Residual seawater from salt production (bittern) as a coagulant to remove lead (Pb²⁺) and turbidity from batik industry wastewater

Eddy Setiadi Soedjono, Agus Slamet, Nurina Fitriani, Mega Soekarno Sumarlan, Agus Supriyanto, Dwi Ratri Mitha Isnadin, Norzila Binti Othman

Department of Environmental Engineering, Faculty of Civil, Engineering, and Planning, Institut Teknologi Sepuluh Nopember, Kampus ITS, Sukolilo, Surabaya, 60111, Indonesia
Department of Biology, Faculty of Science and Technology, Universitas Airlangga, Kampus C UNAIR, Jalan Mulyorejo, Surabaya, 60115, Indonesia
Department of Water and Environmental Engineering, Faculty of Civil and Built Environment, University Tun Hussein Onn Malaysia, 86400, Parit Raja, Batu Pahat, Johor, Malaysia

HIGHLIGHTS

• Bittern as residual product from salt production using crystallization process is cheap, abundant, and underutilized.
• Bittern is an effective coagulant to remove Pb²⁺ and turbidity from batik production wastewater.
• Response surface methodology (RSM) helps optimize Pb²⁺ and turbidity removal.

ABSTRACT

Coagulation and flocculation using bittern coagulant are effective methods for processing batik industrial wastewater containing heavy metals and high turbidity. Bittern as residual seawater product from salt production can be used as a natural coagulant as it contains magnesium (Mg²⁺), chloride (Cl⁻), and sulfate ions (SO₄²⁻) which can react with Pb²⁺ and turbidity to produce precipitation. This study focused on Pb²⁺ and turbidity removal from batik wastewater by introducing different variations of coagulant doses and variations in fast-stirring speed. Bittern coagulant dosage (v/v) of 5%, 15%, 25%, and 35% were used while fast-stirring speed were 55 rpm, 90 rpm, and 125 rpm. Results of this experiment showed that variations of coagulants and stirring speed to give Pb²⁺ maximum removal of 99.3% happened when coagulant dose and stirring speed at 35% and 55 rpm, while maximum turbidity removal at 97% happened when coagulant dose and stirring speed was 15 % and 125 rpm, respectively. Optimum dose using Response Surface Methodology (RSM) was at coagulant dose of 25% with 55 rpm, of which Pb²⁺ and turbidity removal were 99% and 93%, respectively.

1. Introduction

Batik industry in Indonesia is experiencing a rapid development. International recognition by UNESCO in 2009 for batik increased consumer demand for batik and number of batik centers in various regions of Indonesia. Based on data from Ministry of Industry, there were as many as 56,000 units of small and medium batik enterprises (SMEs) in 2018 (Utama, 2018). Development of batik industries definitely affected the increase of its wastewater.

Batik industry wastewater is generated from different processes like coloring, washing, and rinsing of batik fabric. Use of synthetic dyes produces wastewater that contains dyes of high turbidity concentration (Apriyani, 2018). Turbidity disrupts aquatic life of receiving water bodies as it hinders photosynthesis (Yasril, 2018) while synthetic dyes contain heavy metals like lead (Pb²⁺). Based on its toxicity, US Agency for Toxic Substances and Disease Registry classifies Pb²⁺ as compound with significant influence on human health (Misran, 2009). Lead is mordant dying substance that binds dyes in the form of PbCrO₄ (Suharty, 1999). Lead can also be used as a dye mixture: white color comes from white lead [Pb(OH)₂.2PbCO₃] and red color is from red lead (Pb₃O₄) (Latifah et al., 2014). Lead has a dangerous impact on health as it can enter human body and cause poisoning. Lead poisoning in humans can cause...
dysfunction and damage to kidneys, reproductive system, liver, brain, and central nervous system. Lead can even cause mental retardation in children and can also cause death (Dewi, 2009). Therefore, this research is concentrated to study on lead removal using bittern as compared with other heavy metals which may be associated with batik wastewater. Besides, other findings regarding lead removal in the study area shows the concern of the issue (Subekti, 2017; Nisa, 2016).

