Removal of Malachite Green and Congo Red Dyes from Water by Polyacrylonitrile Carbon Fibre Sorbents

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ABSTRACT
The present work was aimed at evaluating the adsorption properties of malachite green and congo red dyes by polyacrylonitrile carbon fibre sorbents. The sorbents were activated and oxidized using potassium hydroxide and ammonium persulfate, respectively at mild conditions. Consequently, the sorbents were characterized for surface area, surface functional groups and thermal decomposition. The activated sorbent displayed a 18.8 mg/g (94 %) of malachite green removal at Co = 20 mg/L, while both modified sorbents showed a 17.5 mg/g (87.5 %) removal of congo red at the same concentration. All sorbents showed a rapid equilibrium of malachite green and congo red dyes in water. Also, the sorbents are somewhat tolerable against different solution pH conditions despite a slight change due to possible electrostatic interactions. Thus, the materials could be successfully employed to treat dyes-laden wastewater.

Keywords*: Adsorption, congo red, malachite green, polyacrylonitrile carbon fibre, sorbent, wastewater treatment*

1.0 INTRODUCTION

Synthetic dyestuffs are widely used in textile, paper, printing, plastic, leather and cosmetic industries [1]. Over the last few years, there has a surge of demand, leading to an increase of production and consistent expansion of these industries. However, poor waste management has resulted in dyes finding their ways into water resources, thus affecting the properties of fresh water, the living creatures therein and also public health [2]. Malachite green and congo red are among the common textile dyes in wastewater, wherein the discharge of dyes worldwide contributes around 20 % of water pollution [3].

The release of dyes into water bodies has become a subject of significant concern as it causes water pollution and health issues. Congo red, for example can be metabolized into benzidine, a compound that has been reported to be carcinogenic and mutagenic for aquatic organisms [2]. The presence of dyes in aquatic system is also aesthetically displeasing, reduces light penetration for photosynthesis, thereby reducing the oxygen solubility for live therein [1].

Several physicochemical treatment methods are available to combat dyes-laden wastewater [1,4]. Often, these treatment strategies end-up with several drawbacks such as low efficiency, high maintenance and operating costs, and sludge generation. Among others, adsorption has gained research attention in dyes wastewater treatment [4]. The process is known to be simple, cheap and easy to scale-up. Various low-cost sorbents have also been developed to accommodate the ever-changing and ever-challenging global water pollution [3]. To broaden the body of knowledge, the present work is embarked to evaluate the adsorption properties of polyacrylonitrile carbon fibre sorbents to challenge malachite green and congo red dyes in water. Systematic batch adsorption studies were carried out at different contact times, concentrations, solution pH conditions to shed some light on the promising application of the material in wastewater treatment.

2.0 MATERIALS AND METHODS

2.1 MATERIALS

The polyarcylonitrile carbon fibre was supplied by Toho Tenax, Japan. Malachite green (mw = 365 g/mol) and congo red (mw = 697 g/mol) were obtained from HmbG Chemical, while potassium hydroxide, ammonium persulfate, sodium hydroxide and hydrochloric acid were purchased from VNK Supply.

2.2 PREPARATION AND CHARACTERIZATION OF SORBENTS

Polyacrylonitrile carbon fibre was cut into pieces of 1 cm × 1 cm, washed using distilled water to remove debris and dried in an oven at 105 °C for 24 h. The sample was designated as as-received PAN. Chemical activation was performed via potassium hydroxide impregnation of as-received PAN at a ratio of 1: 0.5 (as-received PAN: KOH), and dried in an oven. Next, the dried material was soaked in 0.1 M HCL solution overnight and washed using distilled water to a constant pH. The resultant material was designated as activated PAN. Then, the activated PAN was later soaked in 3 M ammonium persulfate solution at room temperature for 48 h for oxidation procedure. The material was washed using distilled water to a constant pH and was designated as oxidized PAN. All sorbents were dried in an oven at 105 °C prior to use.

The sorbents were characterized for surface area, surface functional groups and thermal decomposition. The thermal degradation profiles were obtained using a TGA 4000 (Perkin Elmer) at a N2 flow of 40 mL/min and a heating rate of 10 oC/min from 30 oC to 900 oC. A PulseChemisorb 2705 (Micrometrics, USA) was used to measure the specific surface area of sorbents, while the surface functional groups were detected using a Spectrum GX FT-IR (Perkin-Elmer, USA).

