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Application of peanut shell ash as a low-cost support for fenton-like catalytic removal of methylene blue in wastewater

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ABSTRACT

Hazards and colour of industrial wastewater due to organic compounds such as dyes are becoming a significant problem with increased urbanization owing to its direct effects on photosynthesis, ecosystem and human health. This research attempts to use for the first time Peanut Shell Ash (PSA) based Fenton-like catalyst, impregnated with iron (Fe^{+3}), to study the decolourization and decomposition of methylene blue (MB). The materials have been characterised by using several techniques, namely, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-rays spectroscopy (EDS), N_2 adsorption and pH changes by mass transfer (for point of zero charge). Then, the catalytic, adsorption and hydrogen peroxide alone processes were compared. The effects of several reaction parameters such as initial hydrogen peroxide amount, initial dye concentration, initial pH, temperature, catalytic doses and adsorption on the removal efficiency of MB were studied. Furthermore, the effect of an electrolyte (hydroxyl radical scavenger) on the decolourization of dye was evaluated. The results revealed that catalytic process was the most efficient as compared to others. The results further revealed that the optimum decolourisation of MB occurred, when solution contained 0.1 g catalyst, 4 mM of hydrogen peroxide at temperature of 30°C and initial pH value of 3. The decolourisation efficiency was 84% with 0.2 g of catalyst, 16 mM of hydrogen peroxide at a temperature of 30°C, pH value of 3, and at initial MB concentration of 15 mg/L. The study, therefore, concluded that Peanut Shell Ash based Fenton-like catalyst shows good decolourisation and degradation efficiency at acidic pH values (pH = 3–5).

Keywords: Fenton-like process; Methylene blue; Peanut shell ash;Wastewater; Oxidation

1. Introduction

The need for the removal of minor concentrations of obnoxious and toxic pollutants in the industrial wastewater is increasingly becoming significant due to increase in urbanization [1]. The acidic wastewater discharged from various industries is hazardous to ecosystem and to human health [2]. Many organic compounds such as dyes, pharmaceuticals and pesticides need advanced oxidation and degradation treatments due to their mutagenic, tetratogenic and carcinogenic effects [2,3]. Over the past few years, coloured effluents owing to potential environmental hazard have drawn much attention [4,5]. The presence of dyes in aqueous streams may lower the light penetration hence may affect the photosynthesis process and adversely affect aquatic life. Therefore, the removal of such coloured dyes is important for the sustained aquatic environment [3,6].

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Different physical, biological and chemical methods have been used for the treatment of coloured wastewater [5]. Unfortunately, these conventional treatment methods have limited efficiency in the removal of these toxic substances [7]. Additionally, these are non-destructive, have high operational cost and result in the production of by-products [7]. Therefore, it is important to study novel methods for effective treatment of wastewater containing dyes. Advance oxidation processes (AOPs) like catalytic oxidation [8–10], Fenton process [8,11], photo-Fenton process, photo catalysis have gained much attraction in recent years [12,13]. Among all AOPs, Fenton reactions may be the most appropriate due to their feasibility, low toxicity and simplicity of reaction [4]. In the past two decades, the homogeneous Fenton reaction was reported as an effective method for the removal of hazardous pollutants. However, this process has some disadvantages such as limited operational pH range for effective oxidation and sludge production [14].

Consequently, the heterogeneous Fenton process was developed to avoid the sludge formation and to widen the pH range. It was observed that the nature of support, type of pollutant and its adsorption on catalyst can affect the degradation efficiency of catalysts [15]. Recently, several materials were reported as supports in heterogeneous Fenton-like processes for the effective removal of pollutants [4,11,15–18].

This study concerns the decolourisation of a dye methylene blue by heterogeneous Fenton-like catalyst based on peanut shell as has a support. The peanut shell is an agricultural by-product and is available in large quantities, particularly in winter. It is often burnt and discarded. It is also used as an absorbent for the removal of coloured dye and heavy metals [19–21]. It can be used as a raw material to make Fenton-like catalyst. It can bring economic and environmental benefits in wastewater purification. Lithium modified PSA has been successfully implied as a catalyst for biodiesel production [22]. Recently, magnetic carbon composites were fabricated from raw peanut shells and successfully implied as support in Fenton-like catalytic process for the removal of MB in water [23]. In our work, ash obtained from peanut shells was used as a support in Fenton-like catalytic process. To the best of our knowledge, this is the first report using peanut shell ash as a support in Fenton-like decolourisation processes.

