Progress in Engineering Application and Technology Vol. 3 No. 2 (2022) 37–45

PEAT

Homepage: http://publisher.uthm.edu.my/periodicals/index.php/peat
e-ISSN : 2773-5303

A Comparison of *Moringa Stenopetala* and *C.Arietinum* (*Cicer Arietinum L*) Absorbance Efficiency As A Natural Coagulant For Domestic Wastewater Treatment

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DOI: https://doi.org/10.30880/peat.2022.03.02.004
Received 27 January 2022; Accepted 07 November 2022; Available online 10 December 2022

Abstract: Domestic wastewater is produced due to usage of water for various daily activities and it is hazardous to other water sources that receive it such as rivers as it contains various contamination and heavy metals such as Chromium (VI). Thus, domestic wastewater treatment is required where natural coagulant were used for coagulation process. In this project, *Moringa Stenopetala* seeds and *Cicer Arietinum* have been chosen as natural coagulants to study their efficiency in treating the domestic waste water that been collected from the cafeteria at Universiti Tun Hussein Onn .The characteristics of both material was determined through FTIR, adsorption efficiency was determined by Langmuir and Freundlich and the effectiveness as natural coagulant determined through Jar Test. The physiochemical properties that studied was turbidity, COD and pH value. The Chromium (VI) removal by both M.*Stenopetala* and C. *Arietinum* in different dosages determined where 200 mg/L of M.*Stenopetala* showed the highest percentage removal with 42.44 %. M.*Stenopetala* is more efficient as natural coagulant than C. *Arietinum* an optimum dosage of 200 mg/L with 63.00 % of turbidity removal, 75.00 % of chemical oxygen demand removal and higher efficiency to neutralise the pH level of wastewater in acidic medium.

Keywords: Natural Coagulant, Absorbance Efficiency, *Moringa Stenopetala, CicerArietinum*

1. Introduction

The water quantity and quality has always played a major role where it determines organism quality of life and the residency of humans. The toxic that presents in wastewater can cause dangerous effect living organism especially aquatic organism or plants that growth in the water. It can be also harmful to human that accidently have a contact or utilise the water such as from river, without knowing the

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harmful compounds contain from waste. Thus, wastewater from all sources, including domestic wastewater, must be purified before consumption to ensure the health and well-being of the people and animals who drink it. This purification is known as water treatment and there are various types of water treatment to treat the water and make it safe to consume [1].

Coagulation- flocculation is one of the water treatments which has been utilised widely to treat the waste water. Synthetic coagulants or chemical coagulants are often used [2]. For example, alum is often used in the coagulation-flocculation process to purify the water in Malaysia where the cost of alum is high and as Alum is a non- biodegradable thus the usage coagulant can produce large sludge volume which results in water pollution turning worse if the process does not undergo accurately. This will increase the turbidity of water. Besides that, the presence of heavy metal such as chromium in domestic waste water is hazardous to the environment and causes death to the organism that consumes the water without any treatment. Cr (VI) is dangerous because of its ability to easily penetrate cell membranes and its powerful oxidising strength. It produces a variety of soluble and mobile anions in the atmosphere. Due to the extreme toxic nature of Cr (VI), intestinal and lung cancer can be resulted as well as nausea, serious diarrhea and kill the aquatic organism. The maximum concentration of Cr (VI) permitted in drinking water is 0.1 mg/L. [3] [4]. Thus, removal of chromium from the domestic wastewater during the treatment process is important.

