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Removal of Vat Green 3 Dye from Aqua Solution using Chemical Coagulants and Okra Pods as Natural Coagulant by Coagulation-Flocculation Process

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ABSTRACT

This article presents that the coagulation-flocculation process is one of the water treatment processes that mainly removes dyes from aqua solution by using chemical and natural coagulants. This research was conducted to evaluate the use of chemical coagulants (ferric chloride ($FeCl_3$), aluminum chloride ($AlCl_3$) and natural coagulant (okra pods) to remove Vat Green 3 (VG 3) dye from aqua solution by the coagulation-flocculation process. Various experimental parameters were studied by jar test experiments such as pH, coagulant dosages, initial VG 3 dye concentration, mixing speed, and settling time. The results showed that the maximum removal efficiency of VG 3 dye was for FeCl3 97.261%, AlCl3 94.466% and okra pods 92.572% at optimum conditions pH 6 for FeCl3 and okra pods, pH 7 for $AlCl_3$, coagulant dosage 400 mg/L for $FeCl_3$ and AlCl3, 200 mg/L for okra pods dosage, concentration of dye 80 mg/L, mixing speed 150 rpm, and settling time 60 min for FeCl3 and $AlCl_3$, 70 min for okra pods at room temperature 25 ± 2 oC. The maximum volume of sludge at optimum conditions was 33 mL/L, 20 mL/L, 3 mL/L for $FeCl_3$, $AlCl_3$, okra pods, respectively. The kinetics of the coagulation-flocculation process was obeying pseudo first order kinetics more than pseudo second order kinetics. These results indicated that the natural coagulant (okra pods) could be an alternative to chemical coagulants for removal of VG 3 dye from textile effluent due to its low cost, biodegradable, non-polluting and lower sludge production.

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INTRODUCTION

Yearly allot of fresh water is spend in textile industrial process, therefore, reuse of textile industrial wastewater is very important to face high water consumption required for its process (Shirmardi et al., 2013). The main problem of textile industry for a long time is treatment of wastewater because it is strongly pollutant with many chemical pollutants such as dye, fluctuating pH, high temperature, turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), and total dissolves solids (TDS) (Loloei et al. 2013). Dyes are organic compound have high molecular weight and complex structure resulting difficulty biodegrade (Obiora-Okafo & Onukwuli, 2017). There are about seven thousand chemical structures in over forty thousand different dyes and pigments. Textile wastewater contain dyes which because of their synthetic nature and high water solubility, most of them are difficult to remove (Hussein & Jasim, 2021). Vat Green 3 is a vat dye that is commonly used in the textile industry for coloring

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cotton fabrics. As a result, it is frequently discharged in huge quantities into the environment. Due to vat dyes weak exhaustion properties about 5-20% of initial dye remain unfixed and end up in effluents (Arabi et al., 2013). If textile wastewater discharged to environment without treatment caused serious and very harmful to environment and human body which lead to many disease such as anemia, and damage to lung, brain, and kidney therefore, it is important to treat textile wastewater to avoid environment pollution (Kristianto et al., 2019). There are many techniques for textile wastewater treatment such as physiochemical (Yadav et al. 2013), chemical (Nourmoradi et al., 2015), membrane filtration (Xia et al., 2017), oxidation with ozone carbon (Venkatesh et al., 2017), filtration (David et al., 2020), ion exchange (Hassan & Carr, 2018), and adsorption (Puchana-Rosro et al., 2018). All above techniques suffer from one or more limitations such as they are often very costly and accumulation of concentrated sludge caused a disposal problem (Arabi et al., 2013). Coagulation-flocculation process is an essential process for textile wastewater treatment because it has been found to be cost effective, easily operated, energy saving, and efficient (Loloei et al., 2013). Coagulation process is used in wastewater treatment plants to remove particles ranging in size from 0.1µm to 10µm (Adnan et al., 2017). The process of coagulation/flocculation is the binding of microscopic particles in water into larger, heavier clumps that settle away relatively quickly. The bigger particles are known "flock", the majority of the dye in the water will be removed by well formed flock that settles out of the water rapidly in the sedimentation basin (Ratshilivha et al., 2014; Jindal et al., 2016). Coagulants are classified as natural coagulants and chemical coagulants. Chemical coagulants used in the treatment of color from wastewater such as alum ($Al_2(SO_4)_3.4H_2O$), magnesium chloride ($MgCl_2$), aluminum chloride ($AlCl_3$), ferric sulfate ($Fe_2(SO_4)_3$, calcium chloride ($CaCl_2$), ferrous sulfate ($FeSO_4$), ferric chloride ($FeCl_3$), and PAC or polyaluminum chloride ($AlCl_3.6H_2O$) (Gelebo et al., 2019). The disadvantage of chemical coagulants is using a lot of chemical quantity which caused many hazards for the environment, and produce a lot of non-biodegradable sludge, to overcome this problems, natural coagulants are used (Solanki et al., 2013; Ahmad et al., 2018). Zemmouri *et al*. 2013 studied using chitosan as primary flocculant and aluminium sulfate (alum) as coagulant for treatment the raw water from Beni-Amrane dam with high turbidity by coagulation-flocculation process. Various chitosan doses were examined, the results reveal that turbidity removal was 85% when chitosan used alone and 97% when chitosan used in combination with alum with chitosan dose 0.15 mg/L and alum dose 20 mg/L, pH 7.8 after settling time 45 min. Vijayaraghavan & Shanthakumar, 2015 evaluating alginate extracted from marine brown algae, *Sargassum sp.* and alum to remove direct blue 2 dye from aqueous solution by coagulation-flocculation process, experiment carried by jar test using various parameters pH, alginate dose, initial concentration of dye, calcium dose. The maximum dye removal was 86.1% with optimum conditions: pH 4, initial dye concentration 200 mg/L, calcium dose 6 g/L, alginate dose 40 mg/L. Sludge volume index was 2.14 mL/g with alginate coagulant, and with alum 16.43 mL/g, kinetic study showed that coagulation process obey second order kinetic model. Gelebo & Ahmed, 2019 studied removal of direct blue/ red, reactive red/ blue, industrial wastewater and the mixture of both dyes using moringa stenopelata seed extract by coagulation-flocculation process, simple extraction with distilled water and with saline have been used to obtain seed extract, different parameters were tested pH, coagulant dose, mixing time, colour and turbidity. The maximum removal for reactive red 195, blue19, direct Red 81, blue 86, Industrial waste water and the mixture was 98.4, 86, 94.45, 89.3, 90.5 and 85.8% and 97.3, 84.45, 96.6, 84.8, 87.73 and 84.6% for both simple and saline extract respectively at optimum coagulant dose 70 mL/L and pH 10. Ahmad et al., 2018 assessed removal of reactive yellow dye from textile wastewater by coagulation-flocculation process using potato starch. Interaction of parameters was indicated by analysis of variance (ANOVA), different parameters were examined pH, coagulant dose, and temperature. Taguchi optimization technique was used to optimized parameters. Maximum dye removal about 27% with optimum parameters temperature 55 °C, pH 10, coagulant dose 0.5% (w/v). The advantages of natural coagulants are low cost, easily obtained, biodegradable, low toxicity, and produce small sludge volume (Jagaba et al., 2020).