One effective processing method to remove Pb^{2+} and turbidity from batik industry wastewater is by adding coagulant to conduct coagulation and is followed by flocculation (Permana et al., 2014). Coagulant added can be either synthetic or natural coagulant (Hendraawati, 2016). As bittern magnesium ions (Mg^{2+}), chloride ions (Cl^{-}), and sulfate ions (SO_4^{2-}) that can react with Pb^{2+} and turbidity from batik wastewater, then bittern is used for coagulant in this study. Furthermore, bittern is abundant residual solution which is underutilized in salt production using crystallization process.

2. Research method

2.1. Location and time of research

Batik industry wastewater was obtained from batik industries at Kampung Batik Jetis, located in Jalan Pasar Jetis, Sidoarjo Regency, East Java Province. Bittern was obtained from salt ponds located in Jalan Mondung Selatan, Pamukasan Regency, East Java Province. Preparation of coagulant, wastewater sample, tools, and materials, as well as analysis for turbidity were conducted at the Ecology and Environmental Laboratory of the Faculty of Science and Technology, Universitas Airlangga. Bittern characterization was carried out by measuring several parameters, including pH (SNI 06-6989.11-2004), temperature (SNI 06-6989.23-2005), turbidity (SNI 06-6989.25-2005), and lead concentration (Pb^{2+}) (SNI 06-6989.8-2004).

2.2. Tools and materials

Main tool and instrument used in this experiment were a complete set of jar test and an AAS of Shimadzu AA-7000 with wave length of 283.3 nm or 217 nm. Materials used in this study comprised of 5 L of bittern and 5 L of batik industry wastewater. Scanning electron microscope (SEM) was conducted to perform surface analysis from flocs from batik wastewater with bittern and precipitates of bittern. A volume of 200 mL of batik wastewater with 15% bittern (v/v) was prepared through coagulation and sedimentation which the precipitate was dried at 105°C or 217 nm. Materials used in this study comprised of 5 L of bittern and 5 L of batik industry wastewater. Scanning electron microscope (SEM) was conducted to perform surface analysis from flocs from batik wastewater with bittern and precipitates of bittern. A volume of 200 mL of batik wastewater with 15% bittern (v/v) was prepared through coagulation and sedimentation which the precipitate was dried at 105°C or 90 min before scanning. Bittern precipitates was filtered and dried in 60 °C for 30 min before scanning. Response surface methodology (RSM) was used to get to know best variable conditions.

2.3. Preparation of bittern

Bittern characterization was carried out by measuring several parameters, including pH (SNI 06-6989.11-2004), temperature (SNI 06-6989.23-2005), turbidity (SNI 06-6989.25-2005), magnesium (Mg^{2+}) (SNI 06-6989.55-2005), chloride (Cl^{-}) (SNI 06-6989.19-2004), and sulfate (SO_4^{2-}) (SNI 06-6989.20-2004).

2.4. Preparation of batik industry wastewater

Five liters of wastewater samples in the form of residual solutions from batik cloth coloring was taken from batik industry at Kampung Batik Jetis in a 5 liter jerrycan. Initial characterization tests were performed on the coagulant samples obtained which included pH (Indonesia National Standard) (SNI) 06-6989.11-2004), temperature (SNI 06-6989.23-2005), turbidity (SNI 06-6989.25-2005), and lead concentration (Pb^{2+}) (SNI 06-6989.8-2004).

2.5. Implementation of jar test

Using the jar tests, batik industry wastewater was mixed with bittern. The volume of batik industry wastewater was 200 ml, while bittern coagulant doses (v/v) varied from 5%, 15%, 25%, and 35%. The fast-stirring speed varied at 55 rpm, 90 rpm, and 125 rpm for 5 min and continued with slow-stirring at a speed of 30 rpm for 15 min. Samples were allowed to stand for 60 min to form two layers, namely filtrate and precipitate (Qasim and Zhu, 2018). Filtrate was used to measure turbidity while precipitate was further filtrated using filter paper for Pb^{2+} analyses using AAS. Replication was conducted twice for each treatment. Removal for turbidity and lead is based on ratio between remaining concentration after experiment to initial concentration.

