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Evaluation of Fenton Reagent Treatment to Anaerobically Digested Spentwash in Combination with Biological Treatment

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ABSTRACT: Applicability of Fenton treatment on anaerobically digested spentwash (ADSW) was investigated for chemical oxygen demand (COD) and color reduction. Effect of pH and variable doses of Fenton's reagent for COD and color removal was investigated. Overall experiments obtained 71 % COD and 75 % color reduction. Subsequently, an optimized Fenton dose was employed to carry out adsorption experiment to study the effect of adsorption on COD and color reduction. Adsorption reduces COD in the range of 45 to 55% in ash, 8 to 17 % in coco pith, 30 to 51% in bagasse and 39 to 60 % in charcoal. Similarly color reduction was found to be 10 to 40 % in ash, only 8% in coco pit, 7 to 32 % in bagasse and 15 to 65 % in charcoal. Adsorption removes 44% color reduction and 65 % COD.

KEYWORDS: Anaerobically Digested Spentwash (ADSW), Fenton reagent, Oxidation, Hydroxyl radical, Adsorbent

I. INTRODUCTION

Molasses based distillery effluent (spentwash) is considered to be one of the highest-polluting industrial wastewater and characterized by very high chemical oxygen demand (COD), low pH and dark brown color. The brown colour of spentwash is hardly degraded by the conventional treatments. Anaerobic treatment is an accepted practice for spentwash treatment. However, even after anaerobic treatment, spent wash does not meet the stringent effluent standards laid down by CPCB, India, in terms of very high levels of BOD, COD, solids etc. [4]. Therefore, it is necessary to explore additional treatment methods to remove the color and COD from spent wash.

Fenton's oxidation is one of the oldest advanced oxidation processes which is used successfully, as it is comparatively cheap and uses easy to handle reagents. It has been used to treat a variety of industrial wastes containing toxic organic compound, such as phenols, formaldehydes and dyestuffs [17]. The Fenton reaction is catalytic Advanced Oxidation Process (AOPs). Fenton's reagent is mixture of hydrogen peroxide and ferrous iron for the generation of hydroxyl radicals from hydrogen peroxide and it is based on an electron transfer between hydrogen peroxide and iron ions. This is illustrated by the following mechanism

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH- + OH^{\cdot} \quad (1)$$

Fe3+ ions which decompose H_2O_2 and produce HO2˙ hydroperoxide radicals

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^{+} + HO_2^{\cdot} \quad (2)$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} [16].These radicals are very strong oxidizing agent capable of reacting with a wide variety of organic compounds under ambient conditions [5].

$$OH\bullet + Fe^{2+} \longrightarrow OH^{-} + Fe^{3+} \quad (3)$$

Fe^{3+} catalytically decomposes H_2O_2

$$Fe^{3+} + H_2O_2 \rightleftharpoons Fe\text{-}OOH^{2+} + H^{+} \quad (4)$$

$$Fe\text{-}OOH^{2+} \longrightarrow HO_2\bullet + Fe^{2+} \quad (5)$$

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$Fe^{2+} + HO_2\bullet \longrightarrow Fe^{3+} + HO_2^-$ (6)
$Fe^{3+} + HO_2\bullet \longrightarrow Fe^{2+} + H^+ + O_2$ (7)
$OH\bullet + H_2O_2 \longrightarrow H_2O + HO_2\bullet$ (8)

The objective of this study was, to examine and optimize Fenton reagent treatment to ADSW at variable pH and Fenton reagent doses for maximum color and COD reduction. Subsequently optimized Fenton reagent was studied to examine the effect of bio-adsorbent in COD and color reduction.

II. EXPERIMENTAL METHODS

A. Material

Anaerobically digested spent wash (ADSW) sample was collected from distillery of Bhima Sahakari Sakhar Karkhana Limited, Pune Maharasthra, India. Ferrous sulphate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (Merck, India, 30% w/w, density 1.1), pH of the ADSW solution was adjusted by using 1N H_2SO_4 and 1N NaOH. Fenton's reaction was performed in the glass beaker of 500ml capacity with constant stirring on magnetic stirrer. Analytical reagent chemicals were used for the preparation of reagents, experimental treatment and analytical methods.