Okra plant is also known as *Abelmoschus esculentus* L. (Moench) or *Hibiscus esculentus* L.. It is a plant that grows in the tropics, sub-tropics, and warmer areas. Okra can be used as a coagulant for the treatment of wastewater because it contains protein in various sections of the plant (Dantas et al., 2021). Okra pods powder is a non-toxic, biodegradable plant product with coagulant and coagulant aid properties. Okolo et al., 2015 revealed okra pods as natural coagulant to remove turbidity from paint wastewater by coagulation-flocculation process, different parameter were tested pH, coagulant dose, and settling time. The maximum turbidity removal was 80% and 95% at settling time 3, 30 min, respectively with optimum parameters pH 4, okra pods powder dose 200 mg/L.

This present paper investigates the application of the coagulation-flocculation process to remove Vat Green 3 (VG 3) dye from aqua solution using different chemical coagulants (aluminum chloride, ferric chloride), and a natural coagulant (okra pods). The experiments were carried out using the jar test to find the best operating factors for pH, dosage, dye concentration, mixing speed, and settling time on the VG 3 dye removal efficiency. As well as sludge production of chemical and natural coagulants and kinetic models (pseudo first-order and pseudo second-order) were studied.

MATERIALS AND METHODS

Vat green 3 (VG 3) dye preparation

Vat Green 3 (VG 3) (CI: Vat Olive Green B) dye was used as a pollutant in this study and was supplied from Al-Khadmya cotton factory of textile industries in Baghdad, Iraq. Vat Green 3 has a molecular formula of $C_{31}H_{15}NO_3$ (molecular weight 449.465 g/mol). Fig.1 shows the molecular structure of VG 3 dye. The stock solution of dye was prepared by dissolving 1000 mg of dye in one liter of distilled water (DI) of 3-8 μS/cm conductivity to obtain a concentration of 1000 mg/L and then saving it in a conical flask to be used in the experiments. Stock dye solution was diluted to obtain different dye concentrations (10, 20, 50, 80, 120, 140) mg/L.

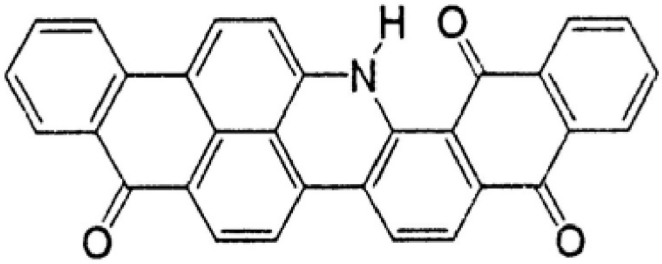

Fig. 1. Chemical structure of VG 3

Calibration curve of Vat Green 3 (VG 3) dye

Fig. 2 shows the calibration curve of VG 3 dye was conducted by using different concentration solutions. A spectrophotometer UV (Thermo-genesis 10 UV, USA) at a wavelength of 643 nm was used to measure absorbance for each concentration. For each concentration, the value of absorbance obtained was recorded. After that, a linear relation was plotted between absorbance and VG 3 dye concentration in order to calculate the unknown VG3 dye concentrations during the removal process.

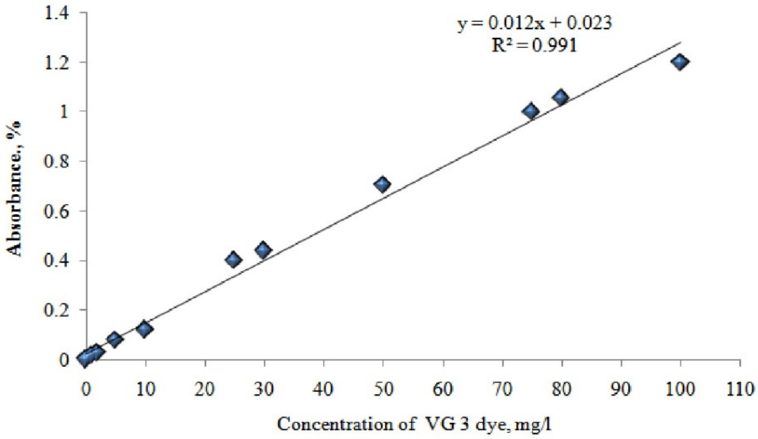

Fig. 2. Calibration curve of VG 3 dye

Chemical coagulants

Ferric chloride ($FeCl_3$) (molecular weight 162.21 g/mol), and aluminum chloride ($AlCl_3$) (molecular weight 133.33 g/mol) were used as chemical coagulants. The stock solution of coagulants was prepared by dissolving 1000 mg of these salts in 1L of deionized water to obtain a concentration of 1000 mg/L, and then the prepared solutions must be well stirred at an agitation speed of 400 rpm for 15 min using a magnetic stirrer (LMS-1003, Korea) until the coagulants are completely dissolved. Sodium hydroxide (NaOH) or hydrochloric acid (HCl) were used for pH adjustment. The chemical components delivered from Lobachemie, India, were used in this study.

