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Catalytic Wet Peroxide Oxidation of Phenolic Industrial effluent using $PrCo_{0.2}Fe_{0.8}O_3$ Perovskite

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ABSTRACT

Perovskite oxide has been effectively used in CWAO/ CWPO process for removal of organic effluents in waste water. In this study, $PrCo_{0.2}Fe_{0.8}O_3$ perovskite oxide was prepared by Glycine combustion method. Synthesised Perovskite Samples were analyzed by X-ray Diffraction (XRD) for structure and Brunauer-Emmett-Teller (BET) method for surface area analysis. SEM (Scanning Electron Microscopy) has been performed on sample to study the morphology and analysis reveals the data of pore size below 300nm and particle size in range of 50-250nm. In this study, organic effluents like phenolshows degradation up to 78-85% with the minor doping of Cobalt (Co) in the $PrFeO_3$catalyst. Double beam spectrophotometer has been used to study degradation of Phenol.

Keywords*: *Self combustion, CWPO (Catalytic Wet Peroxide Oxidation), Pr based Perovskite, Phenol

I.INTRODUCTION

Wastewaters from industries such as Polymer, Agro Chemical, Resins, Pulp and paper, Dyeing, Fine chemical, Petrochemical etc. contain heavy metals, oil emulsions, inorganic and organic compound, which are difficult to remove due to their solubility in water or due to the presence of persistent and recalcitrant compounds. The nature of pollutants and their concentrations in industrial wastewater depend on their source. Because of the high concentrations of toxic materials in industrial wastewater, it is necessary to apply specific processes for their separation, transformation and further decomposition. **[1]**

Conventional technologies like gravitational separation, centrifugation, coagulation, flotation, adsorption, biological, thermal, and physicochemical treatments have been used to remove or minimize the water pollutants. Among the different technologies degradation of pollutants using microorganism is widely applied for the treatment of residual wastewaters, but it requires a long residence time and is not suitable to treat the toxic contaminants due to biomass poisoning**[2]**.

The chemical industry generates wastewater that contains toxic compounds in small concentrations so that their economic recovery is not feasible and, in many cases their biological treatment is not feasible since they are poorly biodegradable or toxic. For example, aromatic compounds such as phenols are considered to be toxic to the microbial population at concentrations above 70-200 mg/L.**[3,4]** Aromatic chlorinated compounds are not removed efficiently by existing biological treatment techniques, either they are metabolized very slowly or resistant to microbial attack under prevailing treatment conditions.**[5]** Limitations of technologies have encouraged the researchers to develop more technologies which are efficient and environmental-friendly for waste water treatment.

It is necessary to develop effective treatment options using less conventional techniques, such as chemical and catalytic processes. Chemical oxidation is a popular method since the reactants are inexpensive. Advanced Oxidation Process (AOP) with the capability of exploiting high reactivity of hydroxy radical ($OH^{\cdot}$) in driving oxidation have emerged a promising technology for the treatment of wastewater containing refractory organic compounds. **[6,7]**. In this process,the compounds present in effluent can be oxidized to other species or total mineralization can take place i.e. the organic compound will not have any secondary by-products, sludge or solution resulting in formation of CO_2 and H_2O. There are several types of AOPs used in waste water treatment plants, each one of them can be effective in certain type of waste water and operational conditions. From an economical point of view, Catalytic Wet Peroxide Oxidation (CWPO) is considered to be one of the most effective and promising methods to satisfy the stricter environmental legislations, due to its higher efficiency, lower operating temperature and less harmful by-products compared to other Advanced Oxidation Processes (AOP's).

Many materials have been investigated for waste water treatment, including supported noble metals (mainly Pt and Pd), transition metal oxides (i.e., V, Ce, Mn, Cr, Cu, Co, Ni, and W) and perovskite-based oxides. Though noble metal catalysts such as Ru, Rh, Rd, and Pt generally show higher catalytic activity and higher resistance to metal leaching than others, they are usually very active at low temperature, high cost restricts their wide application.

