Review Article

CHEMICAL TREATMENT OPTIONS OF WASTEWATER FROM SUGARCANE INDUSTRY AND ITS PRIORITY PARAMETERS COMPARISON AS PER SMART RULES OF SINDH ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT: Sugarcane industry is the largest consumer of freshwater and cause of adding wastewater in environment. Wastewater generation by sugarcane industry contains high chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS), and Total suspended solids (TSS), it ultimately reduces accessibility to oxygen. The Sindh Environmental Protection Agency (SEPA) also promulgated legal obligation regarding effluent pollutant level through the Sindh Environmental Quality Standards (Self-Monitoring and Reporting by Industry) Rules, 2014, including priority parameters of effluent discharge for sugar industry such as Effluent Flow, Temparature, pH, BOD_5, COD, Oil and Grease. If wastewater by sugarcane industry is not treated rightly, it will create very worst situation in surrounding areas including, generating foul smelling and septic condition. This toxic wastewater reduces penetration, and threat to crops and aquatic life. There are many treatment techniques such as coagulation, adsorption, membrane, biological etc. by different research studies disclosed that coagulation with different chemicals alum, ferric chloride and ferrous sulphate are very effective for remove of pollution. The adsorption technique followed by coagulation is also a very effective and time saving for sugarcane industry wastewater treatment.

Keywords: Adsorption, Coagulation, Sugarcane industry, Treatment techniques, Wastewater.

(Received 02.01.2021 Accepted 27.02.2021)

INTRODUCTION

Sugar industry is one of the largest agro-based industries and one of the essential substrate for human dietary consumption and it is an important product for human life. The effluent produced from the sugar industry if it is not properly treated before releasing it into the water sources, it can cause pollution to the environment [1]. The sugarcane industry is a very organized and needs huge amount of water for using in different processes. Around two thousand liters fresh water is needed for 1 ton of sugarcane and ultimately its 50% comes in form of effluent [2]. Sugar industry is one of the major high amount water consumer and discharges large quantity of wastewater [3]. Sugar industry produced only sugar but nowadays sugar industries are involved in the production of sugar, electricity and ethanol. So sugar industry is now called as the cane industry [4]. All the industries are bound to fulfill the requirement set in the Sindh Environmental Quality Standards (Self-Monitoring and Reporting by Industry) Rules, 2014 by the Sindh Environmental Protection Agency [5]. Wherein the priority parameters of effluent discharge from sugar industry such as Effluent Flow, Temparature, pH, BOD_5, COD, Oil and Grease ([5]. The limits of the priority parameters are then promulgated in SEQS 2016 by Sindh EPA and mentioned below in Table-1 [5, 6]. Effluents from sugar industries induce environmental pollution. Sugarcane itself contains 70% of water and same can be used for manufacturing of sugar [7]. The industry is responsible for severe impacts in its surrounding areas as well as environment [8]. The sugarcane industry is responsible to produce all types of contamination in environment such as water pollution, degradation of fertile lands, air and noise pollution [11, 12]. 0.56, 0.38 and 2.4 tons of filter press, molasses and bagasse, respectively are formed from around 8.5 ton of sugarcane and this entire process need 17000 cubic meter water in south African countries [14]. Simply, 1250 grams and 300 grams of bagasse and molasses respectively, generated by one kilogram sugar production [15]**.** While 0.27 ton of molasses produced in Mauritius, whereas 103.6 kg sugar and 45.2 kg molasses as a byproduct in Thailand [16]. Due to need of large area, huge investment as well as its maintenance, required huge amount and not feasible in sugarcane industries [17, 18, 19]. Today, sugarcane is produced in over 110 countries [20]. Food processing is one of the most high-water-use industries and the amount of its wastewater is relatively high and dependent on the process details [21]. Food processing wastewaters typically contain high concentrations of biodegradable organic matter [22].

Table 1. The SEQS limits for priority parameters as per Sindh Environmental Quality Standards rules 2014 for Sugar industry Effluent.

Priority Parameters (Units)	Effluent Flow (m^3/day)	Temperature (°C)	pH	BOD (mg/L)	COD (mg/L)	Oil and Grease (mg/L)
Into Inland Waters	-	40 ≥ 3 **°C**	6-9	80	150	10
Into Sewage Treatment	-	40 ≥ 3 **°C**	6-9	250	400	10
Into Sea	-	40 ≥ 3 **°C**	6-9	200	400	10

Wastewater Treatment Techniques

Primary treatment: Often it is famous as mechanical treatment, with adding of some chemicals for increasing efficiency of sedimentation phenomenon by adding of coagulants. This method may reduce suspended solids, BOD and COD.