Natural coagulant

Okra pods (*Abelmoschus esculentus* L. Moench.) were collected from a local market, washed with tap water to remove dirt and dust, and then washed with distilled water to remove salts before being dried in an oven at 45 °C for 24 hours. Dried okra pods were cut into small pieces and ground in a mill until they became fine powder, then sieved with a sieve of 150 µm. A weight of 1gm of okra pods powder was added to 1L of distilled water to obtain a stock coagulant solution of 1000 mg/L, and stirred well by a magnetic stirrer for 10 min, and then filtered through 1µm filter paper so that it could be used in experiments. Table 1 shows the composition of okra pods (Dantas et al., 2021).

Table 1. Composition of Okra Pods.

Proximate Composition of Okra Pods Per 100 g Edible Portion	Quantity
Water	88.60 g
Protein	2.10 g
Fat	0.20 g
Carbohydrate	8.20 g
Energy	144.00 kJ (36 kcal)
Fibre	1.70 g
Ca	84.00 mg
P	90.00 mg
Fe	1.20 mg
β-carotene	185.00 µg
Riboflavin	0.08 mg
Thiamin	0.04 mg
Niacin	0.60 mg
Ascorbic acid	47.00 mg

Experimental work

A jar test (Lovibond, Germany) was conducted for the coagulation-flocculation process as shown in Fig. 3. It was carried out in six beakers, each beaker for each test was filled with 1000 ml with required dye solution concentration. pH was adjusted by adding 0.1 M HCl and/or 0.1 M NaOH as required and measured by a pH meter (BP3001, Trans Instruments, Singapore). Predetermined amount of a coagulant solution was added to each beaker then the was stirred rapidly for 3 min at an agitation speed of 200 rpm to disperse the coagulant solution in all solutions, followed by a slow speed at 50 rpm for 30 min to improve interaction between coagulating particles and facilitate the production of large flocs, then the mixed solution was allowed to settle the flocs for 50 min. Finally, after settling samples 2 ml was withdrawn from 5 cm below the supernatant surface with a pipette, the samples were filtered with Whatman no. 42 filter paper and then analyzed by a spectrophotometer UV for detecting the concentration of VG 3 dye remnants. The effect of various parameters such as pH (2-11), coagulant dosage (10-500) mg/L, concentration of dye (10-140) mg/L, mixing speed (50-250) rpm, and settling time (10-80) min were tested for removal of VG 3 dye at room temperature 25 ± 2 °C. The percentage of removal (R%) after each run was calculated as follows (Desta & Ebba, 2021; Shamkhi & Hussein, 2022):

$$R(\%) = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (1)$$

where C_i and C_e are initial and equilibrium concentrations of VG 3 dye in the water (mg/L), respectively.

The sludge volume production was determined after coagulation-flocculation experiment under optimum conditions according to the following equation (Ramavandi, 2014):

Sludge volume = volume of settled sludge (mL) / total volume of sample (L) (2)

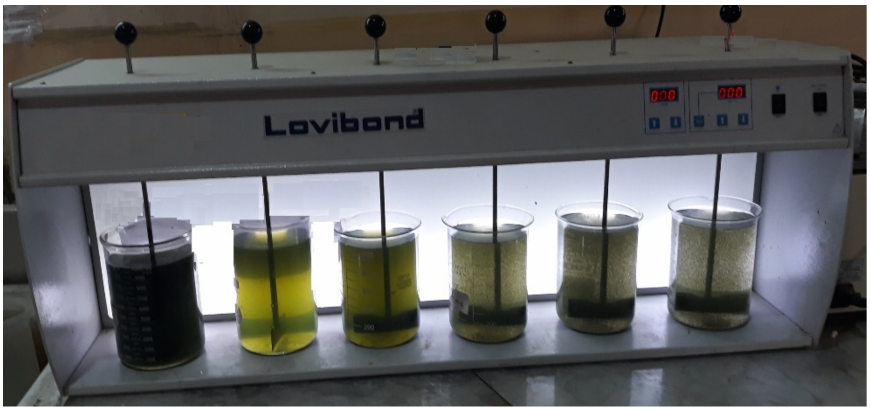

Fig. 3. Jar test experimental work

RESULTS AND DISCUSSION

Results of pH

According to many studies, pH has a vital role in the coagulation flocculation process because it influences not only the reagent characteristics but also the dye hydrolysis and solubility (Karam et al., 2021). The series of experiments have been conducted at different pH values (2, 4, 6, 7, 9, 11), which were adjusted by using 0.1 M NaOH and/or 0.1 M HCl, coagulant dosage kept at 100 mg/L, VG 3 dye concentration of 50 mg/L, mixing speed of 200 rpm, and settling

