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Removal of fluoride and ammoniacal nitrogen from fertiliser wastewater industry using acetylene production sludge (APS)

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Abstract

Wastewater from the fertiliser industry has caused a major problem to the inland water due to the high contaminant of fluoride and ammoniacal nitrogen (AN). Acetylene production sludge (APS) was chosen in this study due to its efficiency. Its properties can aid the wastewater treatment process and it is also environmentally friendly. The characteristics of APS were anaysed by using X-ray diffraction (XRD) and X-ray fluorescent (XRF). This investigation was not only for fluoride and AN removal, but also on chemical oxygen demand (COD) of the wastewater. Jar test was conducted, on the percentage removal of fluoride and AN by varying the parameter such as pH and APS dosage. Fluoride and AN were found to be reduced at an optimum APS dosage of 2.0 g with a pH of 10.18. Meanwhile COD was reduced at an optimum APS dosage of 2.5 g with a pH of 11.38. The maximum percentage removal of fluoride, AN and COD were 15.02%, 51.84%, and 6.64% respectively. The APS performance was then validated by multilinear regression using Excel Data Analysis ToolPak based on the experimental data obtained. The study shows that APS is a waste material that has a potential to be repurposed for treating fluoride and AN contaminated wastewater.

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1.0 Introduction

Malaysia is one of the developing countries that grown economically in the agricultural sector that contributes 8.2% of the economic activity (Department of Static Malaysia, 2020). Based on the data obtained from Our World in Data, Malaysia used about 1,723.4 kg/ha (2020) of fertiliser with about 133,951.80 ha planted area in Malaysia (Deparment of Agriculture, 2020). Nineteen fertiliser companies were recorded in the year 2015 as the member of the Fertiliser Industry Association of Malaysia (FIAM) and more members are expected to register in the following years.

Wastewater from the fertiliser industry was one of the major contributors in contaminating wastewater with excessive amounts of fluoride and ammoniacal nitrogen (AN) contaminants. Fluoride and AN contaminant have contributed a major problem to humans, animals, and plants. Typically, these contaminants are range from 0.44 to 7.3 mg/L (Mourad et al., 2009) and 6 to 1,700 mg/L (Bhandari et al., 2016). Low concentration of fluoride can be beneficial, but excessive fluoride concentration might cause several health issues (Rao, 2003; Yadav et al., 2019). Similarly, AN is an essential nutrient for living organisms, nevertheless its excessive amounts of nitrogen can be toxic (Desai et al., 2016)

Several methods of removing fluoride have been introduced to cope with the high fluoride concentration problem in wastewater. Common fluoride removal methods from wastewater are based on coagulation or precipitation (Wang et al., 2019); ion exchange, reverse osmosis, and nanofiltration (Owusu-Agyeman et al., 2019); electrocoagulation (Behbahani et al., 2011), and adsorption (Ezzeddine et al., 2015).

Meanwhile, several AN removal method have been introduced to control the AN concentration in the environment. Air stripping (Guštin & Marinšek-Logar, 2011); reverse osmosis, chemical precipitation, ion exchange, membrane filtration, oxidation (Meng et al., 2020); and adsorption (Haseena et al., 2016) technology are among the most frequently used and studied technology for the removal of ammonium ions in wastewater treatment (Abdul Aziz et al., 2004; Bhandari et al., 2016).

Few studies have investigated the effectiveness of defluorination using limestone by precipitation of fluoride (Murutu et al., 2012). The addition of limestone to precipitate fluoride as calcium fluoride (CaF_2) into a large concentration of fluoride can lower the fluoride concentration (Mohan et al., 2018; Turner et al., 2005). Previously, Abdul Aziz et al. (2004) had carried out a study on effectiveness of limestone, activated carbon, and addition of both adsorbent for AN removal and the outcome reported a positive impact on the removal.

Although removal of fluoride and AN might be difficult and expensive, low cost and effective solutions should be introduced. Acetylene production sludge (APS) has been found to be applicable in fluoride and AN removal since it contains high composition of calcium hydroxide ($Ca(OH)_2$) (ca. 85 to 95%), which is almost similar to the concentration of an industrial grade lime (Cardoso et al., 2009).

In the acetylene production process, calcium carbide (CaC_2) is mixed with water to produce acetylene (C_2H_2) and ($Ca(OH)_2$), also known as carbide lime or APS (Cardoso et al., 2009). The disposal of the APS as a schedule waste is expensive since the waste is categorised under code SW402 in the first schedule of regulation 2 in Environmental Quality (Scheduled Wastes) Regulations 2005 as can be referred in Environmental Quality Act 1974. Repurposing industrial waste as fluoride and AN removal is one of the cheapest options that can be applied (Singh et al., 2004).

A few studies on wastewater treatment using production waste have been done where some of the waste use are waste eggshell for removal of heavy metal (Park et al., 2007), wastewater treatment using activated carbons derived from agricultural by-product such as coconut shell, coconut shell fibres and risk husk (Mohan et al., 2008) and treatment of dyeing wastewater using coir pith an agricultural waste by-product (Namasivayam & Kadirvelu, 1994). Moreover, Indian Rosewood sawdust (Garg et al., 2004), a lime sludge waste from paper mills was used with the aid of phosphoric acid for fluoride removal (Mohan et al., 2018) and also AN removal from wastewater using clay and zeolite (Desai et al., 2016). From the studies, wastewater treatment using production waste show positive impact on wastewater treatment, and it also helps to minimise production waste disposal. Based on the current research, the study of APS efficiency as the removal of fluoride and AN is still ongoing, hence this forms the basis of this research to determine the effectiveness of this method.