2.6. Statistical analysis

Statistical analysis was conducted using SPSS 26 (Statistical Package for the Social Sciences) software. Statistical analysis was used to determine the effect of coagulant dose variations and fast-stirring speed variations on the percentage of Pb^{2+} and turbidity removal using bittern. Statistical analysis was performed with a normality test and a homogeneity test. If the distribution values obtained are normal and homogeneous (p value > 0.05), a Two-Way analysis of variance (ANOVA) is performed to determine whether the dose of coagulant and speed of fast-stirring affect the percentage of Pb^{2+} and turbidity removal.

2.7. Analysis of optimal coagulant dose and stirring speed

Analysis of optimal coagulant dose and stirring speed was carried out using Response Surface Methodology (RSM) with the help of Design Expert 11.00 software. This program performed optimization according to variable data and response measurement data entered. The output of the optimization stage was the recommendation of several new optimal formulas according to the program. The most optimal formula was a formula with a maximum desirability value. The desirability value which was closer to the value of 1.0 indicated that the ability of program to produce the desired product was better. The purpose of optimization was not to obtain a desirability value of 1.0, but was to find the best conditions that brought together all the objective functions (Raisi and Farzani, 2009).

| Table 1. Characteristics of bittern coagulant. |
|-----------------------------------------------|
| **No.** | **Parameter** | **Unit** | **Value** |
| 1. | pH | - | 6.5 |
| 2. | Temperature | °C | 25 |
| 3. | Colour | - | Clear yellowish |
| 4. | Turbidity | NTU | 11.4 |
| 5. | Chloride (Cl^{-}) | mg/L | 251,732 |
| 6. | Sulphate (SO_4^{2-}) | mg/L | 38,750 |
| 7. | Magnesium (Mg^{2+}) | mg/L | 63,030 |

| Table 2. Characteristics of batik wastewater. |
|----------------------------------------------|
| **No.** | **Parameter** | **Unit** | **Value** |
| 1. | pH | - | 11 |
| 2. | Temperature | °C | 25 |
| 3. | Colour | - | Dark green |
| 4. | Turbidity | NTU | 500.25 |
| 5. | Lead (Pb^{2+}) | mg/L | 6.34 |
3. Results and discussion

3.1. Characteristics of bittern coagulant

Initial testing of bittern coagulants was performed to determine its characteristics which the results are shown in Table 1. Based on the bittern characteristic test, it was known that concentration of chloride ions (Cl\(^{-}\)) was 251732 mg/L, sulfate ions (SO\(_4^{2-}\)) was 38750 mg/L, and magnesium ions (Mg\(^{2+}\)) was 63030 mg/L. Cations and anions present in bittern would react with suspension in wastewater to form deposition of suspended particles to remove turbidity (Ayoub et al., 2000). Chloride ions (Cl\(^{-}\)) and SO\(_4^{2-}\) which reacted with Pb\(^{2+}\) affected the deposition of Pb\(^{2+}\) (Permana et al., 2014).

3.2. Characteristics of batik wastewater

Characteristics of batik wastewater are shown in Table 2. Based on the batik wastewater characteristics, it inferred that the concentration of Pb\(^{2+}\) was 6.34 mg/L. Lead (Pb\(^{2+}\)) in batik industry wastewater was from mordant substances. These substances were dye binding agents in the form of PbCrO\(_4\) (Suharty, 1999). Lead (Pb\(^{2+}\)) was also used as a dye mixture. Turbidity in batik wastewater was 500 NTU. Turbidity was from residual coloring water which contained suspended dyes and from the waxing process which contained residual wax (Apriyani, 2018).

3.3. Effect of bittern dose and fast-stirring speed on lead removal from batik wastewater

Treatment based on variations of coagulant dose and fast-stirring speed was aimed to discover effects caused by the four coagulant doses used (v/v), namely 5%, 15%, 25%, and 35%, as well as the three stirring speeds used of 55 rpm, 90 rpm, and 125 rpm in removing Pb\(^{2+}\). Average percentage of Pb\(^{2+}\) removal is shown in Figure 1. Anova Two-Way test was performed on the Pb\(^{2+}\) removal using SPSS 26 (Statistical Package for the Social Sciences) software. Two p values were resulted namely p value of the coagulant dose variation which was 0.618 and p value of the fast-stirring speed variation which was 0.280. Thus, both p values from the results were >0.05 which indicated that there was no significant effect of the coagulant dose and the fast-stirring speed variations on Pb\(^{2+}\) removal. Average value of Pb\(^{2+}\) removal produced a uniform value in the range of 98%–99% which also indicated no significant effect of the variation in coagulant dose and fast-stirring speed.

