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Improved Reduction of COD, BOD, TSS and Oil & Grease from Sugarcane Industry Effluent by Ferric Chloride and Polyaluminum Chloride Coupled with Polyvinyl Alcohol

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ABSTRACT

Rapid industrialization and urbanization severely affect our environment and water resources. Disposal of untreated wastewater to environment is a great threat to water bodies and environment. Sugarcane industry is an important industrial sector; globally it is also largest source of pollution of surface water and groundwater resources. It comprises a huge amount of chemicals and inorganic pollutants. Many treatment methods have been employed for the treatment of the sugarcane industry wastewater, such as chemical treatment, physical treatment, ion exchange, electrocoagulation and biological treatment. It is a fact that not a single treatment technique is effective for industrial effluent treatment. In this study, the physicochemical technique was used to remove the major pollutants as per Sindh Environmental Protection Agency (SEPA) effluent standards that include Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Suspended Solid (TSS) and Oil & Grease content. In these techniques e.g. chemical coagulation ferric chloride (FC) and poly aluminum chloride (PAC) coupled with polyvinyl alcohol (PVA), with different doses were used for achieving the optimum results. The best results were observed for COD, BOD, TSS and Oil & Grease reduction by FC and PAC dosing 180 mg/300 ml coupled with 45 mg/300 ml PVA. Further, it was also observed that the FC removal efficiency in slightly acidic to neutral medium (pH = 6–7) for COD (97.5%) and BOD (97.5%) is higher than PAC. However, PAC does perform well in slightly neutral to basic medium (pH = 7.5–8) than FC for the removal of Oil & Grease (95.3%) and TSS (97.4%) from the sugarcane effluent.

Keywords: ferric chloride, poly aluminum chloride, poly vinyl alcohol, sugarcane industry, wastewater treatment.

INTRODUCTION

Discharge from the sugarcane industrial effluent has adverse effect on all flora, fauna and environment if untreated or treated partially, because it has heavy load of organic and inorganic pollutants (Gondudey, 2020). One ton of sugar produces on account of approximately 1.5–2 m^3 of fresh water consumption, resulting in discharge of 1 m^3 of wastewater (Dharm Pal, 2017). Sugar is an essential kitchen item and consumed in large quantities as substrates for human diet. (Poddar and Sahu, 2015).

Sugarcane is a cash crop and largest population is involved in agriculture in rural areas throughout world. The sugarcane industrial sector plays a vital role in the economies throughout of the world, but meanwhile it is also responsible for intensifying the environmental problems by generating heavy pollutant load effluents, which is a threat to the environment, fresh water bodies and aquatic life. Sugar industry is the largest agro-industry. On the other hand, the industry is also source of highly polluted wastewater. Now days, there is a demand by consumer for good quality and refined sugar with low impurities. Many chemical processes are used to achieve good results for removal of the impurities with cost effective with minimum generation of wastewater and damaging environment. Unplanned growth of population, rapid expansion in sugarcane industries and urbanization in developing countries severely affects our ecosystem and as a result, pollute fresh and groundwater resources. Around 30,000–40,000 liters of wastewater are generated due to sugar processing of one ton (Belliappa, 1991). Almost 8% of all generated effluent hardly treated in low-income countries and throughout world more than 80% of the municipal and industrial effluent is discharged without proper prior treatment (UN-Water, 2017).

The dark brown color-causing pigments of molasses spent wash has reported and found huge amount of some parameters including Chemical Oxygen Demand (COD) with range of 110,000–190,000 mg/L, Biological Oxygen Demand (BOD) with range of 50,000–60,000 mg/L, dissolved solids 90,000–150,000 mg/L, temperature 70–80°C, and low acidity (pH 3.0–4.5) (Mohana et al. 2009; Kazemi et al. 2015). The discharge of the unsafe wastewater by sugarcane industries is about 5000 m^3/day. The discharged wastewater is extremely contaminated with high values of BOD, COD; which is a high threat to freshwater and aquatic life and may result in depletion of dissolved oxygen (Khan, 2003). Sugarcane industry is one of the largest consumers of fresh water, used in different processes, including washing. During the release in the course of different processes, wastewater possesses complex composition with high temperature different residuals and heavy metals, phosphorus as well as sufficient amount of grease.