Methodology

2.1 Sample preparation

2.1.1 Wastewater sample

Wastewater sample was collected from a fertiliser production factory in Kedah. The wastewater collected was about 30 L and stored in a plastic container. The initial pH and the temperature of the wastewater were measured on site to avoid any changes by using pH and temperature indicator. The sample was then stored in a refrigerator at 4 °C for preservation before carrying out the experiment.

2.1.2 Acetylene production sludge (APS)

The acetylene production sludge (APS) was collected at an acetylene gas plant in Shah Alam by grab sampling technique. About three kilograms of APS sample was kept in a watertight container. The collected APS waste cake was dried to remove moisture and ground before being used for the experiment. APS sample was weighted (ca. 50 g) using a digital balance, placed on a tray followed by oven dried in a universal oven for 24 h at 100 °C to further reduce the moisture. The dried APS sample was then measured to calculate the moisture content using Eq. (1) below:

$$\text{Moisture Content } \% = \frac{M_W - M_D}{M_W} \tag{1}$$

where, M_W = total mass of wet sample (g)
M_D = total mass of dried sample (g)

The moisture content calculated was 19% (Cardoso et al., 2009). Then, dried APS sample was cooled at room temperature, 25 °C and then stored in airtight plastic container to avoid any moisture absorption.

2.2 Characterisation study

2.2.1 Characterisation of wastewater

Fertiliser wastewater properties was characterised using ICP-AES instrument and HACH method DR6000 spectrophotometer. Most of the element found in the wastewater was originally from the raw material used in the fertiliser manufacturing. HACH DR6000 spectrophotometer was used to analyse the amount of fluoride, AN, and COD before and after the experiment was performed. The analysis was conducted using

Table 1: Component available in fertiliser wastewater

Element	Concentration (mg/L)
ICP-AES	
Potassium, K	3756.163
Calcium, Ca	61.593
Magnesium, Mg	22.262
Aluminium, Al	1.661
Boron, B	0.744
Zinc, Zn	0.190
HACH	
Fluoride, F	2.43
Ammoniacal Nitrogen, AN	3,375
Chemical oxygen demand, COD	782.67

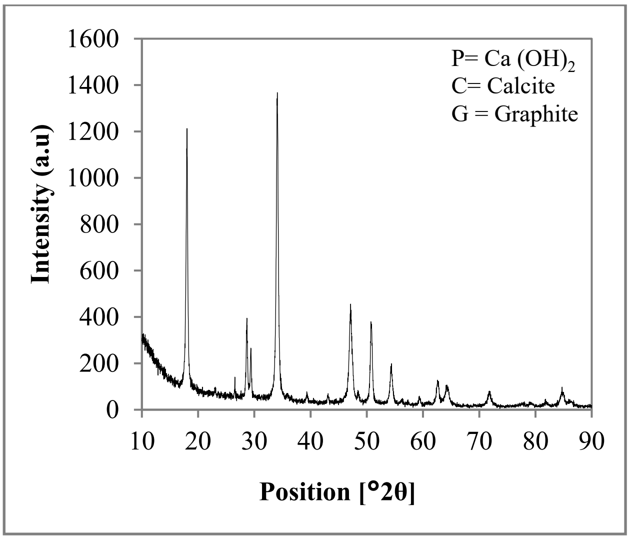

Fig. 1: XRD analysis of APS

reagent such as SPANDS2 (Arsenic Free) Fluoride reagent, ammonia salicylate reagent powder pillow, ammonia cyanurate powder pillow and 20–1500 mg/L COD HR vial for fluoride, AN, and COD analysis, respectively. Meanwhile, another element, such as K, Ca, Mg, Al, B, and Zn exist in the wastewater was analysed using ICP-AES instrument.

2.2.2 Characterisation of APS

APS was characterised by using X-ray diffraction (XRD) and X-ray fluorescent (XRF). XRF is used to characterise the major and trace elements in the APS meanwhile XRD was used to analyse the highest compound found on the APS.

2.3 Jar test

Jar test was conducted to determine the performance of APS for removal of fluoride and AN. Six 250 mL-beakers were prepared by putting 200 mL wastewater sample in each beaker. Then, the beaker was placed on the flocculator and allowed to run at 120 rpm. After that, the initial pH value of the wastewater sample was recorded. The APS dosage was varied at 0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g, and 3.0 g in order to study the effect on percentage removal of fluoride, AN, and COD. The beakers were labelled with their respective APS dosage. The AN removal was analysed using HACH DR6000 spectrophotometer. Then, a graph was plotted to determine the effect of APS dosing and pH towards percentage removal of fluoride, AN, and COD.

Results and discussion

3.1 Characterisation of fertiliser wastewater sample

Most of the elements found in the wastewater were originally from the raw material used in the fertiliser manufacturing. Table 1 shows the available component in fertiliser wastewater from ICP-AES and HACH DR6000 spectrophotometer analysis.

