. Zn removal efficiency continuously increases as zeolite dose is being increased up to the last dose of 1200 mg/L which obtained 79.17% removal. However, Pb, Cu and Mn with highest removal efficiencies of 62.47%, 86.54% and 90.53% respectively all decreases as the zeolite dose is being increased. Thus, 1000 mg/L is the optimum dose of zeolite and most effective in Zn removal.

3.6. Comparison for the performance of coagulants

POME just like many other wastewaters cannot be discharged directly to the land, as it will adversely affect the soil and vegetation system [44]. According to world health organization (WHO), even at low concentration, heavy metal is hazardous. Thus, causes various forms of diseases [45]. It's often difficult to have most heavy metals achieving highest removal efficiencies at the optimum dose which was the reason why this study chose many metals so as to obtain a minimum of three heavy metals at the

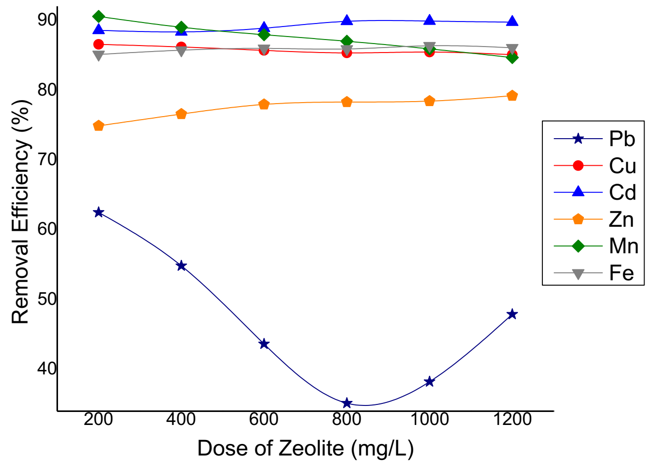


Fig. 11. Contaminants removal efficiencies by Zeolite.

optimum dose. Fig. 12 shows optimum dose of alum, $FeCl_3$, chitosan, *moringa oleifera* and zeolite in the removal of Cd, Mn, Zn, Fe and Pb. It was observed that Pb, Mn and Cd at 91.27%, 95.75% and 92.54% respectively were the only metals that achieved highest removals at alum dose of 4000 mg/L. Pb, Cd and Zn at 94.17%, 93.71% and 78.81 respectively for $FeCl_3$ dose of 1000 mg/L. Optimum chitosan dose of 400 mg/L obtained highest removals of Pb, Cd, Mn and Fe as 89.15%, 94.62% 91.67% and 90.49% respectively. *Moringa oleifera* obtained 86.87%, 94.91% and 91.31% removal of Pb, Cd and Mn respectively at an optimum dose of 2000 mg/L. Lastly, zeolite dose of 1000 mg/L as the optimum was only able to achieve highest removals for Cd and Fe at efficiencies of 89.87% and 86.34% respectively which could be attributed to the presence of some metals in oxide form in the coagulant. However, it would be observed that, Cu could not give highest removal in any of the coagulants.

Adsorption studies by the use of biosorbents have widely been studied . The process have been reported to be costly and not effective for most effluents [22]. The process is also characterised by lower selectivity and mass transfer rate, high toxicity, low adsorption capacity operating complexity, harmful to health, high-energy requirements, very high processing temperatures required for their activation, generation of toxic and voluminous sludge etc [16]. POME as an industrial effluent cannot be treated by adsorption in large scale as most adsorption studies ends at the laboratory scale