2.3 BATCH ADSORPTION STUDIES

A 50 mg of sorbent was added into Beatson bottle containing 50 mL of dye solution of known concentration. For the effect of contact time, the residual concentration was measured at the pre-set time intervals to a point of equilibrium. For the effect of solution pH, few drops of 0.1 M HCl and 0.1 M NaOH were used to adjust the solution pH. The residual concentrations of malachite green and congo red were measured using a Drawell UV-vis spectrophotometer (DU-8200) at a wavelength of 625 nm (a.u. = 0.0938 × Co, R2 = 0.996) and 486 nm (a.u. = 0.169 × Co, R2 = 0.99), respectively. The adsorption capacity at time t, Qt (mg/g) was calculated as, Qt = (Co - Ct)×(V/m), where, V (L) is the volume of solution, m (g) is the mass of sorbent, Co and Ct (mg/L) are the initial concentration and concentration at time, t, respectively.

3.0 RESULTS AND DISCUSSION

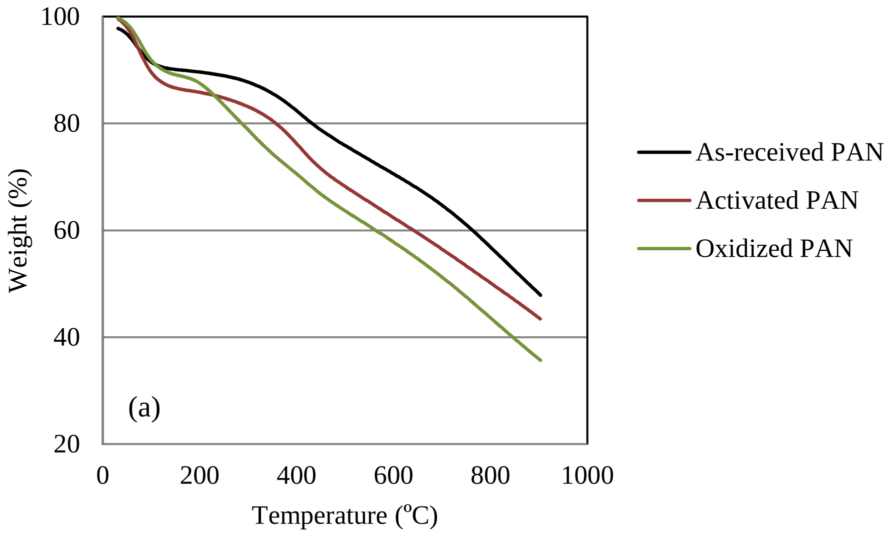
3.1 CHARACTERISTICS OF SORBENTS

Table 1 summarizes the physical characteristics of polyacrylonitrile carbon fibre sorbents. The pH values of sorbents are between 4.4. and 6.7. The yield of activated PAN is 72.5 %. The weight loss could be due to the effect of KOH as dehydrating agent that prompts light burning-off during the drying process [5]. Likewise, the yield of oxidized PAN decreased further to 33.1 % as a result of aggressive surface oxidation reactions. This is in agreement with the trend of decreasing surface area of oxidized PAN from 31.2 m2/g to 14.9 m2/g. From Table 1, the activated PAN exhibits a surface area of 31.2 m2/g because potassium ions intercalate into the carbon network, thus causing pathways development via volatilization under the mild conditions [6].

Table 1: Physical characteristics of sorbents.

Characteristics	As-received PAN	Activated PAN	Oxidized PAN
pH	6.7	4.4	5.3
Yield (%)	96.3	72.5	33.1
BET specific surface area (m^2/g)	-	31.2	14.9