3.2 Characterisation of APS

3.2.1 XRD characterisation of APS

Fig. 1 shows the XRD results of APS where the highest peak represents the highest compound in APS. The major compound found on the APS is P ($Ca(OH)_2$) which is about 92.1 % compared to C and G that prove APS is completely dominant with $Ca(OH)_2$.

Eq. (2) is the equation to produce APS that prove that $Ca(OH)_2$ was found abundantly in APS. APS is the by-product produce from the reaction of CaC_2 with water (H_2O).

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 \tag{2}$$

3.2.2 XRF characterisation of APS

Table 2 shows the element composition found in APS through XRF characterisation analysis. Based on the analysis, calcium is the major element and compound in APS with percentage of 61.12% and 58.56%, respectively. Meanwhile, iron (Fe) is detected as the second highest element and compound with a value of 30.73% and 27.18%, respectively.

3.3 Removal of Fluoride and Ammoniacal Nitrogen using APS

3.3.1 Effect of pH and APS dosing

The effect of APS dosing on pH is depicted in Fig. 2. It is proven that APS can increase the pH of a solution due to its alkalinity behaviour. From the result, the pH increases from the initial pH, which is at 8.5 to 8.69, 9.11, 9.40, 10.18, 11.39, and 11.98, respectively in each six beakers within 30 minutes duration. The increase of pH is due to the existing OH^- ion. Eq. (3) shows the relationship between pH and OH^-. Increasing OH^- concentration can increase the pH value.

$$[OH^-] = 10^{-pOH} \quad (3)$$

3.3.2 Fluoride removal

The removal of fluoride is analysed at different APS dosing and pH after 30 min. Fig. 3 shows the effect of APS dosing on fluorine (F) removal. It is evident that, the optimum pH obtained was at 10.18 with APS dosing of 2 g with reducing of F concentration of 2.43 mg/L to 2.07 mg/L which is about 15.02% removal. Based on the study, F was removed at pH between 6.5 to 8.5 (Ezzeddine et al., 2015). The result shows the removal of fluoride start at pH 8.69 with dosing of APS 0.5 g correlated with the previous study. Since the nature of the wastewater was initially at pH 8.50, the fluoride removal can be achieved with a little dosing of APS. The addition of APS helps the effective removal of fluoride until it reaches the maximum removal which is at pH 10.18 with 2 g of APS dosing. This is due to the precipitation of Ca^{2+} with fluoride ion (F^-)to form CaF_2. With existing element Ca^{2+} in APS and K^+ in the wastewater, it also helps the fluoride precipitation through the formation of struvite crystals (Huang et al., 2017).

Moreover, based on the Lewis structure, the electron configuration of Ca and K shows two and one valence electron at 4th shell for both elements, respectively, making the ion charge for both elements Ca^{2+} and K^+ ion. The valence electron of Ca and K is far from the nucleus, making the electron transfer to fluoride become easy. Meanwhile, the valence electron of fluoride in the Lewis structure is at the 2nd shell with seven valence electron ion which is closer to the nucleus (Lester & Birkett, 2010). The closer the shell from the fluoride nucleus, making fluoride stronger to attract Ca and K to form covalent bond (Pomeroy, 2015).

Based on the Lewis structure, it shows that Ca and K atom lose its electron, and fluoride gains the electron forming an ionic compound CaF_2 and KF. Eq. (4) and Eq. (5) shows the formation of CaF_2 and KF.

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \quad (4)$$

$$K^+ + F^- \rightarrow KF \quad (5)$$

However, at the APS dosing of 2.5 g with pH 11.378, the fluoride concentration was slightly increased. This could happen due to the deposition of fluoride.

Table 2: Element composition found in APS

Element	Raw Material (%)	APS (%)	Compound	Raw Material (%)	APS (%)
C	3.385	3.311	CO_2	10.189	10.222
Mg	0.682	0.774	MgO	0.853	1.019
Si	1.128	0.375	SiO_2	1.909	0.621
Ca	57.947	61.105	CaO	55.635	58.558
Mn	1.016	0.971	MnO	0.817	0.777
Fe	32.863	30.718	Fe_2O_3	28.878	27.183
Ni	2.021	1.893	NiO	1.513	1.43
Cu	0.129	0.12	CuO	0.094	0.089
Zn	0.025	0.022	ZnO	0.017	0.016
Cd	0.084	0.074	CdO	0.057	0.051
Pb	0.06	0.055	PbO	0.037	0.035
O	0.661	0.581			