Lowest dose of coagulant of 5% showed a high Pb\(^{2+}\) removal of more than 98% as shown in Figure 1. Other coagulant doses of 15%, 25%, and 35% also showed Pb\(^{2+}\) removal that were just as good which were more than 98.47 ± 0.62% to 99.26 ± 0.31%

Table 3. Qc value calculation results of PbCl\(_2\).

| No. | Dose PbCl\(_2\) Qc (M) | PbCl\(_2\) Ksp (M) | Notes               |
|-----|------------------------|--------------------|---------------------|
| 1.  | 5%                     | 3.3 × 10\(^{-6}\)   | 1.6 × 10\(^{-5}\)   | Not yet precipitated |
| 2.  | 15%                    | 2.72 × 10\(^{-5}\)  | Precipitation occurred |
| 3.  | 25%                    | 4.24 × 10\(^{-5}\)  | Precipitation occurred |
| 4.  | 35%                    | 6.67 × 10\(^{-5}\)  | Precipitation occurred |

Table 4. Qc value calculation results of PbSO\(_4\).

| No. | Dose PbSO\(_4\) Qc (M) | PbSO\(_4\) Ksp (M) | Notes               |
|-----|------------------------|--------------------|---------------------|
| 1.  | 5%                     | 5.585 × 10\(^{-7}\) | 1.6 × 10\(^{-8}\)   | Precipitation occurred |
| 2.  | 15%                    | 2.27 × 10\(^{-6}\)  | Precipitation occurred |
| 3.  | 25%                    | 4.92 × 10\(^{-6}\)  | Precipitation occurred |
| 4.  | 35%                    | 7.64 × 10\(^{-6}\)  | Precipitation occurred |

Figure 1. Average removal of lead concentration.
than 98%. This was to show that coagulant dose should be less than 5% to have an efficient removal. Massive Pb²⁺ removal was due to very high concentration of Cl⁻ and SO₄²⁻ in bittern coagulants. Very high concentration of Cl⁻ and SO₄²⁻ affected formation of compounds with Pb²⁺ that formed PbCl₂ and PbSO₄ (Permana et al., 2014). Reaction of Pb²⁺ with Cl⁻ and SO₄²⁻ during coagulation is as follows: Table 1 shows that the ratio of Cl⁻ and SO₄²⁻ is quite high (251732 mg Cl⁻/L = 7.1 M while 38750 mg SO₄²⁻/L = 0.403 M). In equilibrium, Ksp ratio for PbCl₂ and PbSO₄ can be combined to have the ratio between Cl⁻ and SO₄²⁻ to show which precipitate to be initially formed. The ratio can be explained as follows:

\[ \frac{[\text{PbCl}_2]}{[\text{PbSO}_4]} = 1.6 \times 10^{15} \text{ or } \frac{[\text{Cl}^-]}{[\text{SO}_4^{2-}]} = 10^{15} \text{ or } [\text{Cl}^-] = \sqrt{1000 \times [\text{SO}_4^{2-}]} \]

Content of SO₄²⁻ in bitter is 0.403 M; to have precipitation of PbCl₂ then minimum concentration of Cl⁻ is \([\text{Cl}^-] = \sqrt{1000 \times 0.403} = 20 \text{ M}, \)

while Cl⁻ concentration in bittern is 7.1 M. Then the precipitation reaction will be:

\[ \text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \]

Based on the above equilibrium then minimum SO₄²⁻ concentration requirement to have precipitation at pH above 9 when 1 mmol Pb²⁺ ≈ 1 mmol SO₄²⁻ ≈ 1 mmol PbSO₄, Then 207.19 mg Pb²⁺ ≈ 96.06 mg SO₄²⁻ ≈ 303, 25 mg PbSO₄. This is to say that 1 mg Pb²⁺ ≈ 0.4636 mg SO₄²⁻ ≈ 1,4636 mg PbSO₄. Jar test results of 200 mL with bittern addition of 5%, 15 %, 25 % and 35 % by volume is equal to mass addition of SO₄²⁻ 38,75 mg; 116,25 mg; 193,75 mg and 271 mg which show Pb²⁺ removal of 99,04% with 5% bittern and 98,81% removal with 35% bittern. This is understood as stoichiometrically to remove 6.34 mg Pb²⁺/L in batik wastewater will need only 0,0305 mmol SO₄²⁻ or equivalent to 2.9276 mg/L. PbSO₄ is basically poisonous while PbCl₂ is considered carcinogenic. PbSO₄ precipitation mainly happens up to pH 8–8.5 while above it is going to dissolve, while PbCl₂ is easily to precipitate in water and it starts to dissolve when water temperature increases.