The majority of plant material may absorb heavy metals and act as a natural coagulant [5].The seeds of M. *Stenopetala* and *C.Arietinum* s do have plenty of benefits where the application and economics are wider. The seeds can be used to clarify muddy water as it contains antimicrobial properties. Whole crushed seeds of M. *Stenopetala* and C. *Arietinum* are effective in lowering turbidity from waters with high initial turbidity due to natural flocculating and antibacterial qualities contained in both raw materials. The proteins extracted from the seeds of the M. *stenopetala* tree and C.*Arietinum* are an important flocculent for particles scattered in water, and they are desirable as a safe and organic product for water purification. Besides that, heavy metals may be removed from water and agricultural wastes using both tree plant based material [6]. Tadesse (2018) has shown that M.*Stenopetala* seed to reduce Cr (VI) in tannery waste [7] The presence of hydroxyl site in C. *Arietinum* that also capable to remove Cr (VI) helps people to treat water from drain to reuse again for daily activities because it is eco-friendly and easily to obtain especially in rural area. Both are also been used in many other application such as cooking purposes or treat illness [8] [9].Thus, this research will show the preparation of natural coagulants which are *Moringa Stenopetala* seeds and *Cicer Arietinum* to treat the domestic waste water by observing their performance towards the turbidity, chemical oxygen demand (COD), pH value and also describe its function as natural adsorbent for chromium removal from the domestic wastewater.

2. Materials and Methods.

2.1 Preparation of natural coagulants

The dried pods or known as the fruits of *Moringa Stenopetala* was from the Moringa tree earlier while Kabuli Chickpea (*Cicer Arietinum* L) was purchased at wet market. The seeds of *Moringa Stenopetala* and *C.Arietinum* are dried naturally till they are fully dried and matured. The seeds are smashed and ground separately using a grinder to obtain fine powder .The powders are allowed to dry under sunlight. The stock of each natural coagulant is prepared for four concentrations which were 50 mg/L,100 mg/L,150 mg/L and 200 mg/L by weighting the powder and dissolved into 1 L of distilled water. The solution is stirred gradually for 20 minutes using magnetic stirred and transferred into beakers. The solution were kept in room temperature.

2.2 Determination of adsorption level in *Moringa Stenopetala* seeds and Kabuli Chickpea (*Cicer Arietinum L*)

A 500 mg/L of Chromium (VI) metal stock solution is obtained by dissolving 1.4144 g of $K_2Cr_2O_7$ in 1 L of deionized water. The solution then stirred gradually using magnetic stirred. 25 mL of metal stock solution will be used for every 25 mL from 50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L of the M.*Stenopetala* and *C.Arietinum* solution that prepared early. The natural adsorbent is added to the metal stock and stirred at 100-350 rpm gradually till 45 minutes. With a wavelength of 279.5 nm, a spectrophotometer is used to measure the removal of Cr (V1) from each of the sample [10].The characteristic of both M.*Stenopetala* and *C.Arietinum* before and after adsorption of Cr (VI) is determine by Fourier Transform Infrared (FTIR). Cr (VI) removal by both material in different dosage was determined using UV-spectrometer and calculated using Eq. 1 below:

$$\text{Adsorption / Re \%} = \frac{(C0 - Ce)}{C0} \times 100 \qquad Eq.1$$

Where, C_0 represents the initial concentration (mg/L) and Ce represents the final value of the concentration (mg/L) [10].In order to calculate the Cr (VI) adsorbed per gram by the raw material, qe, Eq. 2 as below is used.

$$qe = \frac{(C0 - Ce)\,V}{W} \qquad Eq.2$$

Where the solution volume state as V is the volume of Cr (VI) solution and W is the dosage of absorbents [11].

2.2.1 Langmuir Isotherm

Langmuir adsorption isotherm model assumed that the adsorption occurs with monolayer adsorption on specific homogenous surfaces containing finite number of adsorption. The Langmuir equation which been linearized is stated in Eq.3,

$$\frac{Ce}{qe} = \frac{1}{Qmax.b} + \frac{Ce}{Qmax} \qquad Eq.3$$

The maximum adsorption rate of a monolayer state as Q_{max} (mg/g). The Langmuir constant which states b (L/mg) as is proportional to the adsorption energy and the affinity of the binding sites. The Langmuir dimensionless constant separation factor RL, which was used to determine either the adsorption was favourable or no equation through Eq. 4 as below,

$$RL = \frac{1}{1+bCo} \qquad Eq.4$$

If we obtain RL less than 1, it shows that the adsorption is favourable, while if the RL value is more than 1 it is not favourable. If we obtain 1, it is in linear and when then RL is o it shows the adsorption is irreversible [10].