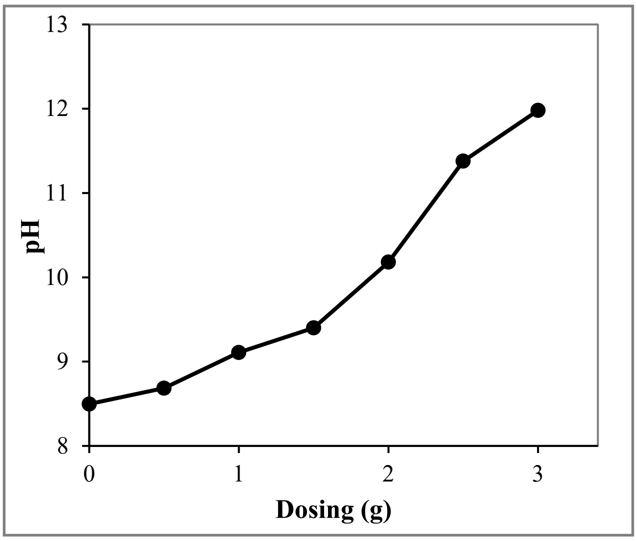

Fig. 2: Effect of APS dosing on pH

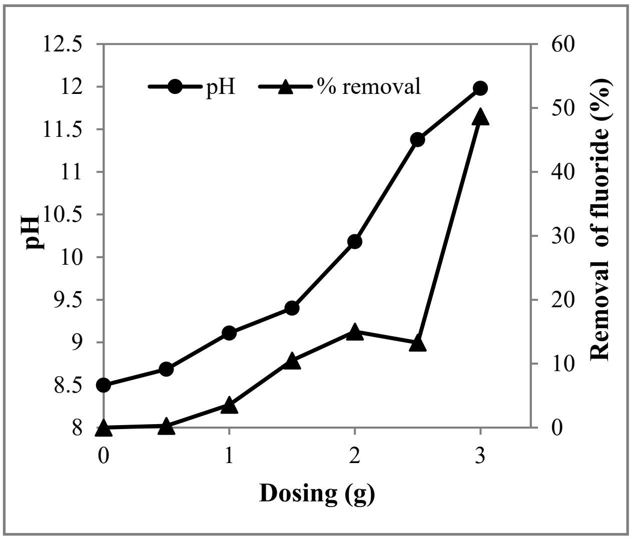

Fig. 3: Effect of APS dosing on fluoride removal

3.3.3 Ammoniacal nitrogen removal

The removal of AN was also analysed at different APS dosing and pH after 30 min. Fig. 4 shows the effect of APS dosing on AN removal. It is observed that the optimum pH obtained is at pH 10.18 with the APS dosing of 2.0 g with AN concentration, reducing from 3131.67 mg/L to 1508.33 mg/L which is about 51.84% removal. Based on the previous study, the optimum pH for AN removal was between 10 to 12 (Abdul Aziz et al., 2004). The result shows the maximum removal of AN was at pH 12 with APS dosing of 3.0 g. The removal of AN was observed to be at the same dosage as fluoride. The presence of OH^- ion from $Ca(OH)_2$ in the APS composition can remove the NH_3^+–N. Eq. (6) shows the precipitation NH_3^+–N and OH^-

$$NH_3^+\text{–}N + 3\,OH^- \rightarrow NH_3^+ + NH_2OH + O_2 \qquad (6)$$

The N^{3-} ion in NH_3^+–N compound will form a covalent bond with $2H^+$ ion and OH^- ion, forming NH_2OH also known as hydroxylamine a crystalline compound. Meanwhile the reaction of NH_3^+–N and OH^- will also form NH_3^+ and O_2. NH_2OH can be further decomposed based on Eq. (7) to form NH_3, HNO and H_2O.

$$2NH_2OH \rightarrow NH_3^+ + HNO + H_2O \qquad (7)$$

Based on Eq. (6) and Eq. (7), NH_3^+ is formed during the wastewater treatment. The formation NH_3^+ is also affected by pH of the wastewater where the formation of NH_3^+ favours at pH 11. Based on a study by Kinidi et.al (2018), the study stated that the formation of ammonia gas favours higher pH, whereas the formation of ammonium ions favours lower pH (Kinidi et al., 2018). Treatment for AN for the ammonia gas form were usually further for the striping process to purify the ammonia gas before it was released to the environment. Meanwhile, at the APS dosing of 2.5 g with pH 11.38 the AN concentration slightly increased. The increase of fluoride concentration could cause the decreasing of AN removal (Huang et al., 2017). From the result, fluoride concentration increases at APS dosing of 2.5 g of 2.067 mg/L to 2.11 mg/L also causing the increase the AN concentration at APS dosing of 2.5 g from 0.11 mg/L to 0.13 mg/L.

3.3.4 COD removal

COD analysis was done in the experiment since it is found that the COD concentration in the wastewater exceeded the minimum discharge condition in fifth schedule, Environmental Quality (Industrial effluent) Regulation, 2009. The COD concentration in the wastewater was contributed by the raw material used in the fertiliser wastewater. Fig. 5 shows the effect of APS dosing on COD removal.

Based on Fig. 5, the maximum removal of COD is at doses 2.5 g with a pH of 11.38 from 782.67 mg/L to 730.67 mg/L which is about 6.64% removal. The maximum COD removal occurs at 2.5 g at pH 11.38 is not in the same dosage amount as maximum removal in fluoride and AN. This might happen since precipitation occurs in fluoride and AN first during the treatment at an APS dosage of 2.0 g at pH 10.18.