PbCl₂ and PbSO₄ compounds can precipitate if they reach saturation point. A saturated solution is a solution that contains the maximum amount of solute (Yazid, 2006). To calculate the precipitation of two

\[ \text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \]
solutions containing ions from insoluble compounds when they are mixed, then it is necessary to calculate the product of ions (Qc) and compare it with product of its solubility (Ksp). Verification of Qc theoretical calculation which was then compared to Ksp in this study was aimed to determine whether precipitation of PbCl$_2$ and PbSO$_4$ occurred due to Pb$^{2+}$ in batik wastewater and Cl$^-$ and SO$_4^{2-}$ from bittern.

Verification of this theoretical calculation is discussed as there are limitations to this study, i.e.; qualitative chemical tests on presence or absence of PbCl$_2$ and PbSO$_4$ from the resulting precipitate were not conducted. Qc calculations of PbCl$_2$ and PbSO$_4$ are shown in Table 3 and Table 4.

Scanning electron microscope (SEM) from coagulated batik wastewater with bittern and bittern precipitates is shown in Figure 2. Bittern shows flat-like area while precipitate becomes far from flat area. Qc results of PbCl$_2$ and PbSO$_4$ were then compared with the Ksp of PbCl$_2$ and PbSO$_4$. Based on the Qc calculation of PbCl$_2$ at a dose of 5% in Table 3, the value was smaller than the Ksp of PbCl$_2$, while the Qc values at 15%, 25%, and 35% doses as seen in Table 3 were greater than Ksp of PbCl$_2$. As Qc of PbCl$_2$ at a dose of 5% was smaller than the Ksp, this indicated that the solution was not saturated yet or PbCl$_2$ precipitation was not formed; whereas Qc of PbCl$_2$ at doses of 15%, 25%, and 35% were greater than the Ksp value of PbCl$_2$.
Qc calculation was also performed on PbSO₄ compounds. Results showed that Qc of PbSO₄ at all doses, namely 5%, 15%, 25%, and 35% as seen in Table 4 were greater than Ksp of PbSO₄. Qc of PbSO₄ at all doses i.e.: 5%, 15%, 25%, and 35% were greater than Ksp of PbSO₄ which indicated that the solution was oversaturated or PbSO₄ precipitate.

As discussed in previous paragraph, it proved that Pb²⁺ removal in batik filtered wastewater occurred due to reaction of Cl⁻ and SO₄²⁻ from bittern to form precipitation of PbCl₂ and PbSO₄. This precipitation was theoretically based on comparison between Qc value and the Ksp. Based on the calculation, Qc value of PbCl₂ at a dose of 5% is less than the Ksp value of PbCl₂; hence at 5% dose PbCl₂ precipitation has not been formed. Qc value of PbSO₄, however, at a dose of 5% exceeded Ksp value of PbSO₄, hence PbSO₄ precipitation happened. Although at a dose of 5% PbCl₂ precipitation has not yet been formed, PbSO₄ precipitation could happen at the same dose with good efficiency for lead (Pb²⁺) removal percentage which the removal was 98% as shown in Figure 2. Based on the calculation, Qc value of PbCl₂ and PbSO₄ at doses of 15%, 25%, and 35% are greater than the Ksp.

![Figure 5. 2D contour plot (a) and 3D surface plot (b) of turbidity removal.](image-url)
value of PbCl$_2$ and Ksp value of PbSO$_4$. This indicates that at dose of 15%, 25%, and 35%, PbCl$_2$ and PbSO$_4$ precipitates were formed, causing highly efficient lead (Pb$^{2+}$) concentration removal percentage at more than 98% which can be seen in Figure 1.