2.2.2 Freundlich Isotherm

The multilayer adsorption of metal ions on heterogeneous surfaces is explained by the Freundlich isotherm equation. The Freundlich equation which been linearized is stated in Eq. 5 as below,

$$\text{loq}\ (qe) = \log kf + \frac{1}{n} \log (Ce) \qquad Eq.5$$

Where n shows the effectiveness of adsorbent and k*f* stands for the Freundlich constant, which describes the strength of the adsorptive bond [11].

2.3 Determination of Efficiency *Moringa Stenopetala* seeds and *Cicer Arietinum* as Natural Coagulants through Physiochemical Parameters.

Domestic wastewater were collected from the drain of café UTHM,Pagoh, Johor and the initial turbidity, pH and COD value were recorded. 200 ml of four different dosage (50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L) of both Moringa Stenopetala seeds and *C.Arietinum* were mix into 800 mL of domestic wastewater that been collected. The samples were undergoes Jar Test under flocculator. Rapid stirring at 100 rev/min for roughly 4 minutes was followed by gentle agitation at 30 rev/min for approximately 16 minutes so that the coagulant was well mixed with the water. The mixing stop to let the compounds in the beaker to settle down well within 30 minutes [8].

2.3.1 Determine the Turbidity Level

Turbidimeter was used to record the turbidity level where the final turbidity level were recorded after the Jar Test. Turbidity removal % of every samples were calculated by using Eq. 6 as below,

$$Turbidity\ removal\ efficiency\ \% = \frac{NTU0 - NTU}{NTU0}\ x\ 100 \qquad Eq.6$$

Where the NTU_o is the initial turbidity reading and NTU is the final turbidity reading.

2.3.2 Determine pH level

pH value is taken to observe the effect of natural coagulants toward the pH of the water sample. pH meter is used to record the pH value of all the water samples.

2.3.3 Chemical Oxygen Demand (COD)

The COD determination begins with measuring 2.5 mL from each of jar test sample including blank sample that consisting the waste water into standard 10 mL digestion tube. Then, 1.5 mL of standard potassium dichromate digestion solution is added into every digestion tube. In each tube, every 3.5 mL of sulphuric acid reagent is run into carefully to form an acid layer under the sample-digestion solution. The tubes are properly closed, inverted numerous times to ensure proper mixing, and then placed in a COD reactor. The tubes are allow to cool till room temperature and placed in test tube rack. The solution is transfer into a conical flask and 1 to 2 drops of Ferroin indicator is added. The solution is titrated with FAS solution slowly. Changes colour to reddish brown or pink colour is the end point. The value of COD is obtained based on Eq.7 as below,

$$COD\ \left(\frac{mgO_2}{l}\right) = \frac{(X-Y)N\ X\ 8000}{sample\ volume} \qquad Eq.7$$

The above equation is derived where X is state as the volume of FAS used for blank titration and Y is the volume FAS of sample titration. N is the constant for FAS solution which the value is 0.10M and 8000 is the multiplication of 1000mL/L and milliequivalent weight of oxygen [12].