B. Test Procedure

1. Optimization of pH

Optimum pH was determined by primarily reactions under varying pH, however amount of H_2O_2 and $FeSO_4.7H_2O$ reagent were kept constant. Fenton's reaction is only effective in the acidic pH range [11]. ADSW pH was above 7.0, hence, the samples were acidified at pH 2, pH 3, pH 4 (using 1N H_2SO_4 and 1 N NaOH) with the constant dose of H_2O_2 (1ml/100ml ADSW) and $FeSO_4.7H_2O$ (0.15 g/100 ml) at ambient temperature (25-32^0 C). The ADSW with variable pH and constant Fenton dose were gently stirred with on magnetic stirrer at 160 RPM. After 2 hrs reaction samples were analyzed for COD and color reduction. Optimized pH was studied for variable doses of Fenton reagent.

2. Optimization of H_2O_2 dosage

Fenton reaction was carried out with different doses of H_2O_2 ranging from 0.5 ml to 2.5 ml /100 ml ADSW. H_2O_2 were added drop wise to ADSW, while keeping Fe^{2+} 0.15 g/100 ml and other parameters constant. Reaction was allowed to continue for 2 hrs. Samples were then analyzed for color and COD reduction.

3. Optimization of Fe^{2+} dosage

The reactions were carried out with constant H_2O_2 dose (1 ml) but variable dosage of Fe^{2+} to 0.25 g/100 ml ADSW while keeping other parameter constant. Fenton reaction was continued for 2 hrs and sample withdraws for analysis after 30 min equal time interval.

4. Adsorption experiment

Previously dried Coco pith, Bagasse and Ash sieved to get 0.5 mm particle size and commercially available charcoal powder of size 0. 2 mm were used as adsorbent for the treatment of Fenton treated ADSW. Bagasse, Ash, Coco pith & Activated Charcoal each viz 5, 10, 15, 20, 25 g was added in Fenton treated 100 ml ADSW and stirred for five hour at room temperature. Then the samples were filtered through (Whatman 47 filter paper) and analyzed for COD and color removal.

5. Adsorption experiment with combine filter

Combine filter was made with different Adsorbent and on the basis of result obtained from individual experiment with Bagasse, Ash, Coco pith & Activated charcoal. Diagrammatic representation of filtration assembly and other configuration is shown in figure 2. Volume of cylindrical glass filter was 49.45 m^3. Adsorbent quantities were taken in order to fit in the space provided to each adsorbent as shown in fig 1.

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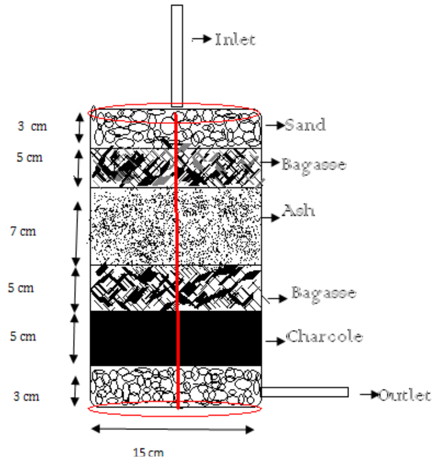

Fig 1: Combine filter schematic

Experiment were conducted in batch and combine filter initially rinse with distilled water. Subsequently one liter of Fenton treated ADSW sample was poured on the surface gradually and outlet sample was collected after 6 hrs. Collected ADSW sample was filter through whatman- 47 filter paper and analyzed for physicochemical analysis. Experiments were repeated to verify results and to obtain constant results.