Removal of fluoride and AN occurred in the treatment have contributed to decreasing COD concentration as fluoride and AN also one of the contributions for COD concentration. However, the

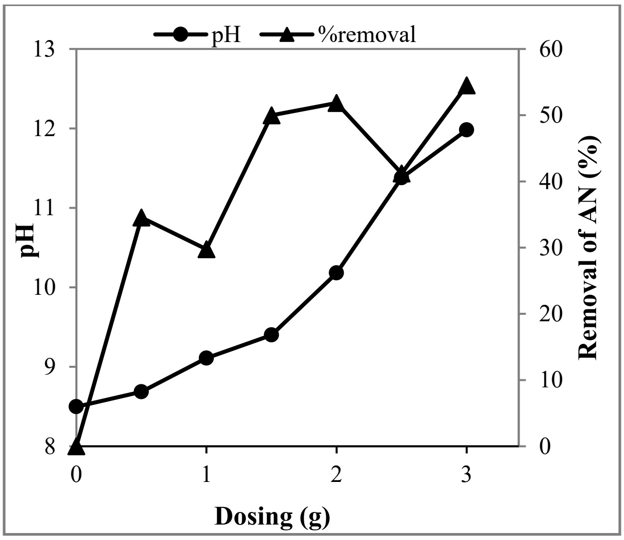

Fig. 4: Effect of dosing on ammoniacal nitrogen

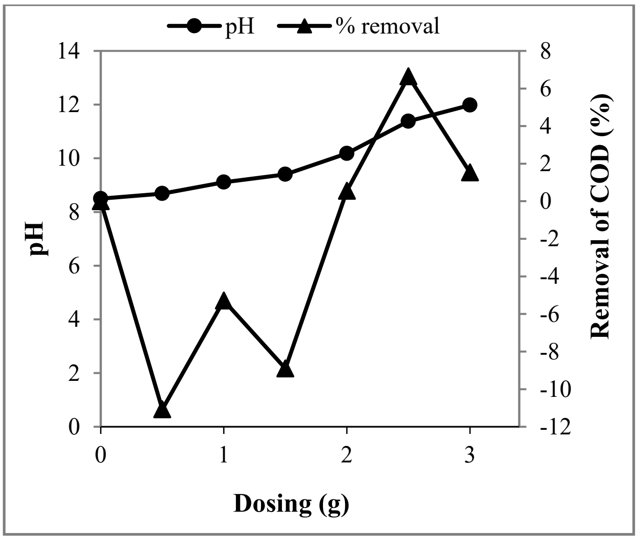

Fig. 5: Effect of APS on COD removal

removal of COD is least comparable to the fluoride and AN. This might happen because of the scavenging effect due to high in OH radical concentration that prevent the removal of COD (Pani et al., 2020). The existence of Fe in the APS can generate the OH radical, but with the right molar ratio of Fe and OH, it can enhance the removal of COD and AN (Gulkaya et al., 2006). Excess amount Fe can hinder the oxidation process as Fe will self –consume the free radical and lead in producing a large amount of sludge (Pani et al., 2020).

3.3.5 Summary of different APS dosing and pH on fluoride and AN removal

Fig. 6 shows the effect of APS dosing on fluoride, AN and COD removal. From Fig. 6 we can observe and compare the highest removal of fluoride, N and COD for the wastewater treatment using APS.

Different APS dosing and pH resulted in different removal percentage of fluoride, AN and COD. The increase of pH is depending on the amount of APS dosing. Excessive amounts of APS dosing can lead to higher pH that can lower the removal effectiveness of fluoride and AN thus optimum dosing and pH for fluoride and AN removal requires further investigation. Based on the study, the optimum pH for fluoride, AN and COD using APS is 10.18, 9.4, and 11.38 with dosing of 2 g, 1.5 g, and 2.5 g, respectively. From the results, it shows that the fluoride and AN were removed first, followed by COD. Fluoride which is in group 17 in the periodic table is more reactive than AN because fluoride element tends to gain electron since it is a halogen that have seven valence electrons in its outer shell (Lester & Birkett, 2010). Even though fluoride is more reactive than AN, the percentage removal of AN is more than fluoride because AN removal is through precipitation with OH^- ion and some of it has become NH_3 gas. Meanwhile, COD concentration decreases after maximum removal of fluoride and AN, since fluoride and AN also a major contributor to the increase in COD concentration. The presence of Fe in the APS does not help in COD removal due to excess amount of Fe that prevent the oxidation process and scavenging effect because of high OH radical produce.

3.4 Validation of APS performance by multilinear regression using excel

3.4.1 APS performance of fluoride removal

The multilinear regression analysis was done based on the data obtained from the experiment. The parameter which is an APS dosing and pH is labelled as X_1 and X_2 respectively meanwhile the responses which are removal of fluoride is labelled as Y_1 and Y_1^* for experimental and predicted data, respectively. Table 3 shows that the comparison is insignificant, but it is still acceptable as the error is below 20%.

The positive value of R square (R^2) from the regression summary output, which is 0.9775 shows that linear regression is suitable to be used to validate the APS performance. When the value of R^2 is rounded to two digits, it means 98% of the value fit the regression analysis model. As for the standard error, it shows the precision of the regression analysis which is about 3.575.

Meanwhile, for Analysis of Variance (ANOVA), one way ANOVA analysis was done using excel data analysis. The significance, F and P-value shows less than 0.05 (5%) which is 0.00569 (0.57%) and 0.0191 (1.9%). The coefficients regression analysis output shows the information involving the component in the analysis. Eq. (8) is the multilinear regression equation obtained based on the coefficient data.

$$Y_1 = -110.45X_1 - 65.32X_2 + 16.94X_1X_2 + 552.89 \quad (8)$$

Table 3: Analysis output for multilinear regression of APS performance on fluoride removal

Coefficient		**F**	**P - value**	**(Y_2) (%)**	**(Y_2*) (%)**	**Error (%)**
Dosing (X_1)	**pH (X_2)**					
0	8.50	0.00897	0.0263	0	4.65	0
0.5	8.69			34.54	23.12	−0.33
1.0	9.11			29.75	35.15	0.18
1.5	9.40			49.97	50.78	0.016
2.0	10.18			51.84	53.07	0.024
2.5	11.38			41.19	43.94	0.067
3.0	11.98			54.50	51.09	−0.063