In recent times, perovskite type oxides have also gained a great interest for the development of catalytic materials. They have been used in processes of combustion of automobile emission**[8]** and treatment of volatile organic compound**[9]**. Some perovskite like $LaTi_{1-x}Cu_xO_3$ by J.L.Sotelo et al. have been previously reported for the waste water treatment also **[10]**. Cerium is usually reported as a good promoter in perovskite lattice. According to several studies, partial substitution of 10% of A site by Ce in cobalt or manganese-based perovskites leads to an increase in catalytic oxidation activity **[11,12]**.Fe^{+2} based Fenton systems (Hydrogen peroxide and iron catalyst, which generate hydroxyl radicals highly oxidative) have been widely implemented to remove recalcitrant organic compounds during wastewater treatment.The previous result prompted us to investigate the performance of Cobalt containing $PrFeO_3$ perovskite ($PrCo_{0.2}\ Fe_{0.8}\ O_3$) for the treatment of phenolic solution through wet peroxide oxidation.

Phenol has been used as a model reactant, because among the harmful organic compounds, phenolic substances have deserved more attention because their wastes are one of the most prevalent forms of chemical toxicity and have higher frequency of occurrence in industrial wastewaters. **[13,14]** They give off unpleasant odour and taste even at very low concentrations **[15]**. Phenolic substances are pollutants with severe toxicity and a poor bio-degradability **[16]**.

II.EXPERIMENTAL

2.1 Catalyst Preparation

Materials

Praseodymium oxide (Pr_6O_{11}), Iron (III) nitrate nonahydrate [$Fe\ (NO_3)_3.9H_2O$], Cobalt (II) nitrate hexahydrate [$Co\ (NO_3)_2.6H_2O$], were obtained from Lobachemie. Concentrated Nitric acid (HNO_3) and Glycine were

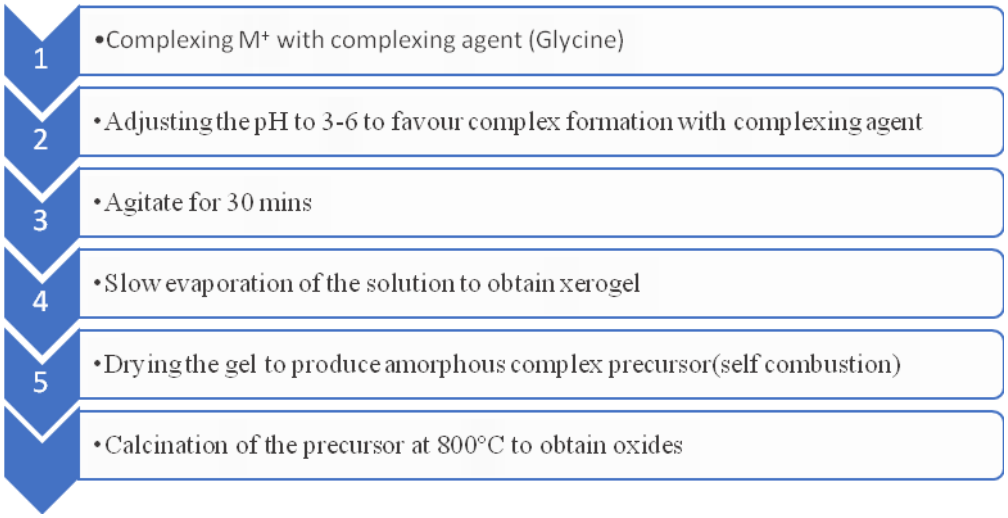
obtained from Merck. All reagents were used as received.

Method

The synthesis was performed under ambient atmosphere. Stoichiometry ratio was used to convert the Praseodymium oxide to its nitrate using concentrated HNO_3.

A solution of Praseodymium nitrate, Cobalt nitrate, and Ferric nitrate was obtained by dissolving calculated equivalent quantity as per catalyst stoichiometry of $Pr(NO_3)_3$, Co $(NO_3)_2.6H_2O$, and Fe $(NO_3)_3.9H_2O$. Adjust the pH to 3-6. Glycine was added to above solution in proportion of 1:1 w.r.t. metal nitrate solution. The mixture was under stirring for 30 minutes. The mixture was heated at 90-100°C with stirring to make thick gel. Formed gel further goes into auto combustion to give semi powder similar to xerogels which is ground to powder. Calcination of powder at 800°C for 8 hours resulted in the desired perovskite oxide of nanosized.

A schematic representation of synthesis can be given as;



2.2 Catalytic Experiments:

Catalytic wet oxidation experiments in presence of hydrogen peroxide were carried out in a 700mL microreactor glass autoclave under continuous mechanical stirring. Such equipment eliminates the possible catalytic effect of the steel wall surfaces. Phenol sample was taken in a beaker, initial pH of the solution was found to be 5.3, to which stoichiometry amount of 30% H_2O_2 (14 equivalents) was added. pH shows slight change towards acidic range and was found to be in range of 4.5-5. The catalyst and solution were placed into the microreactor. Thereafter, the system was closed, air pressure of $1kg/m^3$ is taken and heated up to 60°C with a heating rate of 3°C/min. Then, aliquots were withdrawn during the reaction course with the purpose of monitoring the degradation of phenol. The temperature was further maintained at set value for 120 minutes. Withdrawn samples were analyzed using UV-Visible Double beam spectrophotometer.