Secondary treatment: For achieving more effective results the second step is by using of microorganism (Biological treatment). These microorganisms consume the organic matter for their growth reproduction and convert into small particles (water, CO_2, and energy). Additional settling tank is third step if necessary with full implementation, by this technique the removal efficiency for BOD and suspended solid parameters varies from 70-80%.

Tertiary treatment: In this step mostly activated carbon, Filtration techniques are used for filtration to transparent the treated wastewater. After filtration/using this treatment technique, the treated wastewater may be used in irrigation for cultivation of crops or maybe discharged in water canals.

Chemical Treatment

Chemical coagulation: Chemical coagulation process is a very effective since its inception in 19th century [23]. In this process there is removed all colloidal sized particles. Effectiveness of this process, it is gradually replacing over biological treatment [24]. Aluminum salts are widely used as coagulants in water treatment process due to the effectiveness in removing a broad range of impurities, including colloidal particles and dissolved organic substances [25, 26]. The alum as the coagulant is capable of achieving significant organic removal. The pH of the water during coagulation has profound influences on the effectiveness of coagulation for organic removal. Organic removal is much better in slightly acidic condition. For water of higher organic content, the optimum pH is displaced to slightly more acidic values [1]; chemical coagulation [27], electrochemical treatment [28]. [29] Used different coagulants (Al2(SO4)3.18H2O), polyaluminium chloride (PACl), ferric chloride (FeCl3.6H2O), and ferric sulfate (Fe2(SO4)3.7H2O) for removal of pollutants such as color 63% by FeCl3, turbidity 60-70% by Alum, FeCl3 and Fe2(SO4)3 (Table-2). Coagulation is considerably affected by pH changes and results in a significant removal of colored impurities [30]. From various studies it is found that for coagulants like ferric chloride, alum, ferrous sulfate and aluminum chloride optimum pH values ranges from 6-8. The maximum COD and color removals of 82-78% were achieved through the application of optimum pH values ranges from 6-8. The maximum COD, TSS and Turbidity removals were observed 85%, 90% and 92% respectively by electrocoagulation flotation technique as per Table-2 [31]. Aluminum is easily available, economically fit and highly efficient as compared to other metals for industrial effluent and drinking water treatment [32, 33] reported that Alum shows 80-86% of COD and color reduction as compared to aluminum chloride which showed reductions of 75-85.7% whereas ferrous sulfate gives 76-82% respectively as mentioned in table-2. Coagulation and flocculation are usually followed by sedimentation, filtration and disinfection. The problems with this treatment process include poor % recovery, operational issues, arbitrary guidelines and dependency on various operational parameters [34]. [35] used alum, ferric chloride and Polyaluminum chloride (PAC) for selection of suitable coagulant. The optimum condition of the coagulant (pH, coagulant dosage, fast mixing speed) was determined by using Design Expert software. Results showed that alum can be used to effectively remove 42.9% of COD and 100% of TSS at high dosage as depicted in table-2 (50 mg/l). On the other hand hybrid electrode of iron-aluminum was utilized at 156 A/m^2 current density to achieve maximum removal of COD 90% and color 93.5% from sugar industry wastewater with reaction time 120 min, electrode gap 20mm and Electrolyte concentration 0.5M [36]. This statement can be supported by where the removal efficiency of COD and TSS reached up to 96.1% and 95% by Alum and PAC respectively [37]. In other study, the percentage of Turbidity, color and COD removal by FeCl3 were 79, 94 and 80% respectively as stated in table-2 [38]. Meanwhile, FeCl3 replaced by Alum for comparison and the removal efficiency of Alum were reported 70, 91, 92, and 98% for turbidity, color, COD and TSS respectively as per in table-2 [38]. However, by using PAC as coagulant at around pH 6 can gives removal efficiency for turbidity, color, COD and TSS 93.4, 95, 87 and 98% respectively [38]. Furthermore, by using alum as coagulant, the total dissolved solids were decreased upto 87% and total suspended solids upto 98%, seen in table-2 [39]. Polyaluminum chloride (PAC) allows formation of floc faster compared to other coagulant as it has high positive electrical charge so it can neutralize the charges of the colloidal easily and reduce the repellent between particles thus allows the particles to form larger flocs [40]. By using PAC, percentage of COD that can be removed was 95% and same for TSS removal as mentioned in table-2 [37]. In addition, the percentage removal COD and TSS can be 56.7 to 84.5% and 95.9 to 99.2% depending on coagulant respectively as per table-2 [41]. Three coagulants were chosen to treat the wastewater. The most suitable coagulant was determined based on its efficiency to reduce COD and TSS in the wastewater at different dosages. By using alum and PAC as coagulant, the percentage of turbidity removal was reduced 94.8 to 99.1% for PAC respectively as depicted in table-2 [41]. $FeCl_3$ and alum has high percentage of turbidity removal at high dosage and achieved the reduction target. In contrast, PAC shows decreasing of percentage of turbidity removal at high dosage and did not achieve the target**.** This reduction may be due to charge reversal and re-stabilization of colloidal particles by reason of overdosing [42]. Percentage of turbidity reduction using $FeCl_3$ and alum were higher compared to percentage of turbidity reduction using PAC, it can be concluded that either by using $FeCl_3$ or alum is suitable for turbidity removal of the wastewater. In addition, the percentage reduction of COD increased up to 42.9% as the dosage of alum increasing. According to studies done by [43, 39, 28]. The percentage of removal might be higher if the dosage of the coagulant is increased. For coagulation with ferric chloride, Alum & PAC at around neutral pH can gives turbidity reduction up to 77, 80 and 91% respectively as per table-2 [44]. Similarly turbidity reduction was observed 82.9 to 99% & 93.8 to 99.6% by Alum and PAC coagulant respectively [45]. By using PAC, the percentage of TSS removal can reach 98% as reported in table-2 [38] and 96% [37]. In this study, results showed that TSS can be reduced up to 100% at low dosage of PAC. Similarly, 100% of TSS can be removed by using alum as coagulant**.** This removal is more than a percentage removal achieved by [38, 46]. In this case, PAC is the most efficient in removing TSS in the wastewater since it can reduce the same amount of TSS as alum at low dosage. In contrast, $FeCl_3$ gives less efficient result of TSS removal with only 40% removal.