3. Results and Discussion

3.1 Characteristics of *Moringa Stenopetala* seeds and *C.Arietinum* as natural adsorbent

The functional group of both M.*Stenopetala* and *C.Arietinum* before adsorption of Cr (VI) were determined through FTIR (Figure 1a and 1b). The wavelength range of both *Moringa Stenopetala* seeds and *C.Arietinum* are obtained from 700-4000 cm^{-1}. The absorption peaks can be noticed in the wavelength range of 3302.4 cm^{-1} for M.*Stenopetala* seeds and 3257.7 cm^{-1} for *C.Arietinum* s. The large bands at 3302.4cm^{-1} and 3257.7 cm^{-1} shows the O-H vibration stretching of carboxylic acid where M.*Stenopetala* seeds has higher surface area of O-H active site than *C.Arietinum* s. On the other hand, there are same band has been noticed at 1636.3 cm^{-1} for both M.*Stenopetala* seeds and *C.Arietinum* s. This band shows the presence of stretching vibration of C=0 group in carboxylic acid. Both functional group act as active sit for adsorption of chromium where removal of chromium (VI) occurs. Figure 1c and 1d show the FTIR spectra of both M.*Stenopetala* sees and *C.Arietinum* at different dosage (50mg/L.100mg/L,150mg/l and 200mg/L) after adsorption of Cr(VI) where dosage 200mg/L of M.*Stenopetala* seeds shows has the lowest band with 3261.4cm^{-1} while dosage 50mg/L has highest band with 3249.6 cm^{-1} after adsorption of Cr (VI). The wavelength decrease slightly as the O-H is been used for the removal of Cr (VI) [10].

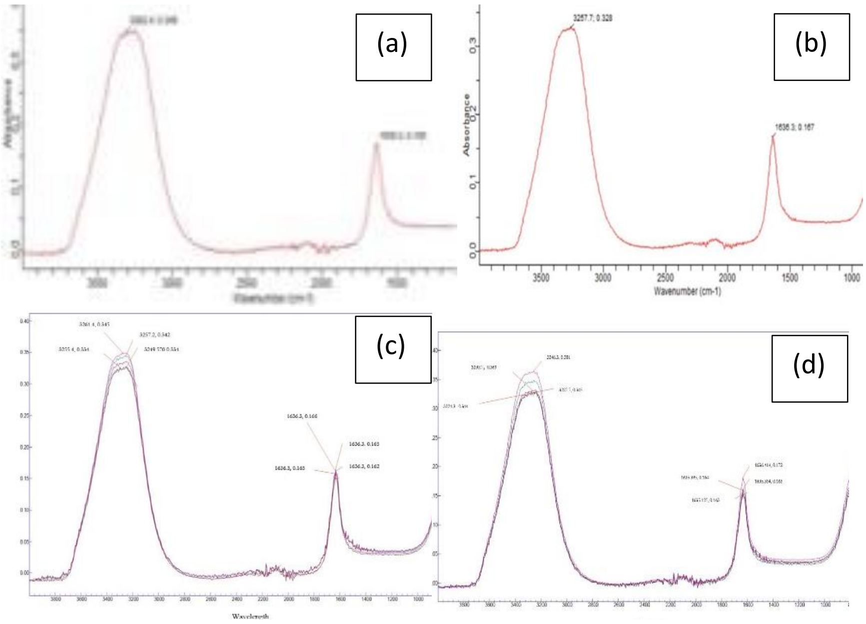

Figure 1: (a) FTIR spectra of M.*Stenopetala* before Cr (VI) adsorption, (b) FTIR spectra of *C.Arietinum* before Cr (VI) adsorption, (c) FTIR spectra of M.*Stenopetala* after Cr (VI) adsorption, (d) FTIR spectra of *C.Arietinum* after Cr (VI) adsorption

3.2 Adsorption Isotherms

The effect of adsorbent dose of M.*Stenopetala* and *C.Arietinum* in Cr (VI) removal is shown as in Figure 2. The maximum percentage of Cr (VI) removal was reached by 200 mg/L of M.*Stenopetala* (42.44%), while the lowest percentage removal was achieved by 50 mg/L of *C.Arietinum* (16.18%). This is because M.*Stenopetala* contains the greatest binding active level of O-H at 200mg/L. Since M.Stenopetala has a larger binding active size than *C.Arietinum*, the removal of Cr (VI) in M.Stenopetala was greater. Both natural adsorbent and synthetic adsorbent show a quick rise in percentage of Cr (VI) elimination up to 150 mg/L, then a slower increase up to 200 mg/L. This is due to the adsorbent binding approximately all ions at 150 mg/L those remaining unabsorbed adsorb more at 200 mg/L of dosage.