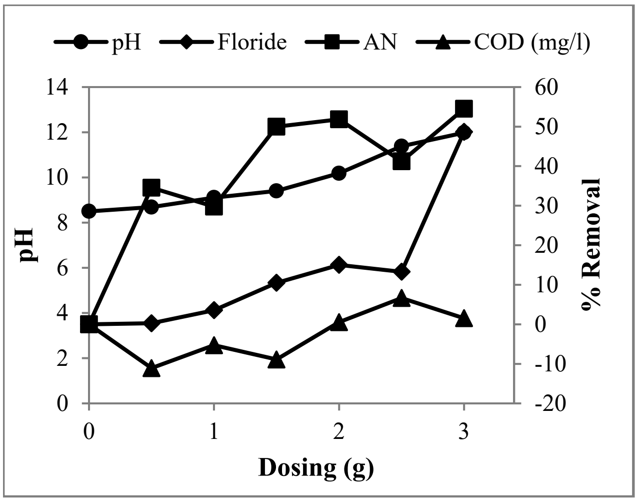

Fig. 6: Effect of APS dosing on fluoride, AN and COD removal

Table 4: output regression for multilinear regression of APS performance on AN removal

Coefficient		F	P - value	Y_1 (%)	Y_1* (%)	Error (%)
Dosing (X_1)	pH (X_2)					
0	8.50			0	−2.12	0
0.5	8.69			0.27	3.97	13.71
1.0	9.11			3.56	1.83	−0.49
1.5	9.40	0.00569	0.0191	10.5	12.13	0.16
2.0	10.18			15.02	12.02	-0.19
2.5	11.38			13.29	15.52	0.17
3.0	11.98			48.68	47.96	−0.01

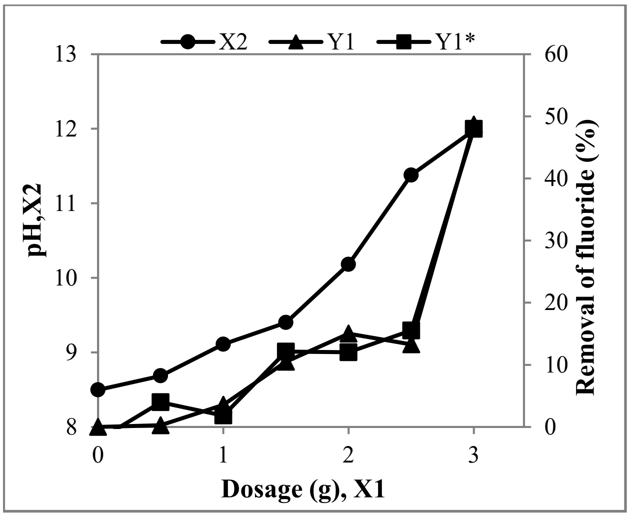

Fig. 7: Percentage removal of Fluoride against APS dosing from experiment and predicted data

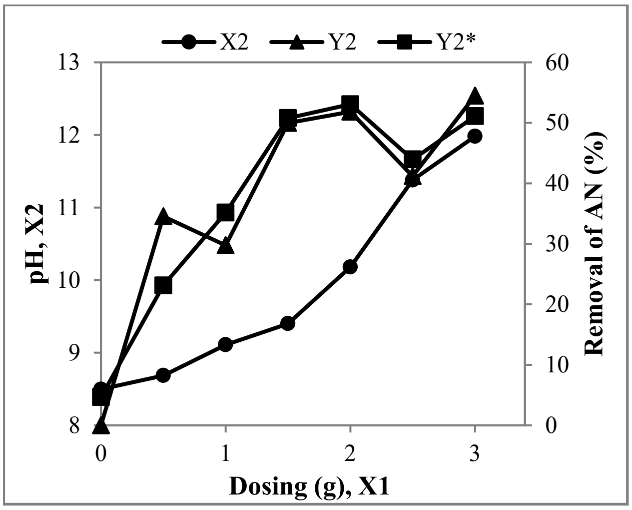

Fig. 8: Percentage removal of AN against APS dosing from experiment and predicted data

Fig. 7 shows a graph of percent removal of F against APS dosing from the experimental data, Y_1 are compared with the predicted data, Y_1* obtained from the analysis. Comparison between the experimental data and the predicted data obtained from the analysis are not much deviated. The percentage error calculated was insignificant, but it is acceptable as the error is below 20%.

3.4.2 APS performance in AN removal

APS performance in removal of AN was also analysed by performing linear regression using Excel. The multilinear regression analysis was done based on the data obtained from the experiment and are shown in Table 4. The parameters which are APS dosing and pH is labelled as X_1 and X_2 respectively. The responses which are removed of AN are labelled as Y_2 for experimental data and Y_2^* for prediction data.

The positive value of R squared of the regression summary output, which is 0.9053 shows that linear regression is suitable to be used to validate the APS performance. When the value of R^2 is rounded to two digits, it means that 91% of the value fit the regression analysis model. As for the standard error, it shows the precision of the regression analysis which is about 71.115.