Sugarcane industries use different chemicals for chemical coagulation process to achieve the required purity and refinedness of the product. $Ca(OH)_2$ is also added to increase the pH of juices. Prior to liming to improve clarification a major amount of H_3PO_4 is added. Additionally, the use of carbon dioxide gas for to maintain low pH in juices (Khan et al., 2003). Chemical coagulation is a very effective and possesses a great potential to treat the industrial wastewater. It is more effective as compared to other methods; these chemicals are widely available and highly effective for the removal of the pollutants from industrial wastewater. Different physicochemical methods to be known as effective and can treat the wastewater discharge from sugarcane industry, but using chemical coagulation is the best technique for sugarcane industries (Aijaz et al., 2020). Due to presence/ high content of organic and inorganic pollutant such as biological oxygen demand, chemical oxygen demand, magnesium, calcium, solids, sulfates, nitrates, etc., makes sugar industries a major player in the pollution category.

Sugar industries pollute the fresh water resources and fertile soil by discharging improperly treated wastewater. It is tragedy in developing countries that there is no proper wastewater management system. The industrial wastewater is highly complex in nature of the wastes generated with the limited technologies to remove all pollutants at a time. It is the issue of utmost seriousness for environmental degradation in developing countries. (Fito et al., 2018, Samuel et al., 2011).

All the industrial units are bound to fulfill the requirements of regulatory bodies of their countries including Sindh (province of Pakistan) set in the Sindh Environmental Quality Standards (Self-Monitoring and Reporting by Industry) Rules, 2014 by the Sindh Environmental Protection Agency (SEPA). Wherein the priority parameters of effluent discharge from sugar industry such as effluent flow, temperature, pH, BOD_5, COD, Oil and Grease (SMART rules 2014). The limits of the priority parameters are then promulgated in SEQS 2016 by Sindh EPA and mentioned below in Table 1 (SMART rules 2014; SEQS 2016).

MATERIAL AND METHODS

Sampling and its preparation

During the study, 10 industrial units were selected (10 sugarcane industries) and 30 samples (10 Liters each; replicated 3×) were collected.

Table 1. Limits for priority parameters as per Sindh Environmental Quality Standards rules 2014 for sugar industry effluent

Priority parameters	Effluent flow (m^3/day)	Temperature (°C)	pH	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	Oil and grease (mg/L)
Into inland waters	-	40 ≥ 3	6-9	80	150	200	10
Into sewage treatment	-	40 ≥ 3	6-9	250	400	400	10
Into sea	-	40 ≥ 3	6-9	200	400	200	10

Before sample collection, all the sampling bottles were washed properly. The wastewater samples were collected in pre-washed plastic sampling bottles from the discharging point for analysis of different physicochemical parameters by standard sampling procedures. Due to the moral obligation with management of the industrial sectors, the information is not disclosed in the paper. During the collection, transportation, and storage of the samples to the laboratory all standard procedures were followed. After receiving samples in laboratory the air tight sampling plastic bottles were placed in icebox to maintain the characteristics of the samples (Aijaz et al., 2020).

Reagents and glassware

The water used throughout the experiments was de-ionized water obtained from the Milli purifier system (Millipore crop Bedford, MA, USA). All chemicals used were of analytical reagent grade and obtained from Sigma-Aldrich (Spain). potassium dichromate, sulfuric acid, silver sulfate, mercuric sulfate, iron ammonium sulfate, ferroin indicator, sodium sulfate and petroleum ether. The coagulants, Ferric Chloride (FC) & Poly Aluminum Chloride (PAC) and flocculent, Polyvinyl Alcohol (PVA) were purchased from the local market (commercial grade).