III. RESULTS AND DISCUSSION

3.1 Characterization

Perovskite $PrCo_{(1-x)}Fe_xO_3$(x= 0.8) was prepared using Glycine as complexingagent according to the procedure mentioned in 2.1 Method.

Various techniques such as XRD and SEM were employed to characterize these powders. For lattice parameter and interplanar distance (d) calculation i.e. X-Ray Diffraction (XRD) patterns, the samples were scanned in the range of 5-90° for a period of 2s in the step scan mode on D8 Advance diffractometer (Bruker). SEM picture was recorded with JEOL model 1200EX instrument at accelerating voltage of 1-20kV. The specific surface area was determined on Smartsorb-93 by the BET method from N_2 adsorption data obtained at -196°C (77K).

X-Ray Diffraction (XRD)

Powder XRD analysis of $PrCo_{(1-x)}Fe_xO_3$(x=0.8) for various composition showed the presence of pure crystalline perovskite phase. The pattern showed sharp and intense peaks corresponding only to crystalline perovskite-like structure, however trace impurity of Praseodymium oxide was observed at 2θ value 28.8 degrees.

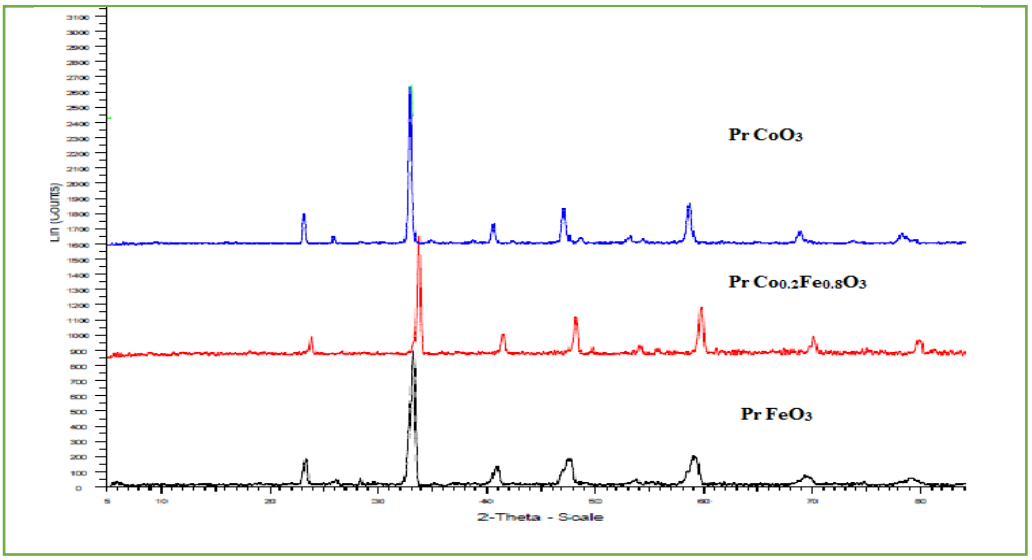


Fig.1 X-Ray Diffraction (XRD) spectra of $PrCo_{(1-x)}Fe_xO_3$ (x=0.8)

XRD patterns reveals that diffraction lines of the $PrCo_{(1-x)}$ Fe_xO_3(x=0.8)show a shift to higher 2θ values with doping of cobalt ions. This shift of diffraction lines is due to transformation of perovskite structure resulting from the alignment distortion of octahedral coordination by gradual substitution of Fe ions by Cobalt**[17]**. This observation of study is in agreement with the study of Hongto Cui et al. for the synthesis of Co -substituted $LaFeO_3$ and $LaNiO_3$.**[18]**

Scanning Electron Microscope (SEM)

SEM (Scanning Electron Microscope) have been also performed for the series of $PrCo_{(1-x)}Fe_xO_3$(x=0.8)to study average particle size and morphology of the prepared materials. The morphology of preparedpowder exhibited homogenous and porous microstructure. SEM analysis reveals the data of pore sizebelow 300nm and particle in range of 50-250 nm.