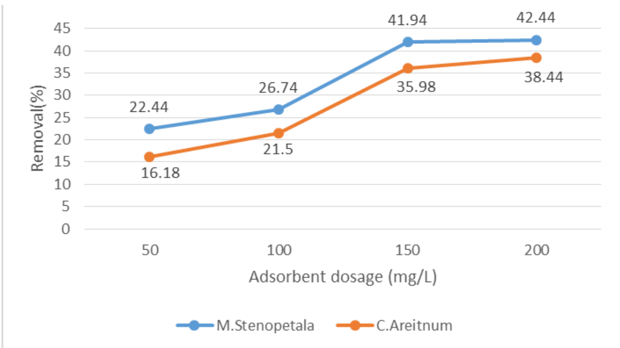

Figure 2: Effect of adsorbent dosage on Cr (VI) adsorption (Orbital shaking speed = 150rpm, Time= 30min)

3.2.1 Langmuir Isotherm

Langmuir isotherm that been linearized as in Eq.3 was used to plot graph of Ce/qe for both M. *Stenopetala* seeds and *C.Arietinum* to obtain b from y intercept and Q_{max} value from slop of the graph. Figure 3a and 3b shows the Langmuir isotherm plots for the removal of Cr (VI) by M. *Stenopetala* seeds and *C.Arietinum* respectively. From Figure 3a, M. *Stenopetala* seeds has the value b, Langmuir

Isotherm constant of 0.634 and q_{max}, the maximum adsorption capacity of 46.512. On the other hand, *C.Arietinum* has the value b, Langmuir Isotherm constant of 0.3124 and q_{max}, the maximum adsorption capacity of 44.643. As the b value is more, the affinity of the adsorbent for metal is stronger and as the q_{max} value higher, total number of binding sites that occupied by Cr (VI) are higher too [13]. RL is computed using Eq.4 to show that the adsorption data of M.*Stenopetala* and *C.Arietinum* are well fitted to the Langmuir isotherm and that the adsorption of Cr (VI) is favorable. M.*Stenopetala* and Chickpea both get less than 1 values of 0.031 and 0.060, respectively. This proved that both natural adsorbents are effective in adsorbing Cr (VI).

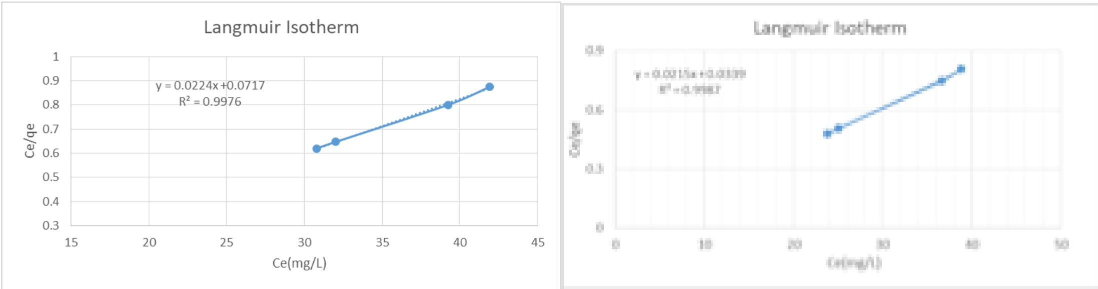

Figure 3: Langmuir isotherm for (a) M. *Stenopetala* seeds and (b) *C.Arietinum*

3.2.2 Freundlich Isotherm

Freundlich isotherm that been linearized as in Eq.5 was used to plot graph of log Ce/ logqe for both M. *Stenopetala* seeds and *C.Arietinum* to obtain n from the slope and Freundlich constant, k*f* from the y intercept. Figure 4a and 4b shows the Freundlich isotherm plots for the removal of Cr (VI) by M. *Stenopetala* seeds and *C.Arietinum* respectively. From Figure 4a, M. *Stenopetala* seeds has the value n of 20.121 and k*f of* 41.419 while *C.Arietinum* obtain n of 11.049 and k*f* of 35.449. Comparison of n value shows that M.*Stenopetala* has higher adsorbent effectiveness compare to *C.Arietinum* as higher the n value, higher the effectiveness of adsorbent [13][14].