Chemical analysis

The physicochemical parameters, such as pH, Chemical Oxygen Demand, Biological Oxygen Demand, Total Suspended Solid (TSS) and Oil & Grease, were analyzed using standard methods for the examination of water & wastewater (21st Edition).

Treatment by coagulant/flocculent

During the study, 300 ml [100 ml from each of triplicate samples] of wastewater sample was taken in 0.5 liter beaker capacity. Different chemical coagulants FC and PAC with and without coupling of PVA in four predefined (Table 3) dosing were added to all samples with 09 pH adjustments (5.0 to 8.5). The mixture was stirred initially at 200 rpm for 30 minutes and then for 15 minute with/without addition of PVA at 80 rpm. The flocculants were then allowed to settle for 30 minutes without stirring. The supernatant was filtered with the help of Whatmann 42 filters and the clear water was then subjected to determination of COD, BOD, TSS and Oil & Grease.

Experimental design

In our experimental design, we proposed eight procedures for the removal of toxic pollutants from the sugarcane wastewater. The different dosages are proposed in Table 3. The combined sample from triplicate was subjected to experimental procedures.

Statistical analysis

Microsoft Office Excel 2010 version software was used for statistical calculations. All analytical data was scrutinized in triplicate and calculations (mean+std) were performed. They were graphically represented by utilization of originpro (2016).

Table 2. Methodology of the study using standard procedure (Aijaz et al. 2019)

Parameters	Results in Units	Instruments used
pH	1-14	Hach pH meter, model # HQ411D
TSS	mg/l	Analytical balance, Shimadzu model # AP x series S-829
COD	mg/l	Titrimetric
BOD	mg/l	Cooled incubator model Muve, UL#121,
Oil & Grease	mg/l	Volumetric analysis

Table 3. Experimental design for dosing of coagulants/flocculants

Coagulant	Exp-1 (mg/300ml)	Exp-2 (mg/300ml)	Exp-3 (mg/300ml)	Exp-4 (mg/300ml)	Exp-5 (mg/300ml)	Exp-6 (mg/300ml)	Exp-7 (mg/300ml)	Exp-8 (mg/300ml)
Ferric chloride	90	90	180	180	-	-	-	-
Poly aluminum chloride	-	-	-	-	90	90	180	180
Poly vinyl alcohol	-	45	-	45	-	45	-	45
Total loading	90	135	180	225	90	135	180	225

Treatment steps

Selection of the best suitable coagulant, determination of experimental conditions, as well as evaluation of pH effects and study of flocculants addition constituted another important step for the use of coagulant. Two different coagulants coupled with poly vinyl alcohol for improved removal of toxic pollutants (Arroub and Alharffi, 2018). In total, 72 samples were prepared by mixing 100 ml from each triplicate at laboratory temperature 25 ± 2 °C**.** Nine (09) samples of each sugarcane industrial effluent for each experiment were adjusted for pH by mixing 1 N HCl or NaOH solution drop wise with the help of a digital pH meter**.** Each sample of 300 ml volume was then subjected to a predefined dose of coagulants/flocculant as per Table 3. The samples were rapidly stirred after the addition of coagulant at 200 rpm for 30 minutes then with or without addition of flocculant at 80 rpm for 15 minutes. The sample was then left for 30 minutes to settle down the flocks. The sample was finally filtered with Whatmann 42 and the filtrate was subject to determination of pollutants i.e. TSS, COD, BOD and Oil & Grease to evaluate the coagulants/flocculant doses efficiency at different pH values.

RESULTS AND DISCUSSION

The major pollutant as identified by Sindh Environmental Protection Agency in its regulation for sugar industries (Table 2) included COD, BOD, TSS and Oil & Grease. It is widely admitted that the effluent from sugar industries is hazardous for environment and must be treated before being discharged. The thirty samples collected from ten different sugar mills were analyzed for Oil & Grease, COD, BOD and TSS and the results are presented in Table 4.