In this study, methylene blue was selected as a model basic dye. It has been found in industrial as well as municipal wastewater [24]. It is frequently used in textile, rubber, plastic, cosmetics, paper, food and pharmaceutical industries [24]. As MB is a highly toxic dye, its decolourisation and degradation is crucial to investigate. This paper aims to study the effectiveness of iron (III) PSA based Fenton-like catalyst for the decolourisation of MB in water. Additionally, the effect of adsorption of MB, pH, catalyst dose, hydrogen peroxide concentration, radical scavengers and reuse performance of catalyst was investigated.

2. Experimental

2.1. Materials and reagents

Methylene blue used in this study was obtained from May & Baker, U.K. A 35% hydrogen peroxide solution was obtained from Merck, Germany. All the chemicals were used without further purification. The pH of solutions was adjusted by using 1N solutions of hydroloric acid and sodium hydroxide. Ultra pure deionised water was used for the whole study. The peanuts were obtained from the local market and shells were separated from the nuts. These shells were washed with de-ionised water, dried in the air for 48 h and were then burnt in a furnace at 600°C temperature to obtain ash.

2.2. Catalyst preparation

The impregnation method [25,26] was used for the preparation of iron (III) oxide loaded PSA catalyst. The PSA was treated according to the method given in literature [17]. The PSA catalyst was prepared by the method described above. The powdered material obtained was dipped in 0.1 M nitric acid solution for 24 h. It was than filtered by using suction filtration assembly and was washed thoroughly with distilled water until a constant pH was obtained [17]. It was then dried in an oven at 110°C overnight [25,26].

2.3. Catalyst characterization

The surface morphology and EDS analysis of PSA and iron-PSA were studied by using (SEM), Model, JEOL JSM-6480 LV JSM-6010LA. The point of zero charge of catalyst was determined by mass transfer method [27]. The structural analysis was studied by PANalyticalX'Pert MPD X-ray diffractometer with Cu K-α radiations (λ = 1.5406 Å) operated at 40 kV and a current of 40 mA in (θ-θ) scan mode. All the specimens were scanned in the 2θ range between 20° and 80° with scan step of 0.02°. The surface area and pore size were determined by Brunauer-Emmett-Teller (BET) method (Micro metrics AS AP 2020).

2.3. Decolourisation experiments

The decolourisation experiments of MB were conducted in 250 mL glass-stopper Erlenmeyer flask. The 100 mL of MB solution (15 ppm for decolourisation and 50 ppm for oxidation) was taken in the flask and weighted amount of catalyst was introduced in it. The 35% hydrogen peroxide solution was used to prepare hydrogen peroxide solutions of different molar concentrations (0–16 mM). The pH of the solutions was adjusted by using 1 N solution of hydroloric acid and sodium hydroxide. The flask was placed in an orbital shaker (PA-16250, Pamico Technologies). The experiments were performed with an agitation speed of 130 rpm. The temperature was kept constant at 30°C for all the experiments. In order to maintain the temperature, the orbital shaker was placed in an incubator (Memmert 854, Schwabach, Germany). All experiments were carried out in dark place and the flasks were also covered with light resisting materials.

The dye removal efficiency was determined by applying following equation.

$$Decolourisation\ efficiency(\%) = \frac{100 \times (A_o - A_t)}{A_o}$$

where A_o = Absorbance at time 0; A_t = Absorbance at time t

2.4. Analytical procedures

2.4.1. Methylene blue concentration

MB concentrations in the aqueous solutions were determined by ultraviolet-visible spectrophotometer (UV-1201, Shimadzu). The maximum absorption value of 664 nm (λ_{max}) was determined. The calibration curves had been prepared before experimentation. The method has been validated by both inter-day and intra-day validations. Each experiment was performed three times and the relative standard deviation was found to be less than 5%.

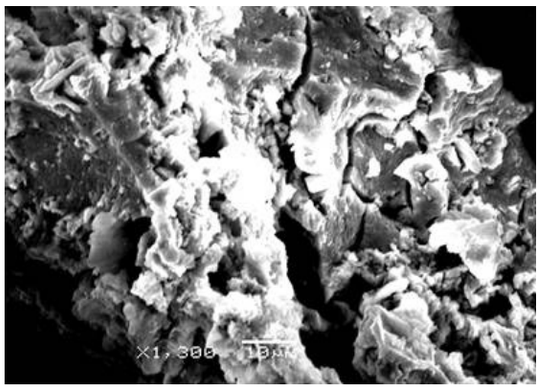
2.4.2. Iron analysis

Concentrations of iron in the aqueous solution at different times were determined by atomic absorption spectroscopy (Perkin Elmer, A Analyst 800). The calibration curves were prepared before the analysis.