Figure 1 displays the thermal degradation profiles of polyacrylonitrile carbon fibre sorbents. The thermal gravimetric analysis was used to analyse the thermal stability of the sorbents. Figure 1(a) can be divided into three stages according to the extent of weight loss. The initial weight loss at around 120 °C may be due to the physisorbed moisture. At this stage, activated PAN exhibits a higher weight loss of 12.7 %, that could be directly attributed to the adsorption of moisture from the surrounding as a result of a higher specific surface area. This is also visualized by a sharp peak centred at 70 °C in Figure 1(b). From Figure 1(a), the moisture content of sorbents are in the range of 11.0 % to 12.7 %. The second stage (121 °C – 430 °C) is associated to the chemical reactions and the release of volatiles such as CO2, CO, H2O, NH3 and HCN. Meanwhile, the profiles at stage three (431 °C – 900 °C) demonstrate a steady decrease in weight, indicating a complete evaporation of polymer chain fragments from the fibre [7]. From Figure 1(a), the as-received PAN shows a somewhat heat-resistant behaviour with a final weight loss of 51.5 % which implies that it is thermally more stable than the other two sorbents. On the other hand, the activated PAN displays a weight loss of 64.3 %. In Figure 1(b), the second peak of activated PAN has shifted to a lower temperature at 258 °C, suggesting that the material has deformed from its original source and becomes more susceptible to heat degradation at higher temperature.



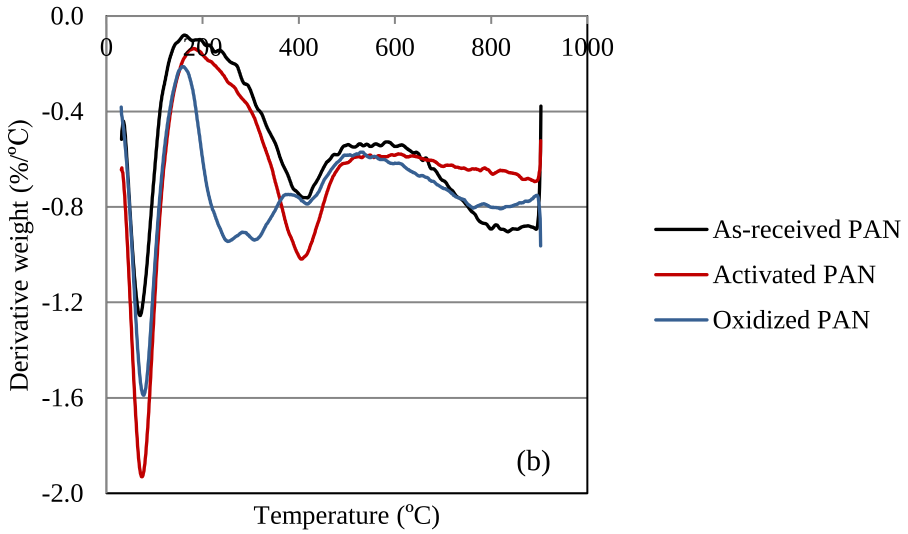


Figure 1: Thermogravimetric analysis of sorbents, (a) weight profiles, (b) derivative weight profiles.

Figure 2 shows the FTIR spectra of sorbents. In general, the spectra are similar but with varying peaks intensities, wherein the spectrum of oxidized PAN has become more simplified as compared to the other counterparts. This could be due to the aggressive oxidation reactions leading to the liberation of some surface functional groups. The peaks centred at 2116 cm-1 and 1987 cm-1 are attributed to the strong stretching of nitrile (C ≡ N) groups, i.e., the main functional groups of polyacrylonitrile carbon fibre. The peaks at 1873 cm-1 and 1209 cm-1 could be assigned to the stretching vibrations of C—O groups. All sorbents exhibit a peak at 1580 cm-1 that corresponds to the stretching vibrations of C=C and/or C=N conjugated bonds in aromatic rings [8]. The broad band at 3360 cm-1 could be associated with the readily adsorbed moisture in the material.