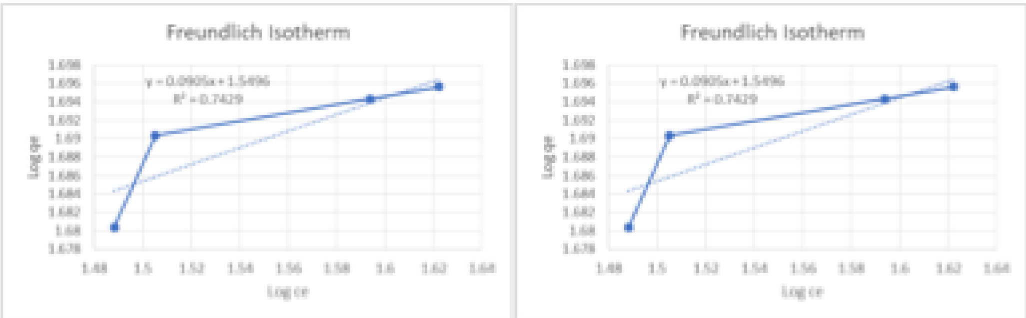

Figure 4: Freundlich isotherm for (a) M. *Stenopetala* seeds and (b) *C.Arietinum*

3.3 Determination of Efficiency of Natural Coagulant through Turbidity Removal.

A graph is plotted against the % turbidity removal which were calculated using Eq.6 as in Figure 5. M.*Stenopetala* seeds has cumulatively higher efficiency in removing turbidity compare to *C.Arietinum* where the higher turbidity removal achieved by 200 mg/L of *M.Stenopetala* with 63.00 % removal. With lower turbidity removal, the final turbidity level were achieved high which indicate the quality of water is low and will give harmful effect to the aquatic organism as the water from the drain will go flow until the pond or maybe river [16].

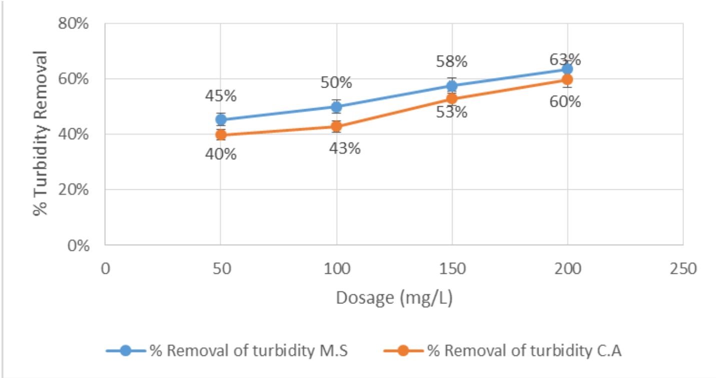

Figure 5: The comparison for % turbidity removal % by M.*Stenopetala* seeds and *C.Arietinum*

3.4 Determination of Efficiency of Natural Coagulant on pH level

Determination of pH value in the domestic wastewater is very important as extreme acidic or alkalinity levels in the wastewater are hazardous to organism who had contact accidently or purposely to the wastewater. The average initial pH value of domestic wastewater from the drainage of café UTHM was 6.25. The final pH value of every samples that undergoes Jar Test with M.*Stenopetala* seed and *C.Arietinum* in different dosages were tabulated in Table 1.

Table 1: Final pH level of domestic waste water after Jar Test

Dosage (mg/L)	pH M.*Stenopetala*				*C.Arietinum*			
	R1	R2	R3	**Average**	R1	R2	R3	**Average**
50	6.410	6.390	6.400	**6.400±0.008**	6.320	6.310	6.320	**6.320±0.004**
100	6.470	6.500	6.480	**6.480±0.012**	6.390	6.350	6.380	**6.370±0.017**
150	6.590	6.580	6.570	**6.580±0.008**	6.440	6.440	6.390	**6.420±0.024**
200	6.610	6.590	6.600	**6.600±0.008**	6.590	6.520	6.540	**6.550±0.029**