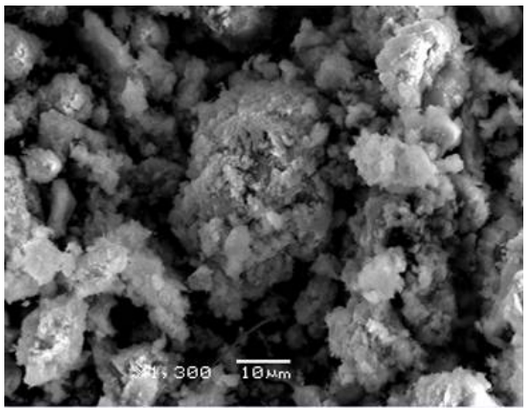
3. Results and discussion

3.1. Catalyst characterisation

The point of zero charge of the catalyst was found to be 9.1 ± 0.4. The SEM images of both PSA and iron PSA indicates (Figs. 1 a,b) that the surface morphology of PSA is retained and no significant change was observed after the incorporation of iron on PSA. Fig. 2 shows the XRD results of (PSA) and the prepared catalyst [iron (III)PSA]. The curve (a) in Fig. 2 showed that the parent material (PSA) is crystalline in nature. Curve (b) showed that Fe doping in the parent material (PSA) reduced the crystallinity and a new peak emerged at 2θ value of 26.081° corresponding to (021) plane reflection of monoclinic $FeSiO_3$ (iron silicate) phase. Moreover,the few peaks present in the parent material disappeared. The decrease in crystallinity may be owing to the broadening of the peaks due to iron doping or the emergence of new phase may also be the other reason as some phases may have appeared at the expense of others or may have hindered their growth. The surface area of PSA catalyst was found to be 17.10 m^2/g and the average pore diameter was 14.10 nm. The chemical composition of PSA and PSA iron was analysed by EDS. Elemental composition with EDS (Fig. 3) confirmed the presence of minute quantities of iron along with Aluminum, Silicon and Zinc as mainly detected components.



(a)



(b)

Fig. 1. SEM images of PSA and PSA/ Fe^{+3} catalysts.

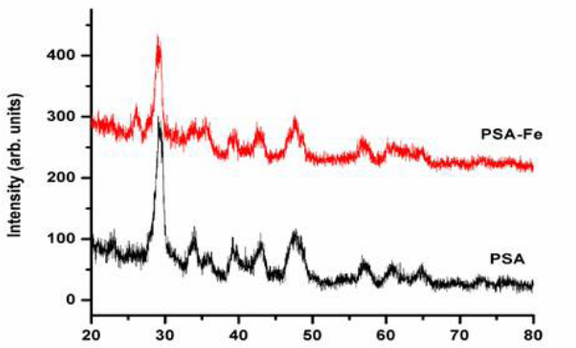


Fig. 2. XRD patterns of PSA and PSA/ Fe^{+3} catalysts.

3.2.Catalytic decolourisation of methylene blue

3.2.1. Comparison between catalytic and non- catalytic processes

Before studying the effect of various parameters, it is indeed important to evaluate the MB removal process, i.e., if MB removal occurs through catalytic process, through simply adsorption or by both processes. For that reason, decolourisation efficiency was compared for catalytic, adsorption and hydrogen peroxide only. Fig. 3 shows that MB decolourisation due to hydrogen peroxide is almost negligible (about < 4% in 120 min). This may be attributed to its low oxidation potential as compared to radical species [15]. The data show clearly (Fig. 3) that the PSA catalyst (in the presence of hydrogen peroxide) decolourise MB more

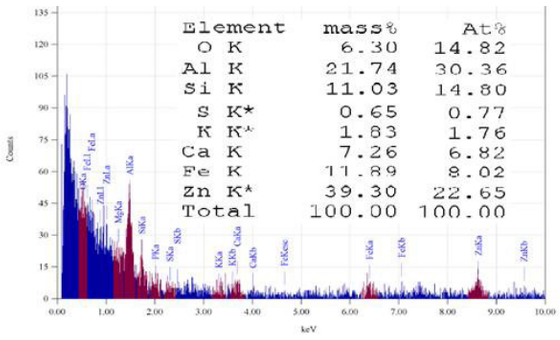


Fig. 3. EDS patterns PSA/ Fe^{+3} catalysts and its composition.