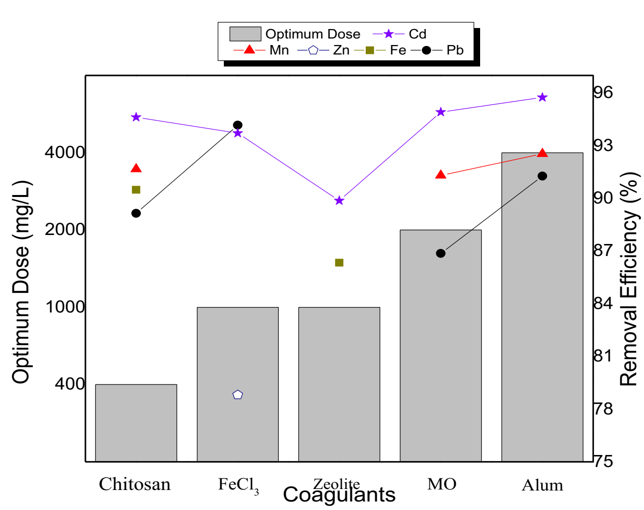


Fig. 12. Optimum dose of alum, $FeCl_3$, chitosan, *moringa oleifera* and zeolite in the removal of Cd, Mn, Zn, Fe and Pb.

level. Whereas, coagulation have been widely employed at bench, laboratory, pilot and full-scale levels [46]. A comparative study by Lee et al [47] between adsorption and coagulation revealed that coagulation is superior to adsorption as a pretreatment process for the performance enhancement of effluent degradation. The coagulation process is reportd to be a cheap and robust method for wastewater treatment [16]. Several studies [48–52] reported adsorption as efficient only when combined with coagulation process. This is to tell how significant the coagulation process is.

4. Conclusion

Treatment of POME containing heavy metals is of extreme importance globally because of its potential effects to both human aquatic ecosystem. Heavy metals are hazardous even at low concentration and thereby causing various forms of diseases. A method that has been tested and found to be effective for heavy metals removal is coagulation-flocculation. In the present study, raw POME obtained from an oil palm mill was characterized and the feasibility of using Alum, $FeCl_3$, Chitosan, *Moringa oleifera* and Zeolite in the removal of Cd, Cu, Fe, Mn, Pb and Zn investigated. Coagulation, flocculation and sedimentation techniques using Jar test were adopted and the determination of heavy metals concentration was carried out using an ICP and AAS. The study further emphasized on determining the optimal doses of coagulants used by analytical methods. Experimental results revealed that Pb achieved highest removal efficiency of 94.17% with $FeCl_3$ at a dose of 1000 mg/L and 91.27% with alum at 4000 mg/L. Chitosan as a biopolymer was highest in the removal of, Pb, Cd, Mn and Fe followed by *moringa oleifera* and lastly zeolite coagulants. Cu achieved excellent removal of 86.54% using zeolite coagulant. However, chitosan and *moringa oleifera* were lower having 82.96% each. Findings also revealed that alum has the highest dose requirement having obtained 4000 mg/L as its optimum. *Moringa oleifera* had 2000 mg/L, chitosan 400 mg/L while both zeolite and $FeCl_3$ at 1000 mg/L. Based on the aforementioned results from the research on the use of the specific natural and chemical coagulants, it can be concluded that different coagulants have variable dosages due to the effect of the interaction between the colloidal particles. Thus, the study recommends the use of natural coagulants (chitosan, *moringa oleifera*, zeolite) as they are less harmful and requires less dosages.

Declaration of Competing Interest

The authors declare that this study does not include any conflict of interest.

Acknowledgement

The authors would like to acknowledge the financial support from the Universiti Tenaga Nasional (UNITEN) under BOLD fund. The authors are also grateful to the Management and staff of Universiti Teknologi PETRONAS (UTP), Malaysia for their guidance, support, suggestions and encouragements from the beginning of the research to the end.

References

[1] Shanmugarajah B. Extraction and characterization of nanocrystalline cellulose from oil palm empty fruit bunch and its potential as adsorbent for dye removal; 2017.
[2] Mba OI, Dumont M-J, Ngadi M. Palm oil: Processing, characterization and utilization in the food industry–A review. Food Biosci 2015;10:26–41.
[3] Dikko A, Alkasim A, Ahmed A. The effect of impurity concentration on activation energy change of palm oil and a its application to identify an adulterated palm oil.