For Analysis of Variance (ANOVA), one way ANOVA analysis was done using excel data analysis. The significance of F and P-value shows a value less than 0.05 (5%) which is 0.00897 (0.9%) and 0.0263 (2.6%) respectively as shows in Table 4. The coefficients regression analysis output shows the information involving the component in the analysis. Eq. (9) is the linear regression equation obtained based on the coefficient data.

$$Y_2 = 47.19X_1 - 27.31X_2 + 236.73 \tag{9}$$

Fig. 8 shows a graph of percent removal of AN against APS dosing from the experimental data, Y_2 compared with the predicted data Y_2* obtained from the analysis. Comparison between the experimental data and the predicted data obtained from the analysis do not deviate much. The percentage error is calculated as in Table 4 which shows that the error is below 0.05 (5%) which is significant and acceptable.

4.0 Conclusions

The characterisation by XRD shows Ca $(OH)_2$ is the major compound found in the APS. Meanwhile, based on the XRF analysis, Ca element is found abundant in APS. Ca plays a crucial role in removal of fluoride by precipitation to form CaF_2. While OH^- also help in removal of AN. For the wastewater contaminant analysis, the analysis was done by using ICP-AES and HACH DR6000 spectrophotometer. From the analysis, it was found that the initial fluoride, AN and COD concentration is about 2.43 mg/L, 3,375 mg/L and 782.67 mg/L, respectively.

Results from the effect of APS dosing on pH in the first study show increments of pH when increasing APS dosing. The pH of the wastewater increased at pH 8.5 to 8.69, 9.11, 9.40, 10.18, 11.39, and 11.98 with APS dosing of 0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g, and 3.0 g, respectively in 30 min duration.

In order to get the highest fluoride, AN and COD removal, the optimum APS dosing and pH was determined and observed from the plotted graph. The optimum pH obtained from fluoride and AN removal is at 10.18 with APS dosing of 2 g. Meanwhile, for COD removal, the optimum pH obtained is 11.378 at APS dosing of 2.5 g. The percentage removal of fluoride, AN, and COD based on the results are 15.02%, 51.84%, and 6.64%, respectively.

Furthermore, multilinear regression was done to validate the APS performance on removal of fluoride and AN. The output of multilinear regression analysis can validate the APS performance in removal of fluoride and AN as the error between predicted values and the experimental value of the removal is below 20%, thus the regression is acceptable.

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References

Aziz, H. A., Adlan, M. N., Zahari, M. S. M., & Alias, S. (2004). Removal of ammoniacal nitrogen ($N–NH_3$) from municipal solid waste leachate by using activated carbon and limestone. *Waste Management & Research*, *22*(5), 371–375. https://doi.org/10.1177/0734242X04047661

Behbahani, M., Moghaddam, M. A., & Arami, M. (2011). Techno-economical evaluation of fluoride removal by electrocoagulation process: Optimization through response surface methodology. *Desalination*, *271*(1–3), 209–218. https://doi.org/10.1016/j.desal.2010.12.033

Bhandari, V. M., Sorokhaibam, L. G., & Ranade, V. V. (2016). Industrial wastewater treatment for fertilizer industry—A case study. *Desalination and Water Treatment*, *57*(57), 27934–27944. https://doi.org/10.1080/19443994.2016.1186399

Cardoso, F. A., Fernandes, H. C., Pileggi, R. G., Cincotto, M. A., & John, V. M. (2009). Carbide lime and industrial hydrated lime characterization. *Powder Technology*, *195*(2), 143–149. https://doi.org/10.1016/j.powtec.2009.05.017

Department of Agriculture, Statistik Tanaman Industri 2020, www.doa.giv.my.

Department of Statistic Malaysia, Statistic Agriculture, 2020, www.dosm.gov.my

Desai, R. N., Vyas, D. S., Patel, S. M., & Mehta, H. (2016). Removal of ammoniacal nitrogen by electrocoagulation method. *International Journal of Advanced Research and Innovative Ideas in Education, 2*, 505–509.

Ezzeddine, A., Bedoui, A., Hannachi, A., & Bensalah, N. (2015). Removal of fluoride from aluminium fluoride manufacturing wastewater by precipitation and adsorption processes. *Desalination and Water Treatment*, *54*(8), 2280–2292. https://doi.org/10.1080/19443994.2014.899515

Garg, V. K., Amita, M., Kumar, R., & Gupta, R. (2004). Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes and Pigments*, *63*(3), 243–250. https://doi.org/10.1016/j.dyepig.2004.03.005

Gulkaya, I., Surucu, G. A., & Dilek, F. B. (2006). Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater. *Journal of Hazardous Materials*, *136*(3), 763–769. https://doi.org/10.1016/j.jhazmat.2006.01.006

Guštin, S., & Marinšek-Logar, R. (2011). Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. *Process Safety and Environmental Protection*, *89*(1), 61–66. https://doi.org/10.1016/j.psep.2010.11.001

Haseena, P. V., Padmavathy, K. S., Krishnan, P. R., & Madhu, G. (2016). Adsorption of ammonium nitrogen from aqueous systems using chitosan-bentonite film composite. *Procedia Technology*, *24*, 733–740. https://doi.org/10.1016/j.protcy.2016.05.203

Huang, H., Liu, J., Zhang, P., Zhang, D., & Gao, F. (2017). Investigation on the simultaneous removal of fluoride, ammonia nitrogen and phosphate from semiconductor wastewater using chemical precipitation. *Chemical Engineering Journal*, *307*, 696–706. https://doi.org/10.1016/j.cej.2016.08.134

Kinidi, L., Tan, I. A. W., Abdul Wahab, N. B., Tamrin, K. F. B., Hipolito, C. N., & Salleh, S. F. (2018). Recent development in ammonia stripping process for industrial wastewater treatment. *International Journal of Chemical Engineering*, *2018*. https://doi.org/10.1155/2018/3181087

Lester J. N. and Birkett J. W. (2010), *Introduction to chemistry*. (1st edition). CRC Press.