C. Analytical method

During the analysis, treated sample was neutralized using 1N NaOH and residual H_2O_2 removed by raising the pH to pH
7-10 with 1N NaOH in order to prevent interference in analytical examination. The residual amounts of H_2O_2 of samples were determined by Iodometric method. Residual H_2O_2 interferes with COD value because it may act as reducing reagent in presence of $K_2Cr_2O_7$ a reagent used in COD analysis. Degradation ability by Fenton reaction was checked by means of Chemical Oxygen Demand (COD) by open reflux method (Titrimetric method) in accordance with standard methods of water and waste water analysis standard methods in *APHA AWWA* [3] Biological Oxygen Demand BOD was determined as 3 days BOD at 27^{o}C by 'Winkler's Iodometric method' given in *APHA AWWA* [3] , pH was measured using a pH-meter (pH−196, WTW Germany). For color assay, ADSW effluent was centrifuge for 10,000 RPM for 10 min and supernatant was diluted 50 times with distilled water. The absorbance were recorded in spectrophotometer (166 Systronics)-at λ_{max} 475 nm [1]

D. Statistical analysis

Results of the all experiments were mean of three duplication of each experimental set. The experiments was laid out in a completely randomize design (CRD). One way analysis of variance (ANOVA) was carried out with all results to confirm the variability of data and validity of results and Duncan's multiple range test (DMRT) was performed to determine the significant difference between treatments. Mean value are taken and treatments mean are significant at 5% level of significance.

III. EXPERIMENTAL RESULT

A. Effect of changes in pH on COD and color reduction

Fenton reaction was continued to 120 min under control pH (pH 2 to 4) conditions with dose of 0.15 g $FeSO_4.7H_2O$ and 1 ml H_2O_2 to ADSW. The effect of pH on COD and color reduction with Fenton reagent treatment is illustrated in fig 2. The optimum pH value was found to be at pH 3 and an average 69% COD, 73% color reduction obtained.

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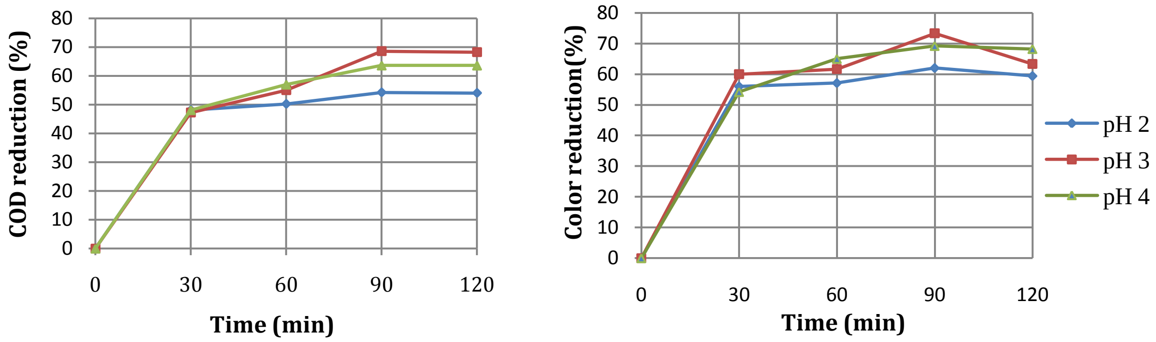
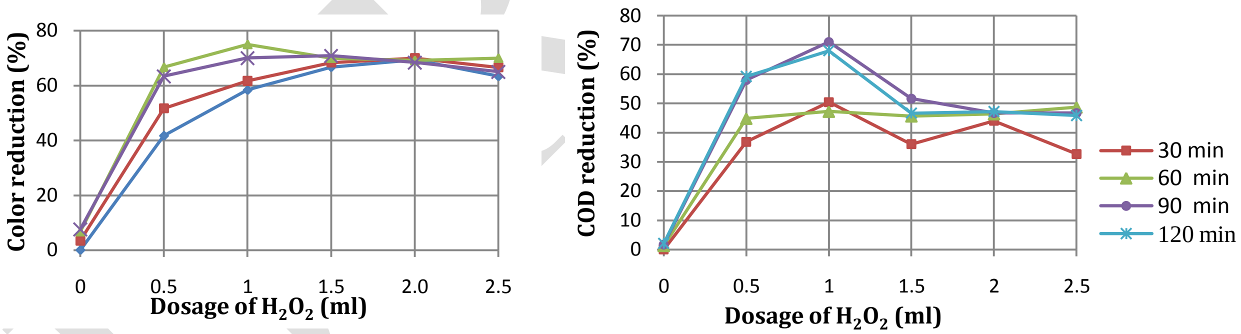