It could be observed in the table above that the pH value merely exceed the limits set by Sindh EPA SEQS limits. However, the COD, BOD and TSS concentrations in all ten sugarcane industrial wastewater samples exceed the SEQS limits. The obtained values are 2 to 10 times higher than the SEQS limits. However, TSS of 6 industries out of 10 exceeds the set limits. The TSS values are by 1.1 to 1.6 times, as compared to maximum limit of 400 mg/L by Sindh EPA. It could be deduced from the data above that COD, BOD and Oil & Grease are the most crucial parameters to be controlled in sugar industry effluent treatment process. A minimum 90% reduction of these pollutants can bring the wastewater pollutant load within SEQS limits.

Effects of pH with removal efficiencies

Figure 1 shows that the coagulation efficiency of FC is higher for oil & grease and TSS at low dosing of 90 mg/300 ml at the pH values of 6.5 and 7.0 respectively. On the contrary, a drastic improvement in the reduction of COD (85.2% at pH: 6.0) and BOD (79.2% at pH: 6.5) could be observed when FC is coupled with 45 mg/ 300 ml of PVA (Figure 2). Similarly by doubling the FC dosing from 90 to 180 mg/300 ml there is appreciable enhancement of pollutants reduction percentage (Figure 3). Subsequently, when this dosing coupled with 45 mg/300 ml of PVA the COD and BOD

Table 4. The result of major pollutants in sample of effluent from ten sugarcane industry (n=3)

Sample ID	pH	BOD (ppm)	COD (ppm)	TSS (ppm)	Oil & Grease (ppm)
S-1	9.3 ± 0.2	1802 ± 23	3279 ± 51	423 ± 7	104 ± 5
S-2	6.5 ± 0.1	1236 ± 11	2105 ± 34	305 ± 5	173 ± 3
S-3	8.7 ± 0.2	1598 ± 13	3056 ± 52	419 ± 7	218 ± 5
S-4	7.1 ± 0.1	607 ± 5	931 ± 8	274 ± 5	137 ± 1
S-5	5.6 ± 0.1	953 ± 7	1647 ± 27	458 ± 9	89 ± 2
S-6	9.5 ± 0.3	524 ± 7	932 ± 18	348 ± 5	73 ± 3
S-7	8.6 ± 0.2	1272 ± 12	2248 ± 43	623 ± 9	98 ± 4
S-8	6.8 ± 0.1	748 ± 9	1101 ± 12	439 ± 7	146 ± 9
S-9	9.5 ± 0.2	479 ± 5	776 ± 5	379 ± 3	65 ± 2
S-10	5.8 ± 0.1	697 ± 9	1074 ± 11	646 ± 9	218 ± 6
SEQS Limits	6-9	250	400	400	10

Note: ppm = mg/L, SEQS limits for industrial effluent into sewage treatment.

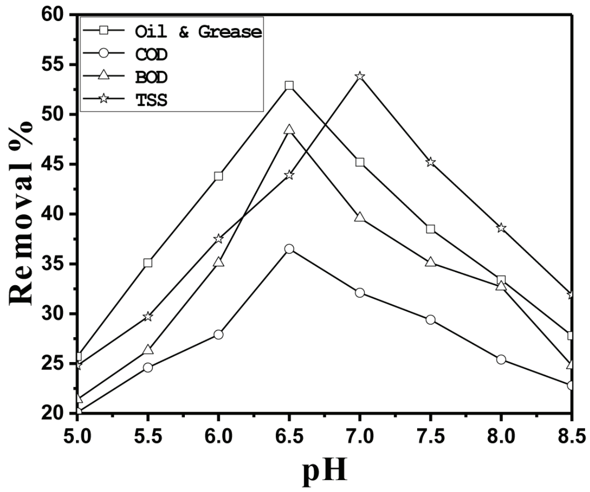

Figure 1. Effect of pH on the removal capacity of Ferric Chloride with 90 mg/300 ml dosing