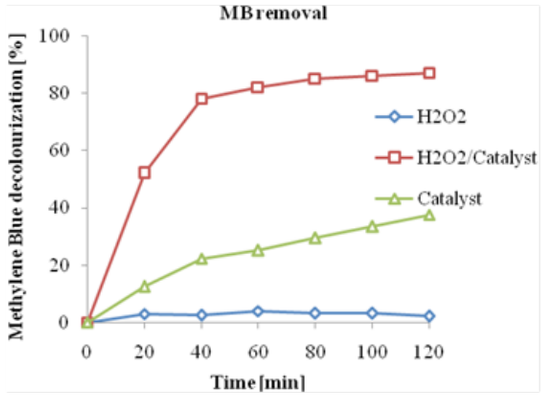


Fig. 3a. Effect of PSA catalyst and adsorption on PSA catalyst for the decolourization of methylene blue ($C_{o\,(MB)}$ = 15 ppm; H_2O_2 = 8 mM; T = 30°C; pH = 3.0; catalyst amount = 0.1 g; V = 100 mL).

effectively than adsorption process. Therefore, the results clearly suggest that iron impregnated PSA catalyses the decolourisation of MB.

3.2.2. *Effect of initial concentration of hydrogen peroxide*

As hydrogen peroxide is the source of hydroxyl radicals therefore, its amount will also influence the rate of decolourisation of the MB. Moreover, the optimum initial concentration of hydrogen peroxide is of great significance owing to its higher cost and environmental concerns. The experiments were also performed at different initial concentration of hydrogen peroxide (1–16 mM).

The Fig. 4 clearly indicates that the rate of decolourisation of MB increases with the increase in hydrogen peroxide concentration. The removal efficiency was 89% when 16 mM of hydrogen peroxide was added. This may be due to lesser production of hydroxyl radicals at lower hydrogen peroxide concentrations and were increased with the increase in hydrogen peroxide concentrations [4]. From the results 4 mM was selected as optimum value of hydrogen peroxide. This concentration is taken by keeping in view its scavenging effect,cost, ecological effects and decolourisation efficiency [4,17].

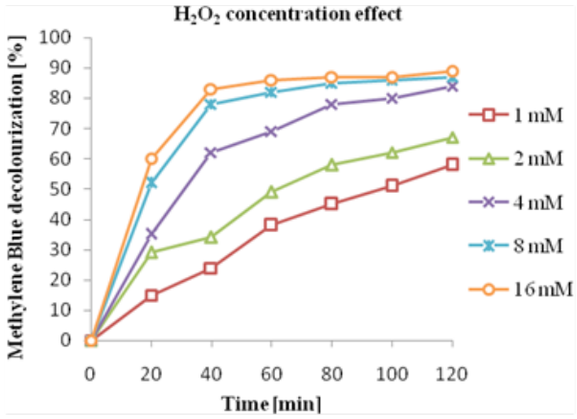


Fig. 4. Effect of H_2O_2 concentration on the decolourization of methylene blue ($C_{o\,(MB)}$ = 15 ppm; T = 30°C; pH = 3.0; catalyst amount = 0.1 g; V = 100 mL).

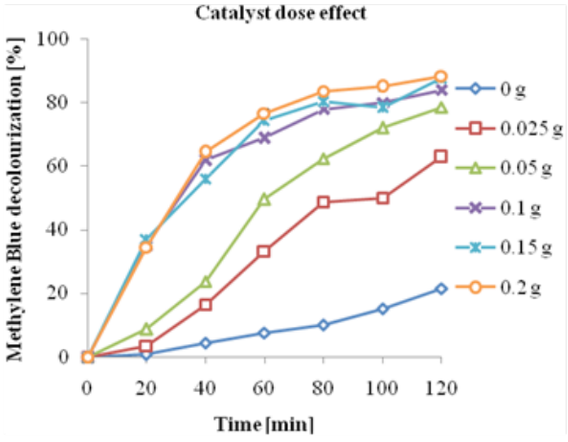


Fig. 5. Effect of catalyst dose on the decolourization of methylene blue ($C_{o\,(MB)}$ = 15 mg/L; H_2O_2 = 4 mM; T = 30°C; pH = 3.0; catalyst amount = 0.025 g – 0.2 g; V = 100 mL).