The variations of the fast-stirring speed used in this study, which were 55 rpm, 90 rpm, and 125 rpm, has the same statistical results in removing Pb$^{2+}$ around 98%–99%. All variations of fast-stirring speed were efficient in dispersing coagulants quickly and evenly, hence there was a better potential for collisions between particles and coagulants (Hadiwidodo, 2019). In the stirring process, contact between Pb$^{2+}$ in batik wastewater and Cl$^-$ as well SO$_4^{2-}$ from bittern will quickly occur. Mixing causes formation of clot core flocs of PbCl$_2$ and PbSO$_4$. It coincides with the formation of flocs between particles that have undergone destabilization as they precipitate (Permana et al., 2014).

### Figure 6. 2D contour plot (a) and 3D surface plot (b) of optimum desirability formula.

3.4. Effect of bittern dose and fast-stirring speed on turbidity removal from batik wastewater

Treatment based on the variation of the coagulant dose and the fast-stirring speed was aimed to discover whether there was a significant effect caused by the four coagulant doses used, namely 5%, 15%, 25%, and 35%, as well as the three stirring speeds used, which were 55 rpm, 90 rpm,
and 125 rpm. This experiment was conducted to know turbidity removal of batik wastewater. The average turbidity removal is shown in Figure 3.

Coagulant dose plays important role in particle collision, so addition of coagulant must correspond with flocs formation. Insufficient coagulant dose reduces collision between particles and hinders floc formation. Likewise, when the dose of coagulant is too much, then flocs are not formed properly and it produces more turbidity (Metcalf and Eddy, 2003). Colloidal particles that cause turbidity in batik wastewater are derived from the residual coloring water that contains suspended dyes. They also come from the wax shedding process which obviously contains residual wax (Apryani, 2018). Colloidal which causes turbidity have positive or negative charges. Hence, addition of bittern with high cation and anion concentrations is highly effective in removing turbidity from batik wastewater.

Lowest dose of coagulant which was 5%, showed a high turbidity removal in the range of 91%–94% as seen in Figure 4. Other coagulant doses i.e.: 15%, 25%, and 35% showed turbidity removal that were just as good, ranging from 91% to 96%. Statistical results of this study indicated that there was no effect of coagulant dose variations. All variations of dose were equally good in removing turbidity from batik wastewater as all the removals were more than 91%. This showed that dose of 5% was more than adequate to remove turbidity. This result was in accordance with the research conducted by Ayoub et al. (2000). In his study, variation in bittern dose did not have a significant effect on turbidity removal from alkaline industrial wastewater. Turbidity removal in the industry was more than 95% (Ayoub et al., 2000). Anova Two-Way test was performed on the obtained percentage of turbidity removal using SPSS 26 (Statistical Package for the Social Sciences) software. Two p values were resulted from the Anova Two-Way test, namely p value of coagulant dose variation, which was 0.439 and p value of fast stirring speed variation which was 0.184. Both p values from the data were >0.05 which indicated that there was no significant effect of coagulant dose and fast-stirring speed variations on the turbidity removal.

Fast-stirring has an important role in coagulation process. The role of fast-stirring is essential and inseparable from coagulation process to increase contact and collision between ion or colloidal particles and coagulants to facilitate floc clumping and assist the deposition process (Lin, 2013). Proper stirring makes the coagulant dispersed quickly and evenly in wastewater. Hence, there is a better chance of collisions between particles and coagulants (Hadiwidodo, 2019).

The fast-stirring process causes ions in the bittern coagulant to be distributed to all parts of batik wastewater which then interacts with turbidity-causing particles dispersed in the batik wastewater. This interaction makes the charge become unstable to undergo colloidal particle destabilization. Destabilized colloidal load reduces the effect of repulsive force (electrostatic force) among colloidal particles and increase attraction forces between colloidal particles (van der Waals force). Particles with different charges attract each other and result in the formation of particles with a larger size, making it easier to precipitate to form flocs (Rambe, 2009).