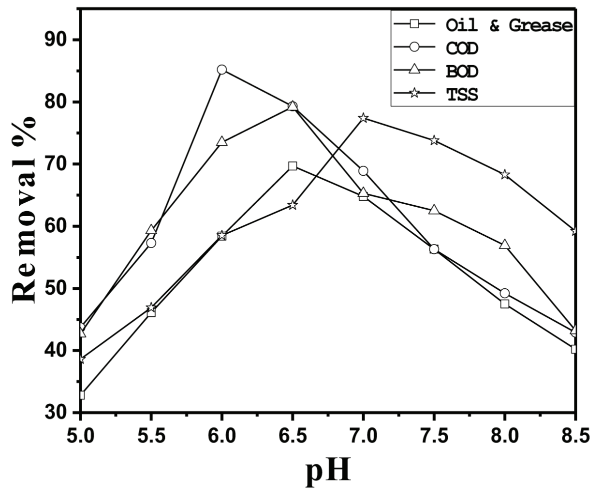

Figure 2. Effect of pH on the removal capacity of Ferric Chloride with 90 mg/ 300 ml dosing coupled with PVA 45 mg/300 ml

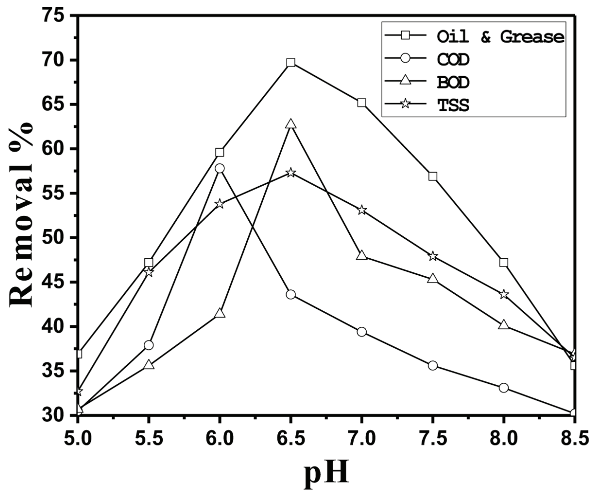

Figure 3. Effect of pH on the removal capacity of Ferric Chloride with 180 mg/300 ml dosing

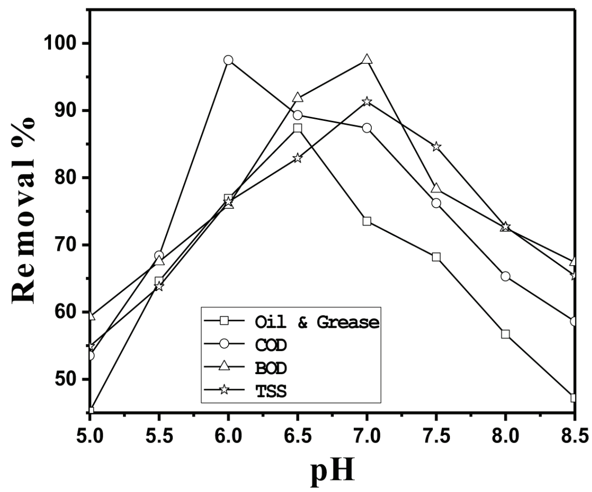

Figure 4. Effect of pH on the removal capacity of Ferric Chloride with 180 mg/L dosing coupled with PVA 45 mg/300 ml

removal percentage increased up to 97.5% for both (Figure 4). The removal percentages were calculated as per following formula:

$$Removal = \frac{C_i - C_f}{C_i} \times 100\%$$

where: C_i – concentration of pollutants before treatment,
C_f – concentration of pollutants after treatment.