[4] Eze SO, Nnenne KU, Eze CN. Polycyclic aromatic hydrocarbons (PAHS) contamination in palm oil samples from major markets of Ohafia agricultural zone, Abia State, Nigeria. Eur J Phys Agric Sci Vol; 2015. 3(3).
[5] Sulaiman F et al. An outlook of Malaysian energy, oil palm industry and its utilization of wastes as useful resources. Biomass Bioenergy 2011;35 (9):3775–86.
[6] Hadi HM, Karuppiah K, Mohd SB. 6 Application of hirarc in palm oil mill industry. Occupational safety and health in commodity agriculture: case studies from Malaysian agricultural perspective; 2014. p. 201.
[7] Khatun R et al. Sustainable oil palm industry: The possibilities. Renew Sustain Energy Rev 2017;76:608–19.
[8] Singh RP et al. Towards sustainable palm oil production: minimizing the environmental damage from oil palm processing. Waste Manage: New Res 2012:161–77.
[9] Loh SK. The potential of the Malaysian oil palm biomass as a renewable energy source. Energy Convers Manage 2017;141:285–98.
[10] Iskandar MJ et al. Palm oil industry in South East Asia and the effluent treatment technology—A review. Environ Technol Innovation 2018;9:169–85.
[11] Jagaba A et al. Sustainable use of natural and chemical coagulants for contaminants removal from palm oil mill effluent: A comparative analysis. Ain Shams Eng J 2020.
[12] Liew WL et al. Conventional methods and emerging wastewater polishing technologies for palm oil mill effluent treatment: a review. J Environ Manage 2015;149:222–35.
[13] Tabassum S, Zhang Y, Zhang Z. An integrated method for palm oil mill effluent (POME) treatment for achieving zero liquid discharge–a pilot study. J Clean Prod 2015;95:148–55.
[14] Ahmad A, Buang A, Bhat A. Renewable and sustainable bioenergy production from microalgal co-cultivation with palm oil mill effluent (POME): a review. Renew Sustain Energy Rev 2016;65:214–34.
[15] Zittel R et al. Availability of nutrients, removal of nicotine, heavy metals and pathogens in compounds obtained from smuggled cigarette tobacco compost associated with industrial sewage sludge. Sci Total Environ 2020;699:134377.
[16] Jagaba A et al. Derived hybrid biosorbent for zinc (II) removal from aqueous solution by continuous-flow activated sludge system. J Water Process Eng 2020;34:101152.
[17] Li X et al. Porous Fe2O3 microcubes derived from metal organic frameworks for efficient elimination of organic pollutants and heavy metal ions. Chem Eng J 2018;336:241–52.
[18] Ghaleb AAS et al. Response Surface Methodology to Optimize Methane Production from Mesophilic Anaerobic Co-Digestion of Oily-Biological Sludge and Sugarcane Bagasse. Sustainability 2020;12(5):2116.
[19] Harsono SS, Grundmann P, Soebronto S. Anaerobic treatment of palm oil mill effluents: potential contribution to net energy yield and reduction of greenhouse gas emissions from biodiesel production. J Cleaner Prod 2014;64:619–27.
[20] Jagaba AH et al. Wastewater Treatment Using Alum, the Combinations of Alum-Ferric Chloride, Alum-Chitosan, Alum-Zeolite and Alum-Moringa Oleifera as Adsorbent and Coagulant. Int J Eng Manage 2018;2(3):67–75.
[21] Abubakar S et al. Aerobic treatment of kitchen wastewater using sequence batch reactor (SBR) and reuse for irrigation landscape purposes. Am J Eng Res 2016;5(5):23–31.
[22] Katheresan V, Kansedo J, Lau SY. Efficiency of various recent wastewater dye removal methods: a review. J Environ Chem Eng 2018;6(4):4676–97.