Fig 2: Effect of pH on COD and color reduction

COD and color reduction was 54%, 64% respectively in pH 2 which lesser compare to pH 3. This could be due to formation of $[(Fe)^{2+}(H_2O)]^{2+}$ occur at low pH , which react more slowly with H_2O_2 produces less amount of reactive hydroxyl radicals thereby reducing the degradation efficiency [7]. At 4 pH 60 % COD and 69 % color reduction observed, lesser compare to reduction at pH 3. Oxidation potential of Fenton reaction decreases with increase in pH 4. This is due to oxidation potential of $OH^{\bullet}$ radicals decreases with an increase in pH. Increasing pH above 3 hinders the oxidation rate significantly and leads to formation and precipitation of $Fe\ (OH)^3$ that hamper the development of Fenton reaction [6].

B. Effect of H_2O_2 doses on COD and color reduction

Fig 3(a) depicts percentage reduction in COD increases with an increase in H_2O_2 concentration i.e. 58%, 71%. However further increase in H_2O_2 dosage decreases in COD reduction. COD reduction 52% in 1.5 ml and 47% in 2.0 and 2.5 ml H_2O_2 dose. This elucidates that degradation rate of organic compounds increases as the H_2O_2 concentration increases until a critical H_2O_2 concentration is achieved. However, when concentration higher than the critical concentration is used, the degradation rate of organic compound was decreased.



(a) **(b)**

Fig 3: Effect H_2O_2 on COD and color reduction

Fig 3(b) demonstrate 75 % color reduction obtain at 1ml dose of H_2O_2 within 90 min reaction time. Further increase in H_2O_2 dosages decreases color reduction. Observed color reductions were 67%, 58%, 57% in 1.5, 2.0, 2.5 ml H_2O_2 respectively.

C. Effect of Fe^{2+} doses on COD and color reduction

The effect of Fe^{2+} dosage on the COD and color reduction was studied by varying dosages of Fe^{2+} from 0.0 to 0.25 g/100 ml of ADSW for a constant dosage of 1 H_2O_2/100 ml at initial pH 3. COD and color reduction were increased with Fe^{2+} dosage. However, further addition of Fe^{2+} over 0.1g decrease in COD and color reduction. Fig 4(a) and Fig 4 (b) depict that the optimum 71% COD and 75% color reduction was achieved with a 0.1 g Fe^{2+} and 1 ml H_2O_2. For lower dose of Fe^{2+} i.e. 0.05 g Fe^{2+}, 52 % COD and 53 % color reduction obtain. This is because lower initial

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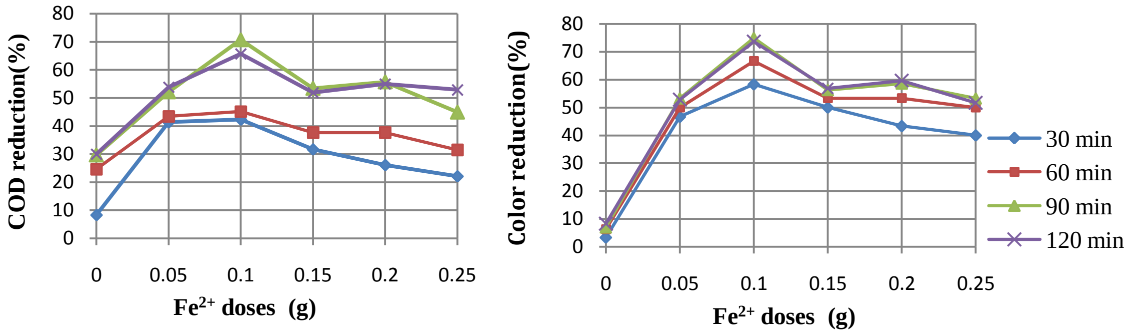
concentrations of Fe^{2+}would cause fewer $OH^{\bullet}$ free radicals to be available for oxidation [16]. For Higher Fe^{2+} dosages 53%, 56%, 45% COD and 53%, 59%, 53% color reduction occur in 0.15, 0.2, 0.25g Fe^{2+}.