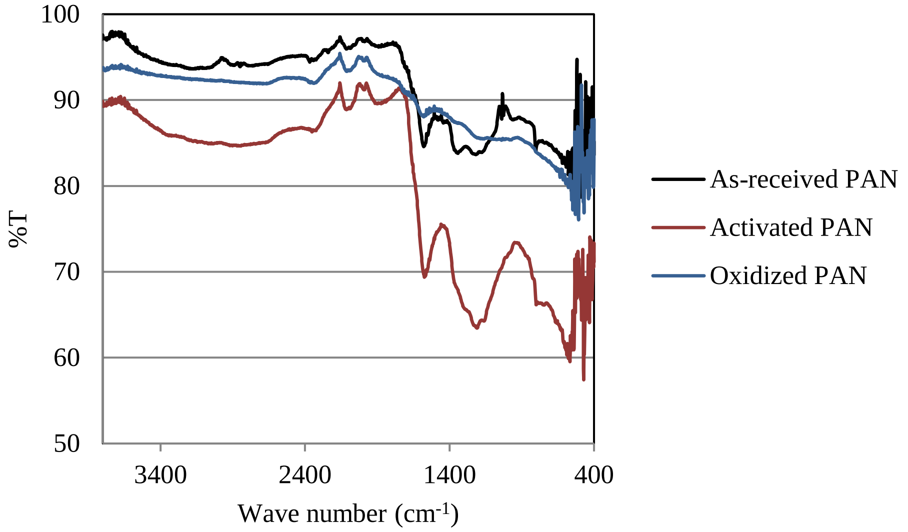


Figure 2: FTIR spectra of sorbents.

3.2 ADSORPTION STUDIES

Figure 3 shows the effect of concentration on dyes adsorption onto polyacrylonitrile carbon fibre sorbents. All sorbents demonstrate an increasing pattern of adsorption with increasing concentration. The concentration of dyes renders a driving force for the solute molecules to overcome the solid phase mass transfer resistance for a greater adsorption at a higher concentration [9]. In Figure 3(a), activated PAN shows a somewhat higher removal of malachite green as compared to the other two sorbents, wherein the as-received PAN and oxidized PAN endow a similar performance. This is true for all concentrations studied. At Co = 20 mg/L, the activated PAN exhibits a dye removal capacity of 18.8 mg/g (94 %). In Figure 3(b), oxidized PAN prevails over the other two sorbents for congo red removal. At Co = 20 mg/L, both oxidized and activated PAN sorbents recorded a similar performance of 87.5 % (capacity = 17.5 mg/g). The modified sorbents display a greater dyes removal due to their specific surface area and surface chemistry that prompt more interaction probabilities for adsorption to take place [10].