Meng, X., Khoso, S. A., Jiang, F., Zhang, Y., Yue, T., Gao, J., Lin, S. Lui, R., Gao, Z., Chen, P., Wang, L. Han, H., Tang, H., Sun, W. & Hu, Y. (2020). Removal of chemical oxygen demand and ammonia nitrogen from lead smelting wastewater with high salts content using electrochemical oxidation combined with coagulation–flocculation treatment. *Separation and Purification Technology*, *235*, 116233. https://doi.org/10.1016/j.seppur.2019.116233

Mohan, D., Singh, K. P., & Singh, V. K. (2008). Wastewater treatment using low cost activated carbons derived from agricultural by-products—A case study. *Journal of Hazardous Materials*, *152*(3), 1045–1053. https://doi.org/10.1016/j.jhazmat.2007.07.079

Mohan, R., Bora, A. J., & Dutta, R. K. (2018). Fluoride removal from water by lime-sludge waste. *Desalination & Water Treatment*, *112*, 19–33. https://doi.org/10.5004/dwt.2018.21918

Mourad, N. M., Sharshar, T., Elnimr, T., & Mousa, M. A. (2009). Radioactivity and fluoride contamination derived from a phosphate fertilizer plant in Egypt. *Applied Radiation and Isotopes*, *67*(7–8), 1259–1268. https://doi.org/10.1016/j.apradiso.2009.02.025

Murutu, C., Onyango, M. S., Ochieng, A., & Otieno, F. A. (2012). Fluoride removal performance of phosphoric acid treated lime: Breakthrough analysis and point-of-use system performance. *Water SA*, *38*(2), 279–286. https://doi.org/10.4314/wsa.v38i2.14

Namasivayam, C., & Kadirvelu, K. (1994). Coir pith, an agricultural waste by-product, for the treatment of dyeing wastewater. *Bioresource Technology*, *48*(1), 79–81. https://doi.org/10.1016/0960-8524(94)90141-4

Owusu-Agyeman, I., Reinwald, M., Jeihanipour, A., & Schäfer, A. I. (2019). Removal of fluoride and natural organic matter from natural tropical brackish waters by nanofiltration/reverse osmosis with varying water chemistry. *Chemosphere*, *217*, 47–58. https://doi.org/10.1016/j.chemosphere.2018.10.135

Pani, N., Tejani, V., Anantha-Singh, T. S., & Kandya, A. (2020). Simultaneous removal of COD and Ammoniacal Nitrogen from dye intermediate manufacturing Industrial Wastewater using Fenton oxidation method. *Applied Water Science*, *10*(2), 1–7. https://doi.org/10.1007/s13201-020-1151-1

Park, H. J., Jeong, S. W., Yang, J. K., Kim, B. G., & Lee, S. M. (2007). Removal of heavy metals using waste eggshell. *Journal of environmental sciences*, *19*(12), 1436-1441. https://doi.org/10.1016/S1001-0742(07)60234-4

Pomeroy R. K. (2015). The Reactivity of Fluorine, *Journal of Chemical Education*, 20(1), 260–264. https://doi.org/10.1333/s00897152651a

Rao, N.C.R. (2003, December 15-17). Fluoride and environment—A Review. In Bunch, M. J. V., Suresh M. and Kumaran T. V. (eds.), *Proceedings of the Third International Conference on Environment and Health, Chennai, India.* (pp.386–399).

Singh, K. P., Mohan, D., Sinha, S., & Dalwani, R. (2004). Impact assessment of treated/untreated wastewater toxicants discharged by sewage treatment plants on health, agricultural, and environmental quality in the wastewater disposal area. *Chemosphere*, *55*(2), 227–255. https://doi.org/10.1016/j.chemosphere.2003.10.050

Turner, B. D., Binning, P., & Stipp, S. L. S. (2005). Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption. *Environmental Science & Technology*, *39*(24), 9561–9568. https://doi.org/10.1021/es0505090

Wang, L., Zhang, Y., Sun, N., Sun, W., Hu, Y., & Tang, H. (2019). Precipitation methods using calcium-containing ores for fluoride removal in wastewater. *Minerals*, *9*(9), 511. https://doi.org/10.3390/min9090511

Yadav, K. K., Kumar, S., Pham, Q. B., Gupta, N., Rezania, S., Kamyab, H., Yadav, S., Vymazal, J., Kumar, V., Tri, D. Q., Talaiekhozani, A., Prasad, S., Reece, L., M., Singh, N., Maurya P., K., & Cho, J. (2019). Fluoride contamination, health problems and remediation methods in Asian groundwater: A comprehensive review. *Ecotoxicology and Environmental Safety*, *182*, 109362. https://doi.org/10.1016/j.ecoenv.2019.06.045