Figure 5 depicts that PAC is a suitable coagulant for Oil & Grease (62.7%) at low dosing of 90 mg/300 ml at pH values of 7.5. However, when coupled with 45 mg/300 ml of PVA, the removal efficiency increased in slightly basic medium for oil & grease from 62.7 to 74.5% and for BOD from 37.4 to 59.2% (Figure 6). However, by doubling the dosing of PAC from 90 to 180 mg/300 ml a drastic improvement in reduction of oil & grease (79.8% at pH: 7.5) and TSS (75.8% at pH: 8.0) were recorded (Figure 7). Finally when 180 mg/300 ml PAC was coupled with 45 mg/300 ml of PVA the maximum reduction of oil & grease (95.3%) and TSS (97.4%) were measured (Figure 8).

The coupling effect of PVA with both coagulants is evident from Figure 9. The maximum dosing of 180 mg/300 ml and coupling of 45 mg/300 ml of PVA gives the best possible reduction percentages for the relevant pollutants of sugar industry effluent. If we evaluate the above bar graph precisely.

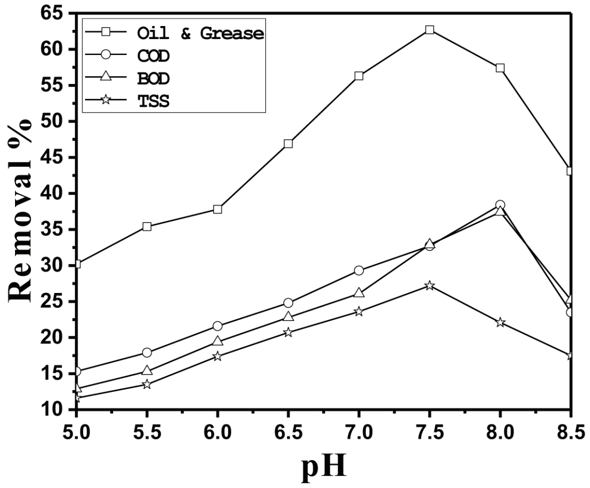

Figure 5. Effect of pH on the removal capacity of PAC with 90 mg/300 ml dosing

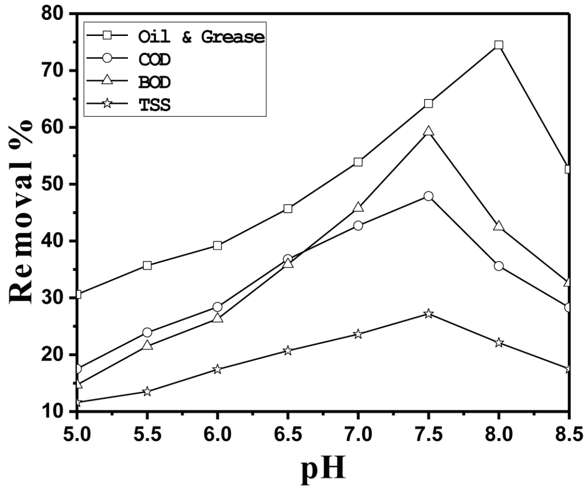

Figure 6. Effect of pH on the removal capacity of PAC with 90 mg/L dosing coupled with 45 mg/300 ml PVA