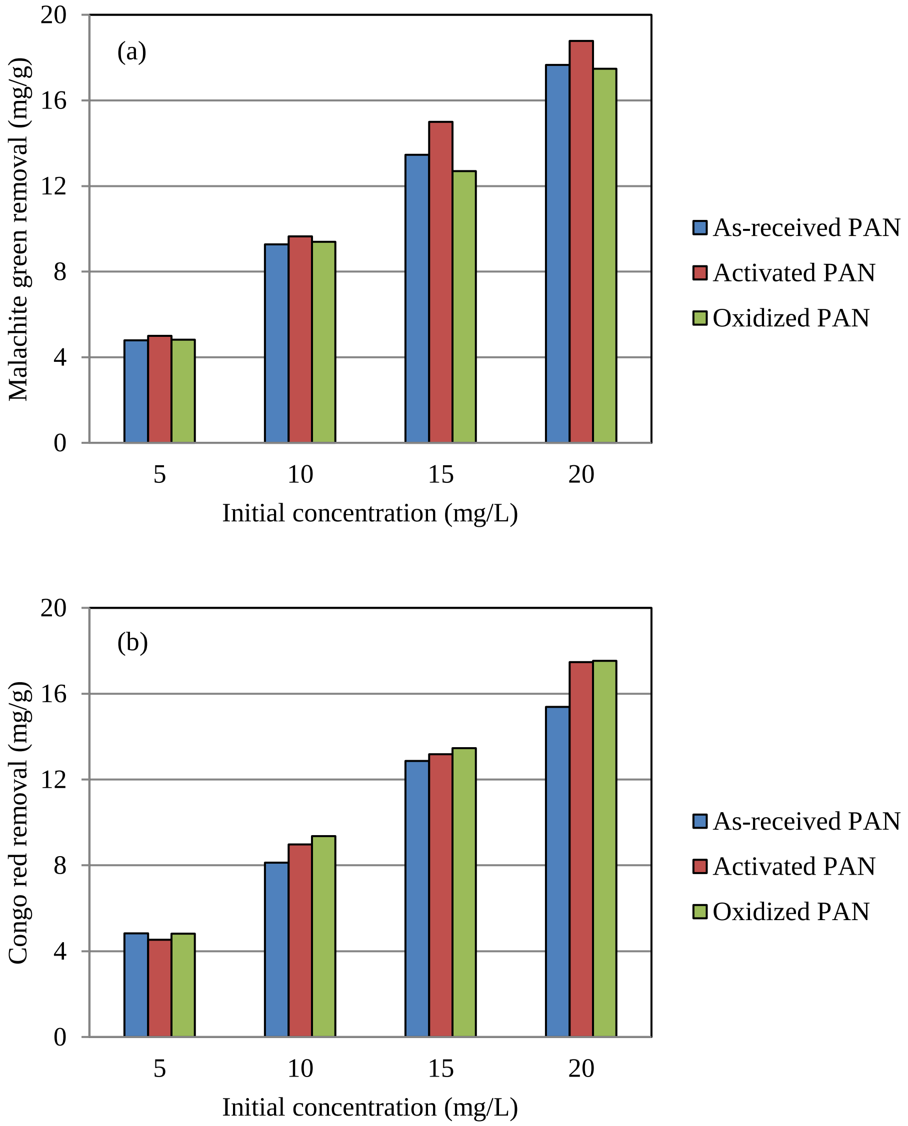


Figure 3: Adsorption of dyes onto polyacrylonitrile carbon fibre sorbents at different concentrations, (a) malachite green removal, (b) congo red removal.

Figure 4 shows the effect of contact time on dyes removal by sorbents. Generally, the adsorption of dyes by all sorbents is rapid. Nearly 77 % of malachite green is adsorbed the moment the sorbents are in contact with dye solution at C_o = 20 mg/L. Similarly, the sorbents demonstrated a missing increasing trend of adsorption with time for congo red removal. From Figure 4(c), the point of equilibrium for congo red adsorption is immediately reached when the solid material is added into the dye solution, suggesting a superfast kinetics. A small increment in adsorption with time can be seen in Figure 4(a,b), especially at a higher concentration of malachite green. The inherent resistance in liquid phase that is partly associated with the chemical properties of malachite green molecules could be the reason for the different kinetics behaviour [11]. The transport of solute from the bulk solution to the sorbent surface occurs rapidly at lower concentration as there is still numerous actives sites available for adsorption. When the amount of molecules are lesser than the number of active sites, the rate of adsorption is rapid and the time to reach equilibrium is almost instant. At high concentration, however, the adsorption sites become the limiting factor, thus restricting the dyes removal. From Figure 4(a), the equilibrium was attained at 16 h for malachite green concentration of 5 mg/L, while the duration increased to 41 h for 20 mg/L solution.