[23] Fagier MAM. Characterization and treatment of sugarcane vinasse by coagulation-flocculation followed by sulfate radical based on advanced chemical oxidation process. Sudan University of Science and Technology; 2016.
[24] Gupta A, Kumar V. New emerging trends in synthetic biodegradable polymers–Polylactide: A critique. Eur Polym J 2007;43(10):4053–74.
[25] Idder A et al. The Porosity of Stabilized Earth Blocks with the Addition Plant Fibers of the Date Palm. Civil Eng J 2020;6(3):478–94.
[26] Jhatial AA et al. Utilization of palm oil fuel ash and eggshell powder as partial cement replacement-a review. Civil Eng J 2018;4(8):1977–84.
[27] Moghaddam TN et al. A Review on the Addictive Materials Paan Masala (Paan Parag) and Nass (Naswar). SciMed J 2019;1(2):64–73.
[28] Jagaba A et al. Water quality hazard assessment for hand dug wells in Rafin Zurfi, Bauchi State, Nigeria. Ain Shams Eng J 2020.
[29] Association APH, APHA. Standard Methods for the Examination of Water and Wastewater. 21st ed. Washington DC: American Public Health Association; 2005. p. 1220p.
[30] Abubakar S et al. Quality Water Analysis of Public and Private Boreholes (A Case Study of Azare Town, Bauchi, Nigeria). Am J Eng Res 2016;5(2):204–8.
[31] Jagaba AH et al. Defluoridation of Drinking Water by Activated Carbon Prepared from Tridax Procumbens Plant (A Case Study of Gashaka Village, Hong LGA, Adamawa State, Nigeria).
[32] Xie Y. Disinfection byproducts in drinking water: Formation, analysis, and control. :RC press; 2003.
[33] Chang H et al. Removal of calcium and magnesium ions from shale gas flowback water by chemically activated zeolite. Water Sci Technol 2017;76 (3):575–83.
[34] Jagaba AH et al. Stabilization of soft soil by incinerated sewage sludge ash from municipal wastewater treatment plant for engineering construction. Sustain Struct Mater, An Int J 2019;2(1):32–44.
[35] Gámiz-González M et al. Kinetic study of thermal degradation of chitosan as a function of deacetylation degree. Carbohydr Polym 2017;167:52–8.
[36] Bhatia S, Othman Z, Ahmad AL. Pretreatment of palm oil mill effluent (POME) using Moringa oleifera seeds as natural coagulant. J Hazard Mater 2007;145 (1–2):120–6.
[37] Kusmawati FN, Kusumaningrum DP. Effect of Red Dragon Fruit Juice on Acrylic Resin Color. SciMed J 2019;1(3):143–50.
[38] Tajuddin HBA. Efficiency of organo-floc as a natural coagulant in the treatment of palm oil mill effluent; 2015.
[39] Amuda O, Amoo I. Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment. J Hazard Mater 2007;141 (3):778–83.
[40] Tan J et al. Chemical precipitation of palm oil mill effluent (POME). Proceedings of the 1st international conference on natural resources engineering & technology, 2006.
[41] Chen C-Y, Chung Y-C. Comparison of acid-soluble and water-soluble chitosan as coagulants in removing bentonite suspensions. Water Air Soil Pollut 2011;217(1–4):603–10.
[42] Chester AW, Derouane EG. Zeolite characterization and catalysis. Vol. 360. Springer; 2009.
[43] Motsi T, Rowson N, Simmons M. Adsorption of heavy metals from acid mine drainage by natural zeolite. Int J Miner Process 2009;92(1–2):42–8.
[44] Jagaba A et al. Treatment of Palm Oil Mill Effluent (POME) by Coagulation-Flocculation using Different Natural and Chemical Coagulants: A Review. IOSR J Mech Civil Eng 2016;13(6):67–75.
[45] Rai PK et al. Heavy metals in food crops: Health risks, fate, mechanisms, and management. Environ Int 2019;125:365–85.