(a) (b)

Fig 4: Effect Fe^{2+} doses on COD (a) and color (b) reduction

D. Adsorption isotherms

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. Fig 5 illustrates COD and color reduction increases with increase in adsorbent concentration. Removal COD ranges from 45 to 55 % in ash, 7 to 16 % in cocopith, and 29.88 to 50.57 % in bagasse 39.19 to 60.63 % in charcoal and color reduction observed in the range of 10 to 44 % in ash, 2 to 8 % in cocopith, 7 to 32 % in bagasse, and 15 to 65 % in charcoal. The logarithmic values of equilibrium concentration (C_{eq}) and removal per unit weight (x/m) are shown graphically for Freundlich adsorption isotherm and Langmuir isotherm model in fig 6 to 9

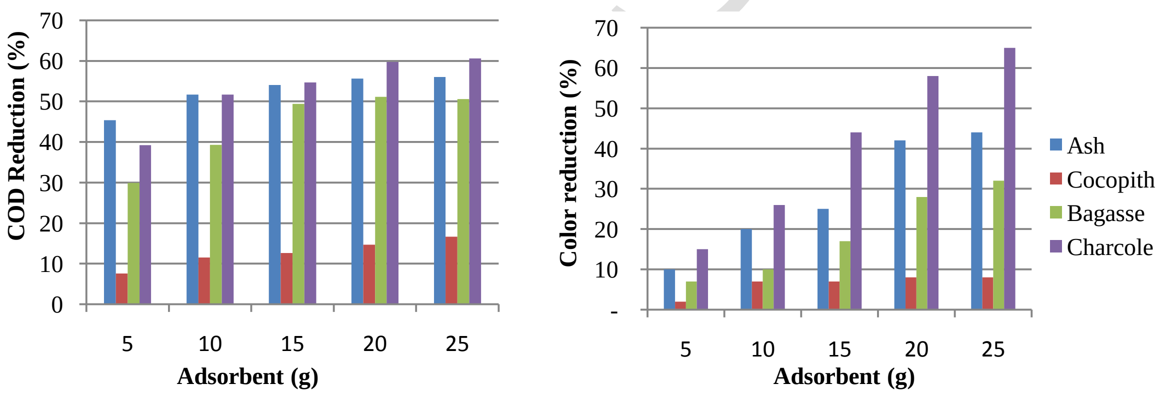


Fig 5: COD reduction through different adsorbent

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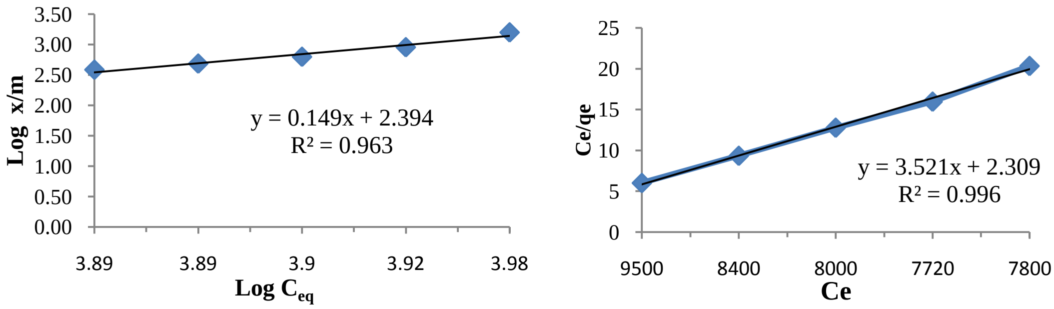
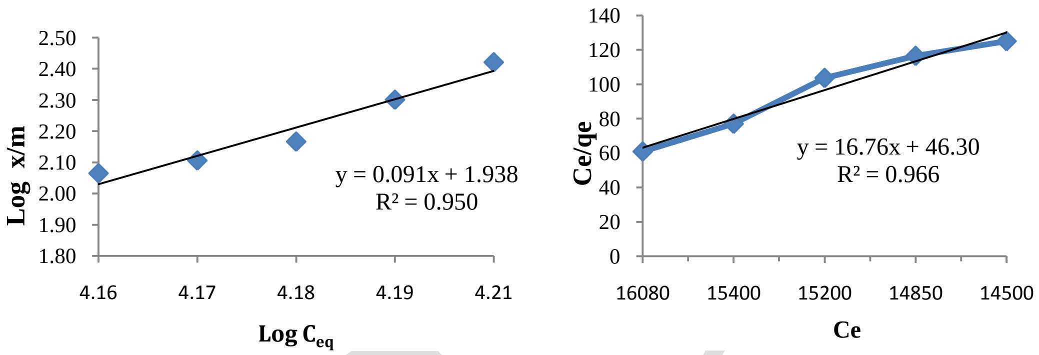


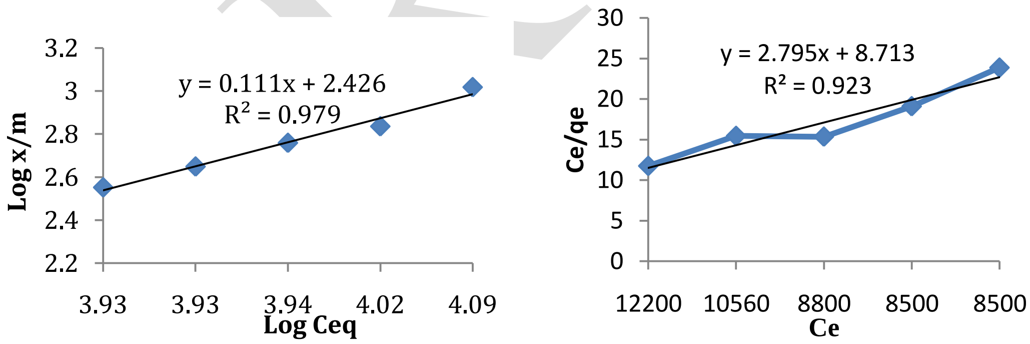
(a) (b)

Fig 6: (a) Freundlich (b) Langmuir adsorption isotherm for COD reduction by Ash



(a) (b)

Fig 7: (a) Freundlich (b) Langmuir adsorption isotherm for COD reduction by cocopith



(a) (b)

Fig 8: (a) Freundlich (b) Lang muir adsorption isotherm for COD reduction bagasse

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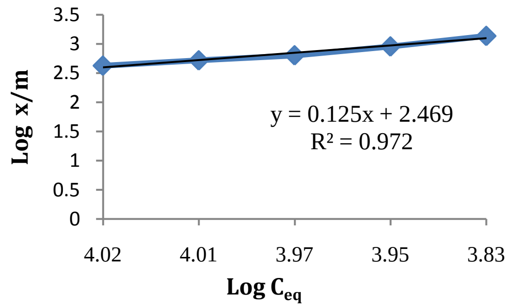
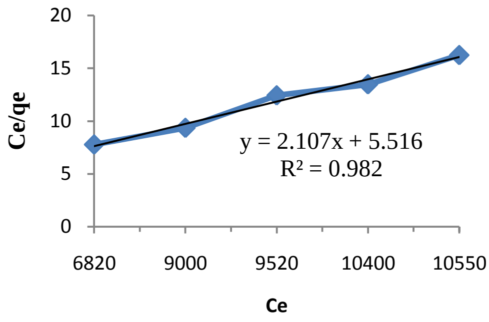