3.2.2. *Effect of catalyst dosage*

A series of experiments were carried out to investigate the effect of catalyst dose. The influence of catalyst concentration on the removal efficiency of MB is presented in Fig. 5. The results show that the decolourisation of MB increased with the increase in catalyst dose, this may be due to increase in active sites with the increase of catalyst concentration [17]. About 88% decolourisation efficiency has been achieved by using catalyst dose of 0.1 g at optimal conditions. Therefore, 0.1 g was selected as an optimum catalyst dosage.

3.2.3. *Effect of pH*

Previous studies revealed that the effective pH range for Fenton-like process has been 2–5 [4,28]. In this study, the effect of initial pH on the decolourisation efficiency

was investigated in acidic and basic medium at optimum conditions. Fig. 6 indicates that colour removal efficiency of the process decreases with the increase in pH. The maximum colour removal efficiency (95.6%) was achieved at pH 3 and it was only 16% at pH 10. At higher pH, the removal of dye may only be due to the adsorption of MB on catalysts [17]. The overall decolourisation efficiency at various pH values was in complete agreement with the available literature [4,28].

3.2.4. Effect of the initial concentration of MB

In order to study the effect of initial MB concentration on the decolourisation efficiency, MB solutions of different concentrations were prepared. Fig. 7 show that MB removal was 12.6 mg/L in 120 min when initial concentration was 15 mg/L and it was 16.8 mg/L when initial MB concentration was 45 mg/L. Therefore, results indicate that the amount of dye removal increases with the increase in dye concentration, as more amount of dye will be available for the catalyst [4].

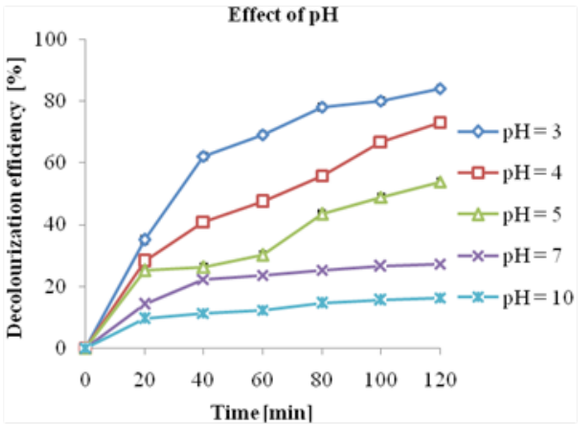


Fig. 6. Effect of pH on the decolourization efficiency of methylene blue on PSA-Fe/H_2O_2 ($C_{o\,(MB)}$ =15 mg/L; T = 30°C; initial pH = 3, 4, 5, 7 and 10; T = 120 min; H_2O_2 = 4 mM; catalyst = 0.1 g; V = 100 mL).

3.2.5. Effect of temperature

The results presented in Fig. 8 indicate that the rate of colour removal of MB speeds up with the increase in temperature. This happens because at higher temperature, the rate of generation of hydroxyl radicals increases; thus, accelerate the reaction rate between catalyst and hydrogen peroxide [4]. However, feasible reaction temperature to be recommended was 30°C as much higher temperature can decompose the hydrogen peroxide and increase the operational cost.

3.2.6. Effect of electrolyte on dye removal

Wastewater usually contains different salts. Therefore, its effect on the dye removal was also investigated. This study may further indicate the radical mechanism in the process. It is well known that sodium chloride acts as hydroxyl radical scavenger. The experiments were conducted under optimum conditions. Fig. 9 indicates that decolourisation efficiency decreased in the presence of salt. The decrease in the rate of degradation may be due to the reaction between chloride ions and hydroxyl radicals [1]. This study further confirms that PSA based catalysts operates through radical mechanism.

3.2.7. Catalyst reuse performance

Catalyst reuse performance has been studied at optimum conditions in order to investigate catalyst stability. The results presented in Fig. 10 indicate that the catalyst has a significant decolourisation efficiency (68%) for MB after four successive runs. Decrease in decolourisation efficiency may be due to the leach out effect of iron from catalyst [4]. Owing to this reason, the leach out test was also conducted and was found to be less than the European Standards (2 mg/L) [4].