[46] Krzemiński P, Popowska M. Treatment Technologies for Removal of Antibiotics, Antibiotic Resistance Bacteria and Antibiotic-Resistant Genes. In: Antibiotics and Antimicrobial Resistance Genes. Springer; 2020. p. 415–34.
[47] Lee J et al. Comparative studies on coagulation and adsorption as a pretreatment method for the performance improvement of submerged MF membrane for secondary domestic wastewater treatment. Sep Sci Technol 2005;40(13):2613–32.
[48] Lee J-W et al. Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes. Dyes Pigm 2006;69 (3):196–203.
[49] Puchana-Rosero MJ et al. a coagulation-flocculation process combined with adsorption using activated carbon obtained from sludge for dye removal from tannery wastewater. J Chil Chem Soc 2018;63(1):3867–74.
[50] Hoong HNJ, Ismail N. Removal of Dye in Wastewater by Adsorption-Coagulation Combined System with Hibiscus sabdariffa as the Coagulant. In: MATEC Web of Conferences; 2018. EDP Sciences.
[51] Hasani A et al. Comparison of adsorption process by GAC with novel formulation of coagulation–flocculation for color removal of textile wastewater; 2008.
[52] Gandhimathi R et al. Use of combined coagulation-adsorption process as pretreatment of landfill leachate. Iran J Environ Health Sci Eng 2013;10(1):24.
[53] Adam A A, Musa M, Sani M. Enhanced optical transmittance of spray deposited zinc oxide thin films for optoelectronic applications. Bayero Journal of Pure and Applied Sciences 2019;12(1):1–5. doi: https://doi.org/10.4314/bajopas.v12i1.1.
[54] Adam A A, Ramamurthi K, Margoni M M. A Study on Low Cost-Highly Transparent and Conductive Molybdenum Doped Zinc Oxide Thin Films Deposited by Spray Pyrolysis Technique. American Journal of Materials Research 2018;5(3):40–5.
[55] Chiromawa L N, Ibrahim K, Ali H M, Gana M U, Musa O A, Mannawi I N, et al. Soft Lithography For Concentrator Photovoltaic CPV System's Application. Bayero Journal of Pure and Applied Sciences 2017;10(1):323–7. doi: https://doi.org/10.4314/bajopas.v10i1.64S.
[56] Kankia Usman Mubarak, Baloo Lavania, Mohammed S Bashar, Hassan B Suhaimi, Ishak Affiana Effa, Zango Uba Zakariyya. Review of petroleum sludge thermal treatment and utilization of ash as a construction material, a way to environmental sustainability. International Journal of Advanced and Applied Sciences 2020;7(12):68–81. doi: https://doi.org/10.21833/ijaas.2020.12.008.
[57] Ehteram Mohammad, Ghotbi Samira, Kisi Ozgur, Ahmed Najah Ali, Hayder Gasim, Fai Ming Chow, et al. Investigation on the Potential to Integrate Different Artificial Intelligence Models with Metaheuristic Algorithms for Improving River Suspended Sediment Predictions. applied sciences 2019;9 (19):1–24. doi: https://doi.org/10.3390/app9194149.
[58] Mustafa Mohammed Hauwa, Hayder Gasim, Jagaba Hussaini Ahmad. Microalgae: A Renewable Source for Wastewater Treatment and Feedstock Supply for Biofuel Generation. Biointerface Research in Applied Chemistry 2021;11(1):7431–44. doi: https://doi.org/10.33263/BRIAC111.74317444.
[59] Mustafa M Hauwa, Hayder Gasim. Recent studies on applications of aquatic weed plants in phytoremediation of wastewater: A review article. Ain Shams Engineering Journal 2020. doi: https://doi.org/10.1016/j.asej.2020.05.009.
[60] Ahmed N Ali, Hayder Gasim, Binti Abdul Rahman Aliya Raihana, Borhana A Abdoulhdi. RAINFALL-RUNOFF FORECASTING UTILIZING GENETIC PROGRAMMING TECHNIQUE. http://www.iaeme.com/IJCIET/index.asp 1523 editor@iaeme.com International Journal of Civil Engineering and Technology (IJCIET) 2019;10(01):1523–34.