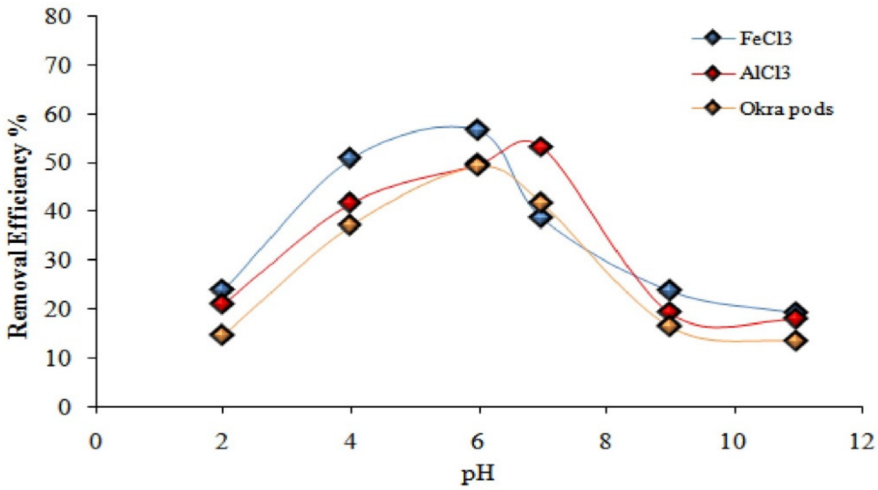

Fig. 4. pH effect on removal efficiency of VG 3.

time 50 min at room temperature 25 ± 2 °C. Fig. 4 depicts the maximum removal percentage of the VG 3 dye: 56.515%, 49.252% for $FeCl_3$, and okra pods respectively at pH 6, and 53.08 % for $AlCl_3$ at pH 7. It is noticed that the removal percentage increases from 23.823% to 56.515% for $FeCl_3$ when pH increased from 2 to 6, 20.98% to 53.08% for $AlCl_3$ with increasing pH from 2 to 7, and finally 14.56% to 49.252% for okra pods with increasing pH from 2 to 6, above these values the removal percentage decreased to 19.052% for $FeCl_3$, 17.84% for $AlCl_3$ and 13.281% for okra pods with increasing pH to 11. This due to increasing the density of positive charge (H^+) at low pH causes the coagulant surface to positively charge, resulting in higher dye removal efficiency (Freitas et al., 2015). On the other hand, increasing in density of negative charge (OH^-) at higher pH causes the coagulant surface to become negatively charged, causing low dye removal efficiency (Irma et al., 2015).

There are many studies consistent with the results of the current study

Kristianto et al., 2019 investigated removal of congo red dye using *Leucaena leucocephala* seed's extract as natural coagulant, the maximum removal dye efficiency was 99.9% at pH 3, further increased in pH removal efficiency decreased.

Dalvand et al., 2017 mentioned that ferric sulfate $Fe_2(SO_4)_3$ used as a coagulant to remove direct red 23 dye from wastewater, the maximum dye removal was 97.9% at optimum pH 7, above pH 7 the removal efficiency dropped. Another researchers (Hussein & Jasim, 2021) used polyaluminum chloride (PACl), aluminum chloride ($AlCl_3$), ferric sulfate $Fe_2(SO_4)_3$, and magnesium chloride ($MgCl_2$) for removal of reactive blue dye, the maximum dye removal was 75%, 86%, 91% and 35% at pH 10, 8, 6 and 10 for PACL, $AlCl_3$, $Fe_2(SO_4)_3$, and $MgCl_2$, respectively.

Results of coagulants dosage

The effect of a coagulant dosage on VG 3 dye removal efficiency were studied. The experiments were carried out with optimum pH values (6 for $FeCl_3$ and okra pods, 7 for $AlCl_3$), initial concentration of VG 3 dye of 50 mg/L, mixing speed of 200 rpm, and settling time 50 min at room temperature 25 ± 2 °C. Different coagulant dosage values (10, 50, 100, 200, 400, and 500) mg/L was used. It was found, as the coagulant dosage increased, the removal efficiency of dye increased until the optimum dosage for $FeCl_3$ and $AlCl_3$ 400 mg/L, for okra pods 200 mg/L, after that the removal efficiency became nearly steady. Figure 5