Formed flocs due to coagulation are then processed further in a flocculation process. Flocculation is the process of combining core flocs so that they become a larger-sized floc by slow stirring. Slow-stirring in this study used a stirring speed of 30 rpm for 15 min (Qasim and Zhu, 2018). In the flocculation process, the force of attraction between colloidal particles occurs to cause particles to become larger and more dominant than the repulsion force. Larger flocs will easily precipitate (Angraini, 2016). After the flocculation process, precipitation is carried out by allowing the samples to stand for 60 min. Flocs will precipitate to the bottom of beaker glasses and form two layers: top layer is supernatant of batik wastewater and bottom layer is floc-like sediment.

3.5. Optimal conditions for bittern dose and fast-stirring speed to remove lead and turbidity in batik wastewater

To acquire the optimal Pb$^{2+}$ and turbidity removal, it is necessary to determine the optimal dose of coagulant and fast-stirring speed. The optimal coagulant dose and fast-stirring speed were determined using Response Surface Methodology (RSM) to find the best conditions to remove Pb$^{2+}$ and turbidity. As compared to the one-variable approach which could not detect frequency of interactions between two or more factors, then RSM was a method which could be chosen to determine the optimal conditions that were affected by interactions between variables (Ratnawati et al., 2). Results of RSM were in the form of 2D contour plots and 3D surface plots. The contour plot and surface plot results of Pb$^{2+}$ and turbidity removal are shown in Figure 3 and Figure 4.

The results of contour plot and surface plot in Figure 3 and Figure 4 show how combination of coagulant dose and speed of stirring quickly influence Pb$^{2+}$ and turbidity removal. Colors in Figure 3 and Figure 4 indicate Pb$^{2+}$ and turbidity removal. Blue color in Figure 3 shows lowest Pb$^{2+}$ removal of 98.36% while blue color in Figure 4 shows lowest turbidity removal at 91.07%. Red color in Figure 3 illustrates highest removal of Pb$^{2+}$ of 99.28% while the red color in Figure 4 points out highest removal of turbidity of 96.62%.

Based on the two figures, it can be seen that treatment with 35% coagulant dose with fast-stirring speed of 55 rpm resulted in the maximum removal of Pb$^{2+}$ of 99.28% whereas turbidity removal is not maximum of 92.25%. Maximum turbidity removal is 96.62% with 15% coagulant dose and stirring speed of 125 rpm while Pb$^{2+}$ removal percentage is 98.60%.

Coagulant dosage and fast-stirring speed can be determined using Response Surface Methodology (RSM). The Expert Design 11.00 program recommends formulas of optimal independent variables based on desirability values. The formula of the most optimal is the independent variable with highest desirability value. Desirability value is the value of objective optimization function that shows the ability of the program to fulfill desired based on the criteria established in the final product (Raissi and Farzani, 2009). RSM results based on desirability values are shown in Figure 5 (see Figure 6).

Based on desirability value in Figure 5, optimal coagulant dose is 25% with optimal fast-stirring speed of 55 rpm. Based on coagulant dose and fast-stirring speed, optimal removal of Pb$^{2+}$ and turbidity are 99.13% and 93.13%, respectively.

4. Conclusion

This study shows that variation of coagulant dose and speed of fast-stirring has no effect on Pb$^{2+}$ and turbidity removal from batik wastewater as the removal is similar (more than 90%); although Pb$^{2+}$ removal is slightly higher than turbidity removal, i.e.: maximum Pb$^{2+}$ removal is 99.3% at 35% coagulant dose and fast-stirring speed of 55 rpm, while maximum turbidity removal is 96.62% with 15% coagulant dose and stirring speed of 125 rpm. Based on the data processing using Response Surface Methodology (RSM), optimal coagulant dose is 25% with fast-stirring speed of 55 rpm of which removal of Pb$^{2+}$ and turbidity are 99.13% and 93.13%, respectively.

Declarations

Author contribution statement

Eddy Setiadi Soedjono & Agus Slamet: Analyzed and interpreted the data; Wrote the paper.

Nurina Fitriani, Mega Soekarno Sunamar & Agus Supriyanto: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Dwi Ratni Mitha Isnadina & Norzila Binti Othman: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.
Data availability statement

Data included in article/supp. material/referenced in article

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Apriyani, N., 2018. Industri batik: kandungan limbah cair dan metode pengolahannya. J. Media Ilmiah Teknik Lingk. 3 (1), 1.