(a)



(b)

Fig 9: (a) Freundlich (b) Langmuir adsorption isotherm for COD reduction by Charcol

Langmuir adsorption isotherm depict the graph of Ce Vs Ce/qe (COD) for ash, cocopith, bagasse and charcoal. The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by

$Q= Q.b.C_e/ 1+b.Ce$

Where q is milligrams of COD accumulated per gram of the adsorbent material; C_e is the residual COD concentration in solution; Q is the maximum amount COD contributing component per unit weight of the adsorbent to form a complete monolayer on the surface bound at high $C_{e.}$ Q represents a practical limiting adsorption capacity. b is the constant related to the affinity of the binding sites. Initial adsorption increases till the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants and is equated by the following equation.

$$C_{eq}/q= 1/q_{max}.b+ Ceq/q_{max}$$

The linear plots of C_{eq}/q versus C_{eq} show that adsorption follows the Langmuir adsorption model

The R^2 values between 0 and 1 indicate favorable adsorption. The R_L for all adsorbent are mentioned in Table 1

The linearised form of **Freundlich adsorption isotherm of** log Ceq Vs log x/m (COD) ash, cocopith-pressmud, bagasse and charcoal was used to evaluate the sorption data and is represented as,

$$\log x/m = \log K + 1/n \log Ceq$$

where C_{eq} is the equilibrium concentration (mg/L) , q is the amount adsorbed (mg/g), 1/n is slope and log K is the intercept of log x/m at log Ceq = 0 . *K* and n are constants include parameters which affect the adsorption process, such as adsorption capacity and intensity, respectively. Details of all value given in Table 2.

Table 2: Adsorption isotherm constants and correlation coefficients

Sr no	Adsorbent	Langmuir Isotherm			Freundlich isotherm		
		Q(mg/g)	b (1/ mg)	R^2	K(mg/g)	1/n	R^2
1	Ash	0.284	0.047	0.9968	316.22	0.1498	0.9636
2	Cocopith	0.0596	0.2794	0.9662	107.15	0.091	0.9509
3	Bagasse	0.35773	0.2329	0.9239	331.13	0.1118	0.979
4	Charcoal	0.0744	0.0744	0.9828	323.59	0.1257	0.972

E. Combine filtration

It has been observed that 65 % COD reduction at 5 hrs

.

Table 3: Effect Fenton treated ADSW followed by Combine filtration

Sr.no.	Parameter	ADSW mg/Lit	Fenton Treatment	Combine filter
1	COD	24481	17280	6000
2	BOD	9792	5000	1800
3	Color	0.326	0.149	0.110

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IV. CONCLUSION

Results indicate that Fenton's oxidation process optimizes at pH 3 and optimal dose of Fe^{2+} and H_2O_2 was 0.1 g and 1 ml /100ml ADSW. It was observed that the Fenton process depends heavily on factors such as the pH of the solution, the amount of both hydrogen peroxide and $FeSO_4$ added. Optimum concentration of ferrous ions was 0.1 g /100ml ADSW produces higher rates of degradation. However, an excessive concentration of the ferrous ions leads to an increase in the unutilized quantity of iron salts. Adsorption efficiency in removing COD increased with increased in Adsorbent concentration. Combine filtration assembly for adsorption experiment made with Ash, Bagasse and charcoal had shown 44% color reduction and 65 % COD reduction at 2 hr of retention time.

Presented adsorption treatment wisely used available adsorbent for the treatment and reduces the cost in treatment. For better cost cutting Biochar of bagasse can be used instead of charcoal. In some reference experiment modified bagasse or activated bagsse showed better result that can be used in combine filtration to achieve maximum reduction in COD and color.

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