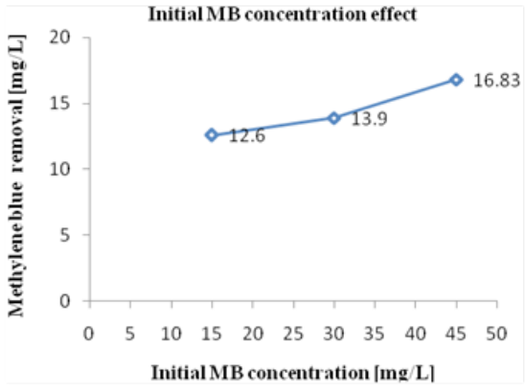


Fig. 7. Effect of initial concentration of MB (T = 30°C; pH = 3.0; T = 120 min; H_2O_2 = 4 mM; catalyst = 0.1 g; V = 100 mL).

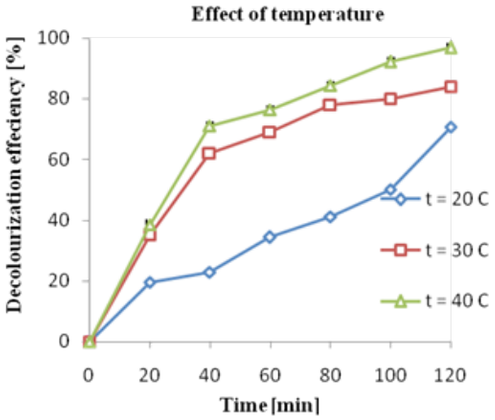


Fig. 8. Effect of temperature ($C_{o(MB)}$ = 15 ppm; pH = 3.0; T = 120 min; H_2O_2 = 4 mM; catalyst = 0.1 g; V = 100 mL).

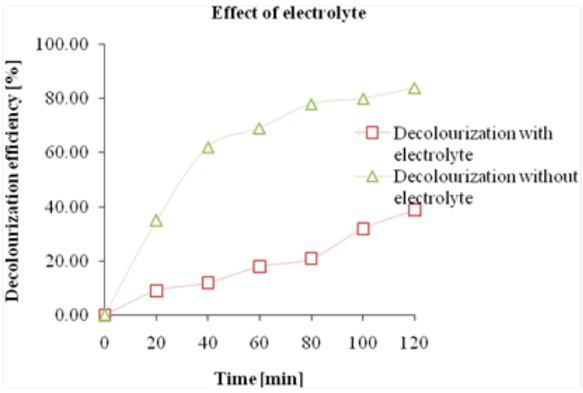


Fig. 9. Effect of electrolyte presence on MB removal efficiency ($C_{o\,(MB)}$ = 15 ppm; pH = 3.0; T = 120 min; H_2O_2 = 4 mM; catalyst = 0.1 g; NaCl = 0.1 M; V = 100 mL).

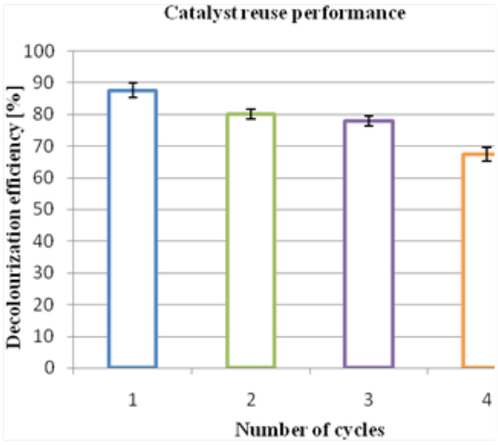


Fig. 10. Reuse performance of PSA-Fe ($C_{o\,(MB)}$ = 15 mg/L; T = 30°C; pH = 3.0; T = 120 min; H_2O_2 = 4 mM; catalyst = 0.1 g; V = 100 mL).

4. Conclusions

The Iron PSA based catalyst was tested and used in Fenton-like process for the removal of a basic dye as MB. Following conclusions have been drawn on the basis of all the experimentation.

1. Peanut shell ash based catalyst is effective in Fenton like process for the removal of methylene blue from water.
2. The catalyst activity is pH dependent and decolourisation was the highest at pH 3.
3. The catalyst has good chemical stability

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