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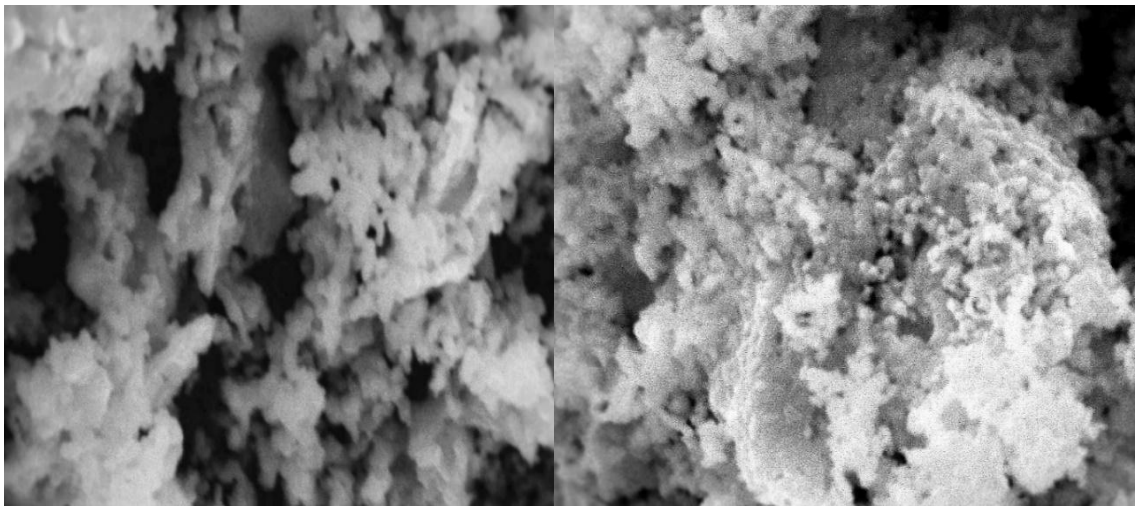

Fig. 2a Fig.2b

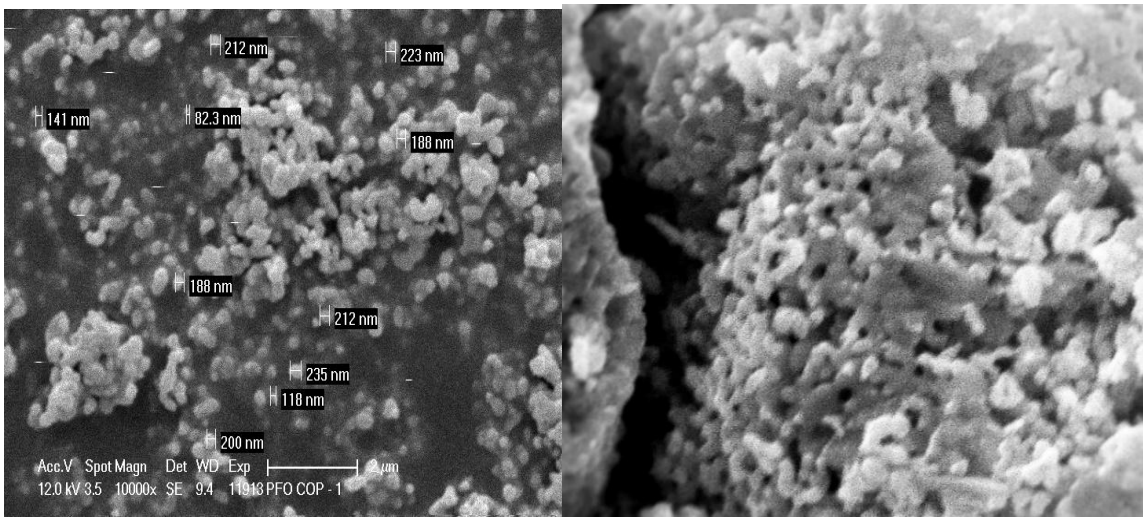

Fig. 2c Fig. 2d

Fig.2 SEM images (a- $PrFeO_3$, b- $PrCoO_3$, c,d- $PrCo_{0.2}Fe_{0.8}O_3$)

Micrographs of $PrCo_{(1-x)}Fe_xO_3$ (x=0.8)clearly showed that each of the particle is low density porous materials which is favourable to a catalytic application.