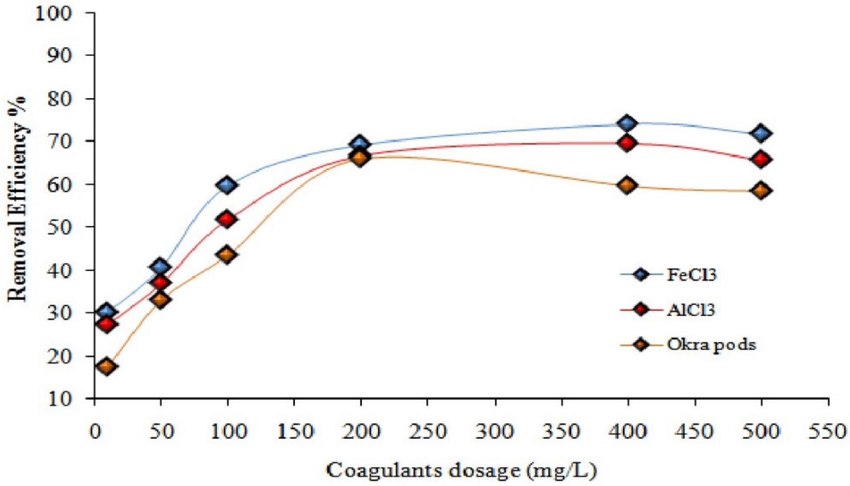

Fig. 5. Coagulants dosage effect on removal efficiency of VG 3 dye

shows the maximum removal efficiency of VG 3 dye is 74.118%, 69.593%, and 65.912% for $FeCl_3$, $AlCl_3$, and okra pods, respectively. This was attributed to the fact that when the coagulant dosage was increased, the active site on the coagulant increased, which caused a large number of binding sites to bind pollutant particles on the surface of the coagulants. After that, the removal efficiency increases nearly steadily due to the saturation of the site with dye (Dalvand et al., 2016). From Fig. 5, the maximum removal efficiency of coagulants for treating wastewater contaminated with VG 3 dye is as follows: $FeCl_3$> $AlCl_3$> okra pods. The previous results were consistent with those of Islam & Mostafa, 2018 who reported that polyaluminium chloride (PAC) and ferric chloride ($FeCl_3.6H_2O$) were used to remove reactive red dye from synthetic waste water using different coagulant dosage range (100-600) mg/L, the removal efficiency of PAC was 93% at dose 100 mg/L and 85% of $FeCl_3$ at dose 200 mg/L, the removal efficiency of coagulants decreased when the coagulant dosage increased above optimum. Also, Chitra & Muruganandam, 2020 have reported a study on use tamarind seeds, *moringa oleifera* seeds, banana peels, fly ash and alum to treat synthetic and real greywater at different coagulant dosage range (200-1200) mg/L, the highest turbidity removal efficiency of synthetic greywater was 61.33%, 85.28%, 90.42%, 93.81%, and 95.79%, and of real greywater was 63.75%, 83.7%, 88.88%, 90.51%, and 93.31% for tamarind seeds, *moringa oleifera* seeds, banana peels, fly ash, and alum at optimum coagulant dosage (400, 600, 1000, 800.1000) mg/L respectively.

Results of initial dye concentration

The effect of initial concentration of VG 3 dye on removal percentage has been determined by varying the dye concentrations (10, 20, 50, 80, 120, 140) mg/L where optimum pH was 6 for $FeCl_3$ and okra pods, 7 for $AlCl_3$, optimum coagulant dosage was 400 mg/L for $FeCl_3$ and $AlCl_3$, 200 mg/L for okra pods, mixing speed 200 rpm, and settling time 50 min at room temperature 25 ± 2 ^{o}C. From Fig. 6, as the initial concentration of dye increased from 10 to 80 mg/L, the removal efficiency of dye increases from 56.898% to 84.631% for $FeCl_3$, 56.883% to 80.144% for $AlCl_3$, and 48.876% to 78.689% for okra pods. When the concentration of dye was more than 80 mg/l, the removal efficiency decreased which reached 79.6%, 72.599%, 70.258% for $FeCl_3$, $AlCl_3$ and okra pods respectively. When dye concentrations increased and there were much coagulant doses that binding the dye particles into flocs,

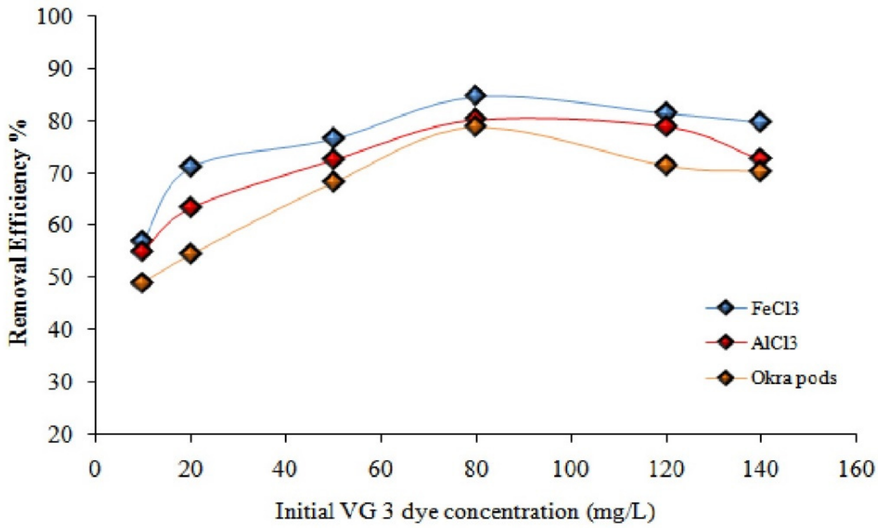

Fig. 6. Initial dye concentration effect on removal efficiency of VG 3 dye

so the removal efficiency increased until the optimum concentration. But when the dye concentration increased higher than optimum concentration, the active sites on the coagulant surfaces became saturated with dye particles, the removal efficiency of dye decreased and several particles remained in aqueous solution (Khader et al., 2018, Jasim & Hussein, 2021). A similar finding was obtained by Goudjil et al., 2021 in which aluminum sulfate (AS) was used as coagulant to treat textile wastewater containing congo red dye. Different initial concentrations of dyes range between (1-50) mg/L, the results showed that the maximum removal dye efficiency was 98.26% at optimum dye concentration (40 mg/L), above the optimum dye concentration removal efficiency decreased. According to Mahmoudabadi et al., 2019 studied using plantago major seed extract as a natural coagulant to remove reactive blue 19 dye from industrial wastewater, different dye concentrations (10-100) mg/L were investigated, the highest removal efficiency was 60% when the initial concentration (40 mg/L), removal efficiency decreased above and below optimum dye concentrations.