Activated Carbon: Activated carbon is one of the most important adsorbent and successfully using with effective for reduction pollution level by sugarcane industry effluent [47, 48]. Activated Carbon is the most powerful adsorbent for wastewater treatment [49]. Some conventional treatment techniques are using by sugarcane industry effluent treatment but adsorption technique as a wastewater treatment has drawn attention in last few decades. Where in commercial activated carbon proved the most effective material for controlling the organic load. Activated carbon found to be most efficient in removal of pollutants from the effluent as compared to the wood ash and bagasse pith [50]. Numerous treatment techniques have been recommended by researchers for treatment of the sugarcane industry wastewater such as adsorbent [50]. [51] Reported regarding the effectiveness of activated carbon. Achieved good results for removal of COD, BOD and pH 2.5/500 ml sample. Presently, adsorption process is being extensively used for the removal of various organic and inorganic pollutants from sugar industry wastewater [52]. In one of the studies [53] reported that, adsorption is a quick, cost-effective and a promising technique for the elimination of pollutants emerging from different refining and recycling technologies. In this study adsorbents like bentonite, Mgo, activated carbon, and fly ash were used as adsorbents for sugar industrial effluents [53]. These adsorbents have been reported in 80% removal of TSS, TDS and oils and grease, along with an effective reduction in BOD, COD, smell and color. The major drawback of adsorption lies in the regeneration of the consumed adsorbent and subsequent treatment of backwash water [54].

Electrocoagulation: Electrocoagulation technology is a treatment process of applying electrical current to treat and flocculate contaminants without having to add coagulations. Electrocoagulation consisted of lower costs for small coagulant requirement, as compared with coagulation, whereas higher requirement may favor conventional coagulation for removal of pollutants [55]. Electrocoagulation is another way to treat the water and wastewater in which aluminum is used as an electrode [56]. In the EC process, coagulation is generated in situ by electrolytic oxidation of an appropriate anode material [57]. This technology gathers the use of electric current and pollutants that are accumulated without the addition of chemicals or coagulating agents. Application of direct current enables the removal of even minor amounts of pollutants from industrial effluents. Moreover, ECF is a proficient technique to eliminate residues for side products [58]. Different reagents such as aluminium sulfate, ferrous sulfate or ferric chloride have been reported to be employed in electrocoagulation process [59]. However, these chemicals were found to be very expensive and dependent on the volume of water treated.

[60] treated wastewater from sugarcane by electrocoagulation and coagulation techniques; shows good result up to reduction of COD 81% and color 83.5% at pH 6 according to table-2. Adding of CuSO4 as a coagulant has shown COD 98% and color 99.5% reduction and PAC results were 97.5% and 99.1% as mentioned in table-2 for COD and color respectively. [61] Used electrocoagulation technique with zinc electrodes as sacrificial anode in bipolar connection system. The achieved results of the treated wastewater were COD, BOD and Total Solids 80.95%, 89.4% and 90.37% respectively at optimal circumstances as per Table-2. The electrochemical reactor performance was analyzed based on with and without recirculation of the effluent having constant inter-electrodes distance. It was found out that the percentage removal of COD increased with the increase of electrolyte concentration and current density. The maximum percentage removal of COD was achieved at 80.74% as depicted in table-2 [62]. [36] Reported that the sludge and slurry generated after electrocoagulation with iron and aluminum electrodes are suitable for agricultural purpose Best removal efficiency was achieved with the pH 6.5, 90% chemical oxygen demand (COD) and 93.5% color removal were attended as stated in table-2.