The initial value of the wastewater indicates that it was in an acidic medium due to the presence of suspended organic compounds from domestic activities. The pH value obtained by 200 mg/L of M.*Stenopetala* was 6.60, which is the closest to the pH value that is safe for aquatic organisms to eat (pH=7). The anion contained in both natural coagulants has neutralised the positive charged ion, H+, [10] present in the wastewater, increasing the pH value. In comparison to *C.Arietinum*, M.*Stenopetala* has a better efficacy in neutralising the pH level of wastewater in acidic medium.

3.5 Determination of Efficiency of Natural Coagulant through COD removal

COD is a measurement of the oxygen equivalent of organic matter in a water sample that can be oxidised by a powerful chemical oxidant. The initial COD value of the residential wastewater collected from the UTHM café's drain was 420 mg/L, indicating a medium level of COD. The final COD level was determined using Eq.7, with the lowest COD value being achieved by M.Stenopetala seeds at a dose of 200 mg/L with a reading of 106.67, and the highest COD value being achieved by *C.Arietinum* at a dosage of 50 mg/L with a reading of 202.67. A higher COD value indicates a larger concentration of organic or inorganic material, as well as a higher rate of oxidation of organic and inorganic material. The elimination of COD is higher in the final wastewater when the concentration of organic and inorganic in the waste sample is lower, indicating a lower final COD value. Due to the higher hydroxyl radical sides (OH-) of M.*Stenopetala* seeds, which oxidise more organic compounds and lower oxidation concentration, 200 mg/L of M.*Stenopetala* seeds removes more COD[15]. To compare the effectiveness of both coagulant in COD removal, a graph were plotted based on the final level of COD from every sample as in figure 6. Conclusion, M.*Stenopetala* seeds shows that it has higher efficiency compare to *C.Arietinum* in the removal of COD in the domestic wastewater.

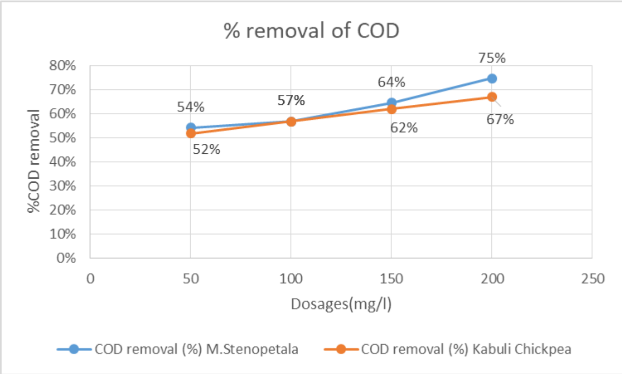

Figure 6: The comparison for % COD removal % by M.Stenopetala seeds and C.Arietinum

4. Conclusion

The FTIR analysis of *Moringa Stenopetala* seeds and *C.Arietinum* s in powder form reveals the presence of OH-, which can function as a binding site for Chromium (VI) adsorption. In comparison to *C.Arietinum*, M.*Stenopetala* has a better effectiveness in removing Cr (VI). M.*Stenopetala* has a better adsorption capacity and affinity of adsorbent than *C.Arietinum*, according to the Langmuir Isotherm. We can determine the effectiveness of an adsorbent using the Freundlich Isotherm, and M.*Stenopetala* has a greater effectiveness than *C.Arietinum*. The effectiveness of *Moringa Stenopetala* seeds and *C.Arietinum* s as natural coagulants for removing turbidity, chemical oxygen demand (COD), and increasing pH levels was tested in a jar test.At 200 mg/L, M.*Stenopetala* had the maximum efficacy for removing turbidity, reducing COD, and improving the acidic pH of waste water. Both natural materials that are affordable to get act as natural coagulants, and both materials may be modified for increased efficiency.

Acknowledgement

The authors would like to thank Faculty of Engineering Technology, Universiti Tun Hussein Onn, Malaysia for its supports.

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