3.2 CWPO of Phenolic solutionover $PrCo_{(1-x)}Fe_xO_3$ (x=0.8)Perovskite: Optimization of reaction condition

According to the above result of characterization, sample with lowest impurity phase and highest surface area among the several preparationshas been selected for further studies. Experiments were carried out over $PrCo_{0.2}Fe_{0.8}O_3$ prepared sample with the purpose of monitoring their catalytic performance for the phenol removal in presence of hydrogen peroxide and simultaneously for optimizing the reaction condition. These catalytic experiments were performed with an initial peroxide concentration of ca. 1.65mL/L (30% H_2O_2), corresponding to the stoichiometric amount for the complete mineralization of phenol, according to the reaction:

$C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O$

In the following section, the effect of pH and effect of temperature have been reported for better optimization of reaction condition.

Effect of pH

The Experimental procedures were same (mentioned in 2.2), only the experiments were carried out at two different pH ranges 3.5-4.5 and 2.5-3.5. These ranges were selected because initial pH of the phenol solution was in the range of 4.5-5.5 which on addition of H_2O_2 further reduced to 4-4.7, which opted us these two-pH range to be monitored.

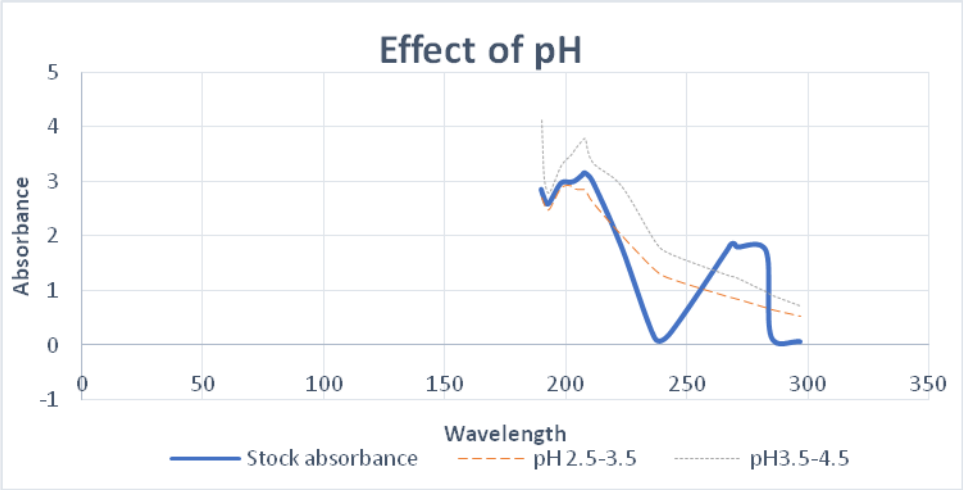

Fig. 3 Effect of pH

The results obtained from the experiments have been shown in Fig.3; it clearly indicates that in presence of $PrCo_{0.2}Fe_{0.8}O_3$ catalyst the rate of reaction is higher at pH 2.5-3.5 in comparison to pH 3.5-4.5.

Effect of Temperature

The effect of temperature has been studied in the range of 60-100°C for the catalytic wet peroxide oxidation of phenol (100ppm) with catalyst loading of 0.6g/L and initial hydrogen peroxide concentration of 1.65mL/L. As expected the total phenol conversion was significantly enhanced by increase in temperature, and this result is in accordance with the study of J. Sotelo et al. **[10]** and J. Barrault et al. [**20]**. However, a lower rate of catalytic performance is observed at 60 °C compared to 80 °C and 100 °C, which might be related to the influence of the temperature on the free radicals formation. But studies also show leaching possibility at higher temperature**[10]** and increase in temperature may add to cost of the process. The environmental factor and obtained result prompted us to investigate the process results at 60 °C. The result obtained from the experimentation has been shown in Fig.4; analysis was done in 60 minutes after achieving the desired temperature.