Results of mixing speed

Mixing speed is a physical parameter that plays an important role in a coagulation process. The impact of the mixing process on the removal of VG 3 dye was investigated by using different mixing speeds (50, 80, 100, 150, 200, and 250) rpm, concentration of VG 3 dye 80 mg/L, pH 6 for $FeCl_3$ and okra pods, pH 7 for $AlCl_3$, coagulant dosage was 400 mg/L for $FeCl_3$ and $AlCl_3$, 200 mg/L for okra pods dosage, and settling time 50 min at room temperature 25 ± 2 °C. Fig. 7 reveals that the highest removal of VG 3 dye was 89.337%, 86.622%, and 81.885% for $FeCl_3$, $AlCl_3$, and okra pods, respectively at an optimum mixing speed of 150 rpm. This is because increasing the mixing speed causes the particles generated during the coagulation process to move faster, encouraging them to agglomerate into larger masses and precipitate, thus increasing the removal rate (Islam & Mostafa, 2020). The removal rate begins to drop when the mixing speed exceeds 150 rpm for $FeCl_3$, $AlCl_3$, and okra pods. This is because as the mixing speed increases, the lumps generated during the coagulation process break and do not precipitate, remaining stuck in the aqueous solution (BinAhmed et al., 2015). The results were in correlation with the studies done by researchers (Nourmoradi et al., 2015; Saritha et al., 2017; Karam et al., 2021).

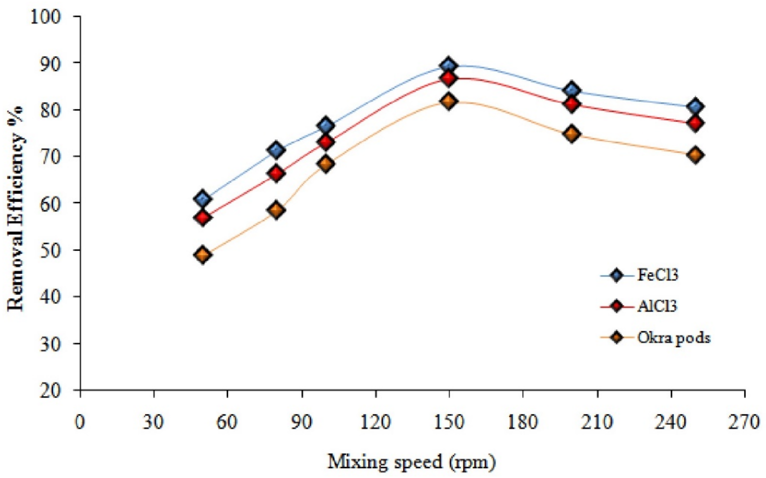

Fig. 7. Mixing speed effect on removal efficiency of VG 3 dye

Results of settling time

One of the operating parameters which give a great consideration in any water treatment plant involved in the coagulation-flocculation process is settling time (Mahmoudabadi et al., 2019). The impact of settling time on VG 3 dye removal efficiency was investigated by various settling times (10, 20, 30, 40, 50, 60, 70 and 80) min, concentration of VG 3 dye 80 mg/L, pH 6 for $FeCl_3$ and okra pods, pH 7 for $AlCl_3$, coagulant dosage was 400 mg/L for $FeCl_3$, $AlCl_3$, 200 mg/L for okra pods dosage, and mixing speed 150 rpm for $FeCl_3$, $AlCl_3$, okra pods at room temperature 25 ± 2 °C. As shown in Fig. 8, the maximum removal efficiency for $FeCl_3$ and $AlCl_3$ was 97.261%, 94.466% respectively at 60 min and for okra pods was 92.572% at 70 min. So, the optimum settling time for $FeCl_3$ and $AlCl_3$ was 60 min and 70 min for okra pods, and when settling time above optimum there is no significant change in the removal efficiency of dye. A similar result was noticed by Vijayaraghavan & Shanthakumar, 2015 in which the maximum removal of congo red dye of 83%, 73%, and 77% obtained at settling time 60 min, 60 min, and 50 min for *Moringa oleifer, Phaseolus vulgaris*, and alum respectively, the results indicated that increasing in settling time increased the removal dye percentage. The removal efficiency of VG 3 dye increases with increasing settling time due to flocs formation, coming together, and settling, which progresses with time until equilibrium is reached, after which no significant flocs formation or settling is achieved (Hussain et al., 2019).