Table 2. The comparison of percent reduction with different coagulants by various techniques.

Turbidity	Color	COD	TSS	BOD	Coagulant	pH	Technique	Reference
60-70%	48%	-	-	-	Alum	6	coagulation	Noppakhun and Ratpukdi (2016)
60-70%	63%				$FeCl_3$			
60-70%	-24%				$Fe_2(SO_4)_3$			
30%	-22%				PAC			
92%	-	85%	90%	-	Aluminum electrode (0-40A, 0-80V)	8	Electro-coagulation-flotation	Shammas NK *et al.,* 2010
94%	-	-	95.4%	**99%**	Stainless Steel electrode (0.2-0.8A)	7	Electro-coagulation	Alaadin A. Bukhari 2008
-	93.5%	**90%**	100%	-	Hybrid Iron-Aluminum Electrode (current density 156 Am^{-2})	6.5	Electro-coagulation	Sahu *et al.*, 2017
-	-	**96.1%**	96.1%	**96.1%**	Alum	6-8	coagulation	Aziz *et al.*, 2017
-	-	**95%**	95%	**95%**	Polyaluminum chloride			
79%	32-94%	69-80%	-	-	$FeCl_3$	6	coagulation	Sahu *et al.*, 2013
70%	91%	**92%**	98%	-	Alum			
93.4%	95%	87%	98%	-	Polyaluminum chloride			
94.8%	92.2%	84.5%	95.9%	-	Alum	6	coagulation	Ghafari *et al.*, 2010
99.1%	97.2%	56.7%	99.2%	-	Polyaluminum chloride			
80%	-	-	-	-	Alum	7	coagulation	Park *et al.*, 2015
91%					Polyaluminum chloride			
77%					$FeCl_3$			
82.9-99%	-	-	-	-	Alum	6-7	-	Zand and hoveidi 2015
93.8-99.6%					Polyaluminum chloride	5-6		
-	80%	-	-	-	Activated Carbon	6	coagulation	Patel and Painter 2017
	83%				Lignite			
57%	-	80.95%	90.37%	89.4%	Zinc Electrode, 20 volt	6-7	Electro-coagulation	Shruti 2017
-	78%	82%	-	-	Alum	6-7	coagulation	Sahu *et al.*, 2014
	76%	82%			Ferrous Sulfate			
	91%	77%			$FeCl_3$			
	85.7%	75%			$AlCl_3$			
68.9%	-	64.8	-	69.9	activated sugarcane bagasse	8	coagulation	Raziya & Desai (2019)
92.4%	90%	79.5%	-	-	Iron electrode (25V, 7.0A, 75min)	8	Electro-coagulation-flotation	Bhattacharya *et al.*, 2018

Conclusion: The wastewater from sugarcane industry is highly polluted, contains huge amount of COD, BOD, TSS,TDS and less DO which severely affect our precious resources including ground and surface water, fertile soil, agricultural land and aquatic life. It is necessary to develop a suitable treatment technique for the sugarcane industry. Many researchers used different techniques and got different results. On the basis of these results it is clear that not a single step of treatment for sugarcane wastewater is sufficient for the treatment and cannot meet the requirements of regulatory bodies. The coagulation technique is more effective for removal of organic pollutants and total suspended solids upto 100% but this single step is not fulfill requirements of the standards. The use of adsorption (activated carbon) with combination of coagulation has produced very impressive results and can meet the limits, set by regulatory bodies. As compared to the biological treatment technique, it has less capacity as compared to coagulation with combination of activated carbon. This technique occupies huge area and takes long time and less effective as compared to other techniques. Also environmental effects of open area treatment. It is recommended that sugarcane industries should use more than one step for treatment. Furthermore, there is less research conducted on oil & grease removal, which must be given preference during preparation of experimental design on wastewater treatment of sugar industry. It could be concluded that among priority parameters set be Sindh Environmental Protection Agency, COD and BOD are the most important ones. The maximum removal above 90% of COD and BOD can be achieved by coagulation and electrocoagulation techniques with pH range from 6 to 9. The choice for coagulant dosage and electrode material & conditions are highly variable in different studies. It is suggested that optimum dosage of coagulants and suitable material & conditions for electro-coagulation may be reviewed in depth with some modeling approach in future.

Funding: This work did not receive any grant from any funding agencies in the public, commercial, or other sectors for this study.

Conflict of interest: There is no conflict of interest to declare by any of the author of this study.

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