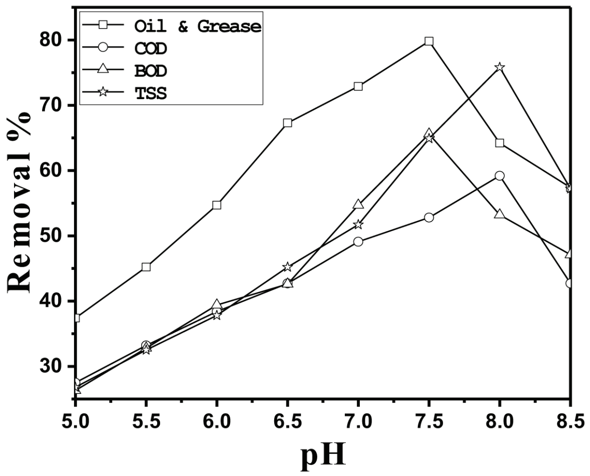

Figure 7. Effect of pH on the removal capacity of PAC with 180 mg/300 ml dosing

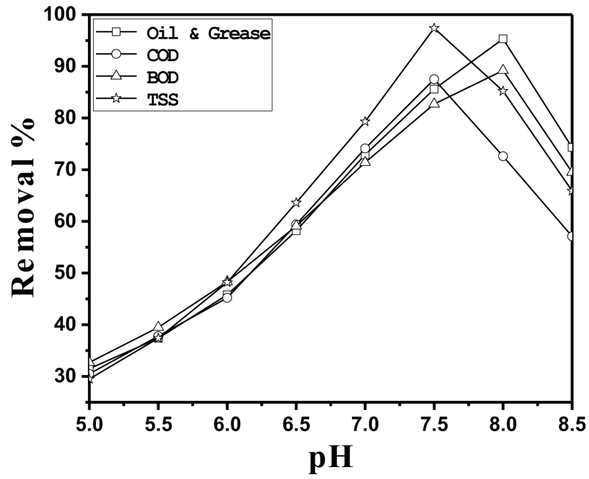

Figure 8. Effect of pH on the removal capacity of PAC with 180 mg/L dosing coupled with 45 mg/L of PVA

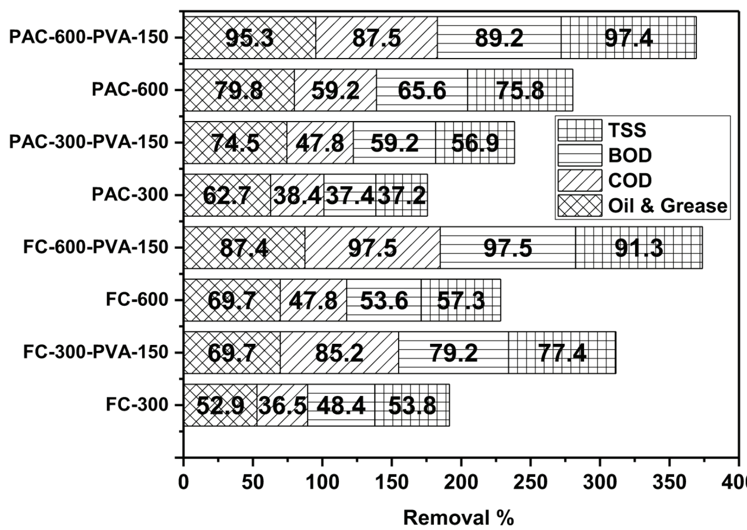

Figure 9. Comparison of eight experiments along with Oil & Grease, COD, BOD and TSS removal percentages

CONCLUSIONS

The sugarcane industry is the largest consumer of fresh water. The concentrations of the reported parameters were beyond the discharging limits as set by Sindh Environmental Protection Agency. The sugarcane industry should use the water quantity wisely in its all processes and avoid the discharge wastewater directly without proper treatment. Zero discharge is the best policy/option for saving of water, which should be ultimately goal of this activity. It can be concluded that FC performs slightly better than PAC. However, it is also evident from the graph above that FC works better for the COD and BOD removal when the medium is slightly acidic to neutral medium (pH = 6–7) than PAC. On the other hand, PAC performs better than FC when it comes to remove oil & grease and TSS in slightly neutral to basic medium (pH = 7.5–8). Finally it can be deduced from the FC bar graph above (180 mg/300 ml) that coupling with 45 mg/300 ml PVA provided better choice for COD and BOD reduction above 97% but oil & grease removal remained slightly below the set target of 90% (Fig. 9). On the other hand, PAC (180 mg/300 ml) – if coupled with 45 mg/300 ml PVA – provided a better choice for Oil & Grease above 95% reduction but slightly below the set target for COD and BOD. It was proposed that mixing of FC and PAC coupled with PVA may be studied to achieve the required target of minimum 90% removal of the critical sugar effluent parameters i.e. COD, BOD and Oil & Grease.