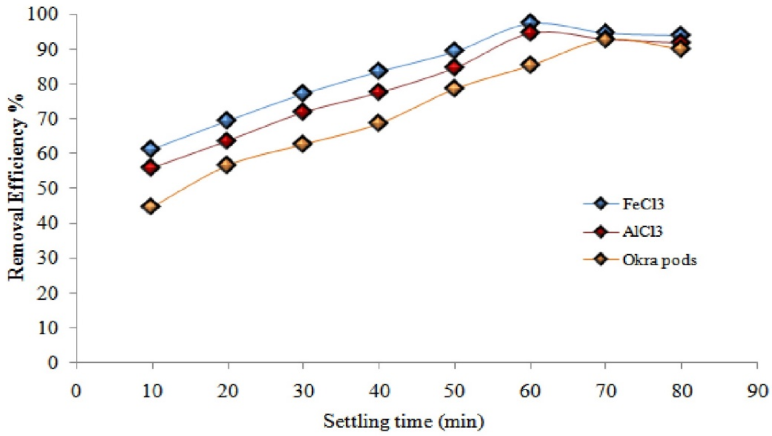

Fig. 8. Settling time effect on removal efficiency of VG 3 dye

Results of sludge volume production measurement

The type of coagulant employed and the operating parameters affect the volume and properties of the sludge produced by the coagulation-flocculation process. During the coagulation–flocculation process, the weight of sludge result at the bottom of jar test beakers was used to quantify the volume of sludge generated (Vijayaraghavan & Shanthakumar, 2020). Sludge produced was measured by using Imhoff cone at the optimum conditions (the concentration of VG 3 dye 80 mg/L, pH 6 for $FeCl_3$ and okra pods, pH 7 for $AlCl_3$, coagulant dosage was 400 mg/L for $FeCl_3$ and $AlCl_3$, 200 mg/L for okra pods dosage, mixing speed 150 rpm, and settling time 60 min for $FeCl_3$ and $AlCl_3$, 70 min for okra pods at room temperature 25 ± 2 °C). Fig. 9 shows the maximum volume of sludge settled was 33 mL/L, 20 mL/L for $AlCl_3$ and $FeCl_3$ respectively, and 3 mL/L for okra pods, this means the sludge produced by using chemical coagulants ($AlCl_3$, $FeCl_3$) was more than the sludge produced by natural coagulant okra pods. In the same context, a study carried out by Bouaouine et al., 2017 on the sludge volume produced by chemical coagulants (aluminum sulfate $Al_2(SO_4)_3$, ferric chloride ($FeCl_3$), lime $Ca(OH)_2$) was 380 mL/L, 380 mL/L and 70 mL/L, respectively, and natural coagulants (Moroccan cactus) was 3.3 mL/L, the result revealled that the sludge volume by natural coagulants was less than the sludge volume produced by chemical coagulants. As reported by (Dwarapureddi & Saritha, 2015; Vijayaraghavan & Shanthakumar, 2015; Aboulhassan et al., 2021), the sludge volume produced by natural coagulant is less than chemical coagulant.

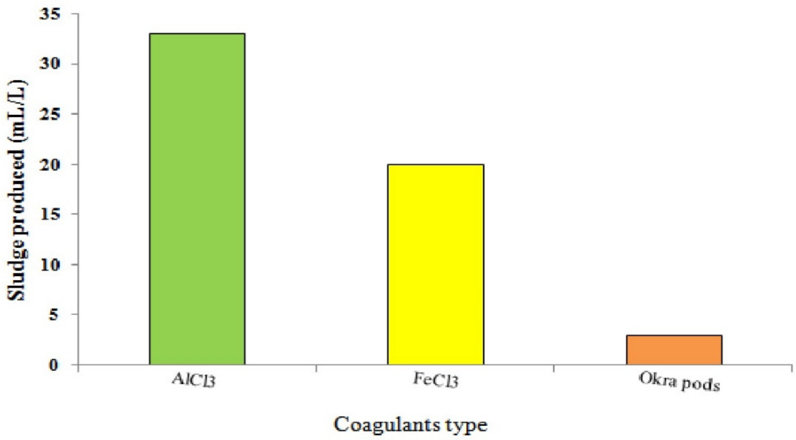

Fig. 9. Sludge volume produced from VG 3 dye at different coagulants.

Coagulation-flocculation Kinetics

Coagulation-flocculation kinetics for removal of VG 3 dye from wastewater was studied, $FeCl_3$, $AlCl_3$, okra pods were used as coagulants. The experimental data was examined with pseudo first order and pseudo second order rate equations. first order equation solution is given in Eq. 3 (Igwegbe et al., 2021)

$$\ln C_t = -k_1 t + \ln C_o \quad (3)$$

where C_o is the initial concentration of VG 3 dye (mg/L), C_t is the concentration of VG 3 dye at any time (t) (mg/L), k_1 is the pseudo first-order reaction rate constant (l/min), and t is the reaction time.

Second order kinetic equation solution is given in Eq. 4 (Sibiya et al., 2021)

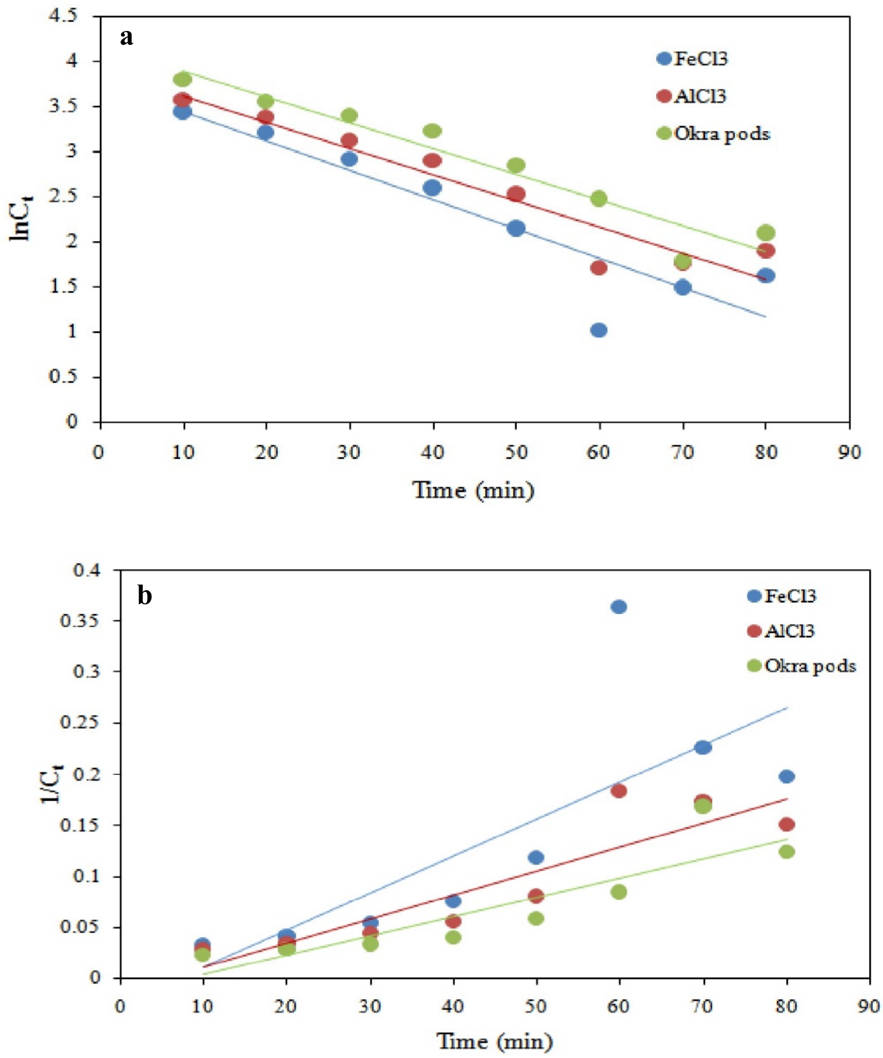

Fig. 10. Coagulation-flocculation kinetics plot for VG 3 dye (a) first-order-kinetic and (b) second-order-kinetic