Angraini, S., 2016. Pengaruh kecepatan pengadukan dan tekanan pemompaan pada kombinasi proses koagulasi dan membrand ultrafiltrasi dalam pengolahan limbah cair industri karet. J. FTEKNIK 3 (1), 5.

Ayoub, G.M., Merhebi, F., Acra, A., Fadel, ., dan Koopman, B., 2000. Seawater bittern for the treatment of alkalized industrial effluents. Water Res. 34 (2).

Dewi, K.S.P., 2009. Kemampuan adsorpsi batu pasir yang dilapisi besi oksida (Fe₂O₃). J. Bumi Lestari 9 (2), 1.

Hadiwidodo, M., 2019. Penggunaan nano-bio koagulan Dari cangkang keong sawa (Pila ampullacea) untuk menurunkan COD, kekeruhan, dan TSS limbah cair industri farmasi. J. Presipitasi 16 (3).

Hadiwidodo, M., 2019. Penggunaan nano-bio koagulan Dari cangkang keong sawa (Pila ampullacea) untuk menurunkan COD, kekeruhan, dan TSS limbah cair industri farmasi. J. Presipitasi 16 (3).

Latifah, R.N., Roro, E., Anistya, L., Erick, R.Y., Nur, J.A., Ayuni, D.R., Rosid, E.M., Edi, P., 2014. Pemanfaatan α-keratin bulu ayam sebagai adsorben ion timbal (Pb). ALCHEMY J. Penelit. Kimia 10 (1), 12.

Lin, J.L., 2013. Enhanced particle destabilization and aggregation by flash-mixing coagulation for drinking water treatment. J. Sepur. Purif. Technol. 115, 145–151.

Metcalf, Eddy, 2003. Wastewater Engineering: Treatment and Reuse Edisi Keempat. McGraw-Hill, New York.

Mistran, E., 2009. Pemanfaatan kulit coklat dan kulit kopi sebagai adsorben ion Pb dalam larutan. J. Sigma 12 (1), 23–29.

Nisa, S.Q.Z., 2016. Adsorpsi Pb²⁺ Pada Limbah Cair Industri Batik Menggunakan Limbah Padat Agar-agar., 50 Skripsi, Fakultas Sains dan Teknologi, Universitas Airlangga, Surabaya.

Permana, R.L., Siti, S.M., dan Nurwachid, B.S., 2014. Penggunaan air laut sebagai koagulan untuk menurunkan kadar Pb dan intensitas warna. Indo. J. Chem. Sci. 3 (2), 143–144.

Qasim, S.R., Zhu, G., 2018. Wastewater Treatment and Reuse Theory and Design Examples. CRC Press, Texas.

Raisi, S., Farzani, R.E., 2009. Statistical Process Optimization through Multi-Response Surface Methodology. World Acad. Sci. Eng. Technol. 267–271.

Rambe, A.M., 2009. Pemanfaatan Biji Kelor (Moringa Oleifera) Sebagai Koagulan Alternatif Dalam Proses Penjernihan Limbah Cair Industri Tekstil. Sekolah Pascasarjana, Universitas Sumatera Utara, Medan.

Ratnawati, S. E., Ekantari, N., Pradipta, R.W., dan Paramita, B.L Aplikasi response surface methodology (RSM) pada optimasi ekstraksi kalsium tulang lele. J. Perik. Univ. Gadjah Mada., 20(1): 46.

Subekti, J., 2017. Pemanfaatan Air Laut Sebagai Koagulan Alternatif Untuk Menurunkan Kadar Pb²⁺ Pada Air Limbah Industri Batik. Skripsi, Fakultas Sains Dan Teknologi, 63. Universitas Airlangga, Surabaya.

Sutharty, N.S., 1999. Studi kualitas fisik kimia 3 (tiga) anak sungai bengawan solo di Kabupaten karanganyar. In: Pusat Studi Lingkungan Hidup, Lembaga Penelitian. Universitas Sebelas Maret, Surakarta.

Utama, S., 2018. Media Industri: 4 Tahun Kinerja Sektor Manufaktur. Kementerian Perindustrian, Jakarta, pp. 34–35.

Yazid, E., 2006. Kimia Fisika Untuk Paramedis. ANDI, Yogyakarta.