REFERENCES

1. Shreyas Gondudey, Parmesh Kumar Chaudhari, Sandeep Dharmadhikari and Raghwendra Singh Thakur, 2020. Treatment of sugar industry effluent using an electrocoagulation process: Process optimization using the response surface methodology. Journal of the Serbian Chemical Society, 85(10), 1357-1369.
2. Dharm Pal, 2017. Treatment of wastewater from sugarcane process industry by electrochemical and chemical process: Aluminum (metal and salt). Journal of Water Process Engineering, 17, 50-62. DOI: 10.1016/j.jwpe.2017.03.005.
3. Pradeep Kumar Poddar, Omprakash Sahu, 2015. Quality and management of wastewater in sugar industry. Applied Water Science. DOI 10.1007/s13201-015-0264-4.
4. Belliappa N. 1991. Physico-chemical properties of sugar mill effluent. Journal of Biological Chemistry, 65, 79-82.
5. UN-Water, 2017. Wastewater: The untapped resource. UN World Water Development Report, 180.
6. Mohana S., Acharya B.K., Madamwar D. 2009. Distillery spent wash: Treatment technologies and potential applications. Journal of Hazardous Materials, 163, 12-25.
7. Kazemi N., Tavakoli O., Seif S., Nahangi M. 2015. High Strength distillery wastewater treatment using catalytic sub- and supercritical water. Journal of Supercritical Fluids, 97, 74-80.
8. Khan M., Kulsoom U., Mahmood T., Riaz M., Khan A.R. 2003. Characterization and treatment of industrial effluent from sugar industry. Journal Chemical Society of Pakistan, 25(3), 242-247.
9. Aijaz Panhwar, Khalida Faryal, Aftab Kandhro, Nazir Brohi, Kamran Ahmed, Mansoor Iqbal, 2020. Treatment of Food-Agro Industry Effluent by Physico-chemical Methods. Pakistan Journal of Science, 72(2), 103-107.
10. Fito J., Tefera N., Van Hulle S.W.H. 2018. Physicochemical properties of the sugar industry and ethanol distillery wastewater and their impact on the environment. Sugar Technology. https ://doi.org/10.1007/s1235 5-018-0633-z.
11. Samuel S., Muthukkaruppan S.M. 2011. Physico-chemical analysis of sugar Mill effluent, contaminated soil and its effect on seed germination of Paddy (*Oryza sativa* L.). Int J Pharm Biol Arch., 2, 1469-1472.
12. Sindh Environmental Quality Standards, SMART Rules 2014. (Self-Monitoring and Reporting by Industry) Rules 2014, limits for priority parameters as per Sindh Environmental Quality Standards rules 2014 for Sugar industry Effluent.
13. Sindh Environmental Quality Standards 2016. Sindh Environmental Protection Agency, Pakistan.
14. Aijaz Panhwar, Aftab Kandhro, Nusrat Jalbani, Khalida Faryal, Saffar Mirjat, Gulzar Jhatial, Sofia Qaiser, 2019. Assessment of groundwater quality affected by open dumping site in hyderabad Pakistan. International Journal of Environmental Chemistry, 5(1), 49-59.
15. Standard methods for the examination of water & wastewater (21st edition, 2017).
16. Arroub H., Elharfi A. 2018. Evaluation of the effectiveness of the new couples Aluminum sulphate/PVAc and aluminum sulphate/PVAs in the clarification of wastewater: case of treatment of liquid effluents resulting from hot galvanization by coagulation flocculation. J. Mater. Environ. Sci., 9(9), 2645-2651.