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_o} \tag{4}$$

where k_2 is pseudo second-order reaction rate constant (L/mg.min)

Fig. 10 a shows the plot of ln C_t against reaction time (t) which yields a straight line with slope k_1 as per pseudo-first-order kinetic. Fig. 10 b shows a plot of $1/C_t$ against time t, which yields a straight line with slop k_2 as per pseudo-second-order kinetic. Kinetic parameters are provided in table 2 show that the regression coefficient (R^2) was favored by pseudo first order kinetics rather than pseudo second order kinetics, so the removal of VG 3 dye using $FeCl_3$, $AlCl_3$, okra pods as coagulants follows the first order kinetic model. Yeheyes et al., 2006 conducted kinetic models on dye (Indantrene Brown (IB) and Imperon Orange (IO)), the results of the experiment obey a pseudo-first-order kinetic model with regression coefficient (R^2) of 0.9366 for IB and 0.9723 for IO.

Table 3 shows the different between results obtained in present study and results obtained in other studies using natural and chemical coagulants.

Table 2. Kinetic parameters for VG 3 dye using $FeCl_3$, $AlCl_3$, okra pods as coagulants

Pseudo-first-order				Pseudo-second-order			
Type of Coagulants	**$FeCl_3$**	**$AlCl_3$**	**okra pods**	**Type of Coagulants**	**$FeCl_3$**	**$AlCl_3$**	**okra pods**
k_1 (1/min)	0.032	0.029	0.027	k_2 (L/mg.min)	0.003	0.002	0.001
y-intercept	3.767	3.912	4.155	y-intercept	-0.025	-0.013	-0.011
R^2	0.833	0.906	0.949	R^2	0.588	0.802	0.837

Table 3. Comparison of pollutants removal using different natural and chemical coagulants

Type of pollutant	wastewater	Flocculant	Optimum dosage	Coagulants	Optimum dosage	Removal efficiency	COD change	Kinetic	Reference
kaolin and hunic acid	Synthetic wastewater	Mallow	12 mg/L	Al^{+3}	0.025mM	97.4%	80% increase	-	Anastasakis et al., 2009
kaolin and hunic acid	Synthetic wastewater	Okra	5 mg/L	Al^{+3}	0.025mM	97.3%	190% increase	-	Anastasakis et al., 2009
kaolin and hunic acid	Biologically treated effluent	Mallow	62.5 mg/L	Al^{+3}	0.025mM	66%	50% increase	-	Anastasakis et al., 2009
kaolin and hunic acid	Biologically treated effluent	Okra	2.5 mg/L	Al^{+3}	0.025mM	74%	40% increase	-	Anastasakis et al., 2009
Naphthalene black dye	Aqueous dye solution	-	-	Alum	1000 mg/L	67.90%	-	Second order	Obi et al., 2019
Alizarin red dye	Aqueous dye solution	-	-	Alum	1000 mg/l	78.89%	-	Second order	Obi et al., 2019
Naphthalene black dye	Aqueous dye solution	-	-	Tiger nut	1000 mg/L	94.43%	-	Second order	Obi et al., 2019
Alizarin red dye	Aqueous dye solution	-	-	Tiger nut	1000 mg/l	96.55%	-	Second order	Obi et al., 2019
Vat Green 3 (VG 3) dye	aqua solution	-	-	$FeCl_3$	400 mg/L	97.261%	-	First order	Present study
Vat Green 3 (VG 3) dye	aqua solution	-	-	$AlCl_3$	400 mg/L	94.466%	-	First order	Present study
Vat Green 3 (VG 3) dye	aqua solution	-	-	Okra pods	200 mg/L	92.572%	-	First order	Present study

CONCLUSIONS

The present work reveals the possibility of using $AlCl_3$, $FeCl_3$, and okra pods for removing VG 3 dye from aqua solution by coagulation-flocculation process. Coagulation-flocculation process carried out using Jar test. The feasibility of VG 3 dye removal efficiency investigated with various parameters pH, coagulant dosage, initial VG 3 dye concentration, mixing speed and settling time. The results showed that the maximum removal efficiency of VG 3 dye was 97.261%, 94.466%, 92.572% for $AlCl_3$, $FeCl_3$, and okra pods, respectively at optimum conditions. Finding revealed that with increasing pH, coagulant dosage, initial dye concentration, mixing speed, settling time removal efficiency increased until reached optimum conditions, more than optimum value the removal efficiency decreased. The flocs settling time for $AlCl_3$, $FeCl_3$ shorter than for okra pods. The sludge volume produced at optimum conditions as a result of the coagulation-flocculation process was for okra pods (3 mL/L), $FeCl_3$ (20 mL/L) and $AlCl_3$ (33 mL/L). The kinetics study of the coagulation-flocculation process revealed that it fit well the pseudo-first-order kinetic model with R^2 = 0.833, 0.906, and 0.949 for $AlCl_3$,

$FeCl_3$ and okra pods, respectively. This study showed that using natural coagulant (okra pods) is environmental friendly compared to chemical coagulants because it produced low sludge volume, non pollutant, biodegradability, recycle, reuse, environmental sustainability in addition sludge handling cost decreased, easy available, easily storied, do not required skilled worker, low cost and requires low dose, therefore, natural coagulants have a promising future.

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CONFLICT OF INTEREST

The author declares that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the author.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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