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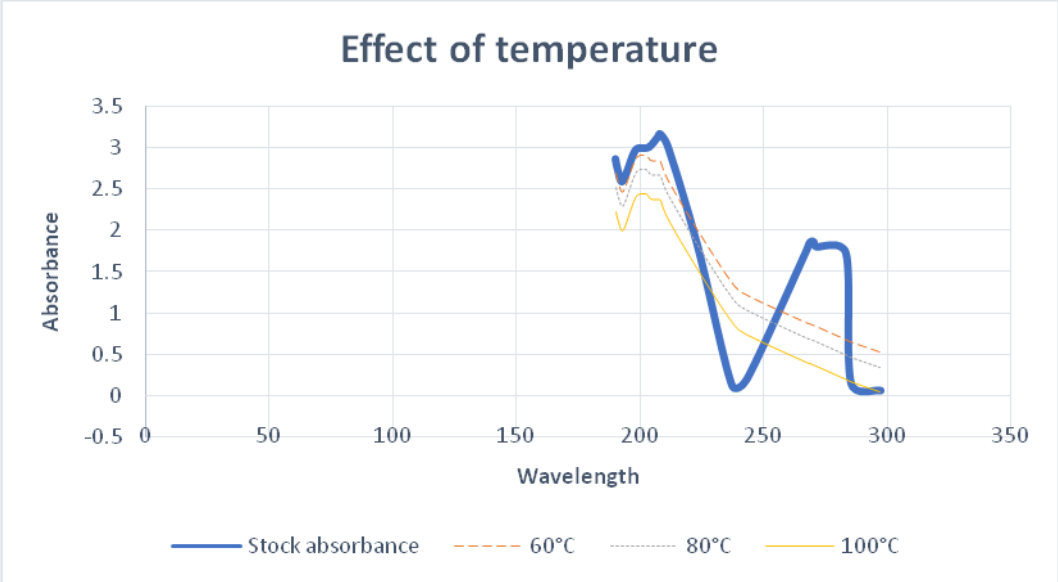

Fig. 4 Effect of Temperature

3.3 Catalytic Performance

The reaction condition has been optimized by performing preliminary experiments on $PrCo_{0.2}Fe_{0.8}O_3$ and on basis of the results, the reaction conditions were set at pH 2.5-3.5 and temperature 60°C. Catalytic performances were analysed using UV-Visible double beam spectrophotometer and total phenol conversion or reduction (i.e. Catalytic Performance) was calculated.

Catalytic performance shows increase in activity with slightdoping percentage of cobalt ion. It can be concluded that increase in cobalt influence the catalytic performance in phenol reduction.

Table 1. Catalytic Performance of Prepared Catalysts

Chemical composition	**S_{BET} (m^2/g)**	**Catalytic Performance (%)**
$PrFeO_3$	6.48	79.0
$PrCo_{0.2}Fe_{0.8}O_3$	4.65	82.0
$PrCoO_3$	3.11	0-5

Note: Reaction conditions: $[phenol]_0$= 100 ppm; $[H_2O_2]_0$= 1.65mL/L; catalyst concentration: 0.6 g/L; temperature = 60°C; Air= 1kg/m^3 reaction time = 120 min

Industrial effluent treatment:

The effluent sample of Phenol based were taken from BOISAR MIDC, the effluent is a processed water from an intermediate of final product. pH of the solution was in the range of 5.4-5.6. (Fig. 5)

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Fig 5 Initial pH of Water effluent

The pH was further reduced to 2.5-3.5 by adding dil. H_2SO_4, there was slight colour change after treatment with diluted acid. (Fig. 6)

Fig. 6 pH of effluent at pH 2.5-3.5

The procedure for treatment remains the same and result obtained are tabulated below:

Table 2. Catalytic Performance of catalyst on Industrial effluent

Catalyst	**S_{BET}**	**Catalytic performance**
$PrFeO_3$	6.48	86
$PrCo_{0.2}Fe_{0.8}O_3$	4.65	89

Sample size:200mL, $[H_2O_2]$= 1.65mL/L, Air= 1 kg/m^3 catalyst=40mg (20% of sample size)

IV. CONCLUSION

$PrCo_{(1-x)}Fe_xO_3$ (x=0.8) powders were successfully prepared by self-combustion process using metal nitrates, glycine. XRD results showed that prepared material was in perovskite phase. The specific surface area of the series is in range 3-6 m^2/g. It can be concluded from the results that series shows decrease in surface area with increase in doping of Cobalt. SEM images reveal the presence of distinct pores on catalyst surface.

The study of the catalytic wet peroxide oxidation of phenolic aqueous solution over $PrCo_{(1-x)}Fe_xO_3$(x=0.8) perovskites has shown a significant removal of aromatic compounds under mild reaction conditions (temperature of 60°C and initial peroxide concentration as per stoichiometric). pH, temperature and peroxide content have significant influence on phenol and its related contaminant reduction in aqueous solution. Catalytic Wet Peroxide Oxidation (CWPO) using cobalt containing ferrite perovskite may be a promising technology for the abatement of many other organic pollutants and its performance can be increased by using slight more pressure of air.

V. ACKNOWLEDGEMENTS

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