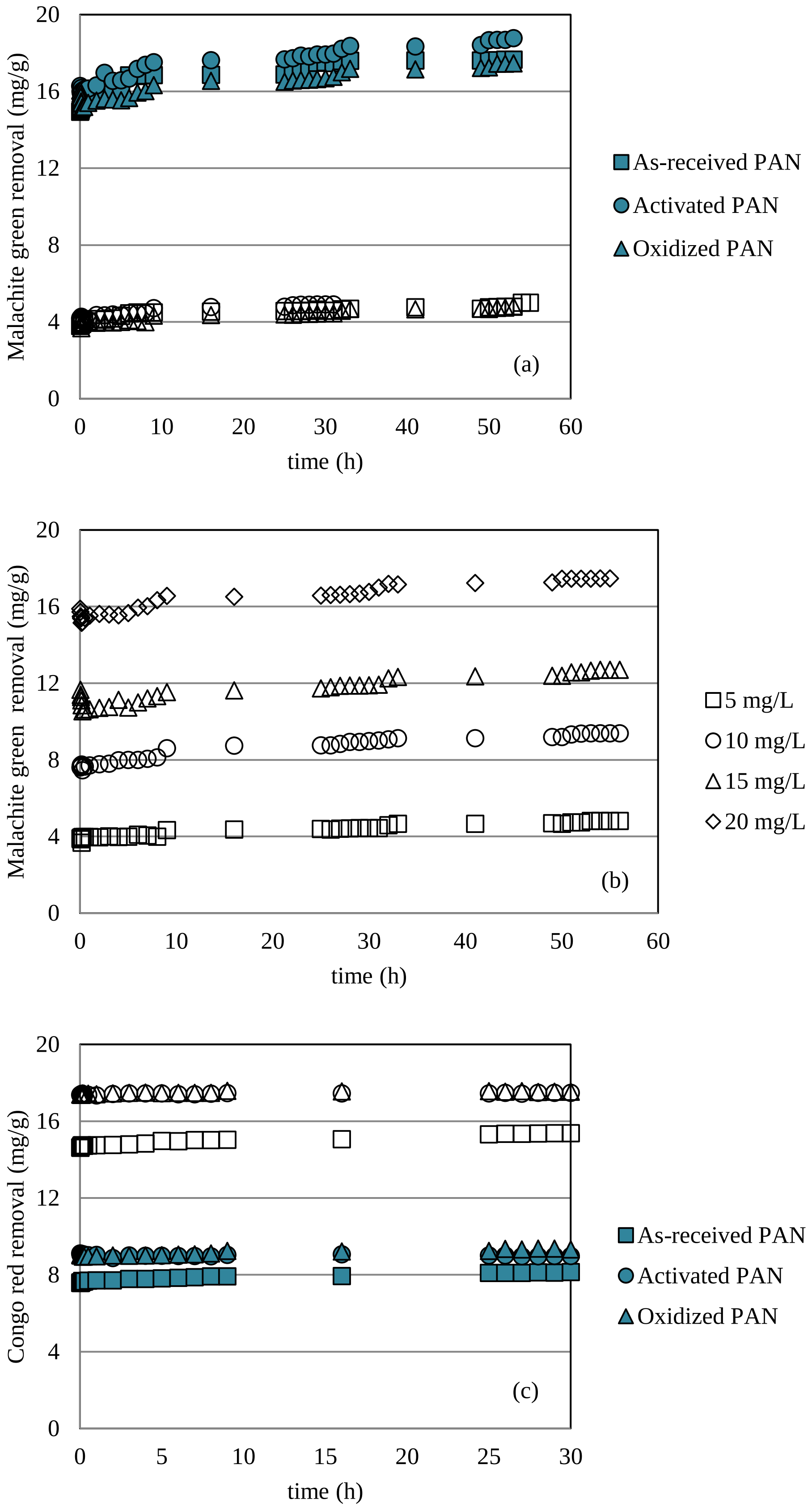


Figure 4: Effect of contact time on dyes adsorption by sorbents, (a) malachite green removal at 5 mg/L (open symbol) and 20 mg/L (closed symbol), (b)

malachite green removal by activated PAN, (c) congo red removal at 15 mg/L (closed symbol) and 20 mg/L (open symbol).

Figure 5 illustrates the effect of pH on dyes adsorption by polyacrylonitrile carbon fibre sorbents. In Figure 5(a), the as-received and activated sorbents display an increasing trend of malachite green adsorption with increasing solution pH, while the oxidized one shows a comparable performance of 93.7 % from pH 3.5 to pH 6.3 before the capacity slightly declines to 92.3 % at pH 7.3. At pH 7.3, the as-received sorbent exhibits a greater performance of 99.1 % as compared to 97.6 % by the activated sorbent. This dissimilar pattern from that at natural pH (Figure 3) could be due to inherent charge of malachite green molecules. Malachite green is a cationic dye, and bears a positively charge in aqueous solution. At high solution pH, the sorbents are surrounded with OH^- ions, at which the increase in adsorption capacity could be stimulated by electrostatic attraction [11]. However, the oxidized sorbent that is likely rich in acidic oxygen groups may undergo surface neutralization at high pH, thus decreasing the OH^- density. This is evident from the distinct equilibrium pH profile of oxidized sorbent as compared with that of the other counterparts. Consequently, the sorption capacity decreases due to less surface attraction. Figure 5(b) shows a decreasing performance of sorbents for congo red removal with increasing solution pH. Congo red is an anionic dye and bears a negative charge in aqueous solution. At low pH solution, the sorbent tends to be surrounded by H^+ ions, hence it will repulse the dye molecules away from the surface. Despite the surface neutralization, the oxidized sorbent still demonstrates a drastic decrease in congo red removal from 91 % at pH 3.3 to 83.7 % at pH 6.1. This could be partly due to the inherent properties of sorbent and congo red solution, and the interaction with foreign OH^- ions that may impede the adsorption to prevail. Nevertheless, all sorbents show a tolerable behaviour against pH with insignificant changes in removal performance between 90 % and 99 %, and 83.7 % and 93.8 % for the removal of malachite green and congo red, respectively. This brings about a promising future of polyacrylonitrile carbon fibre material as sorbent candidate for dyes-laden wastewater treatment.

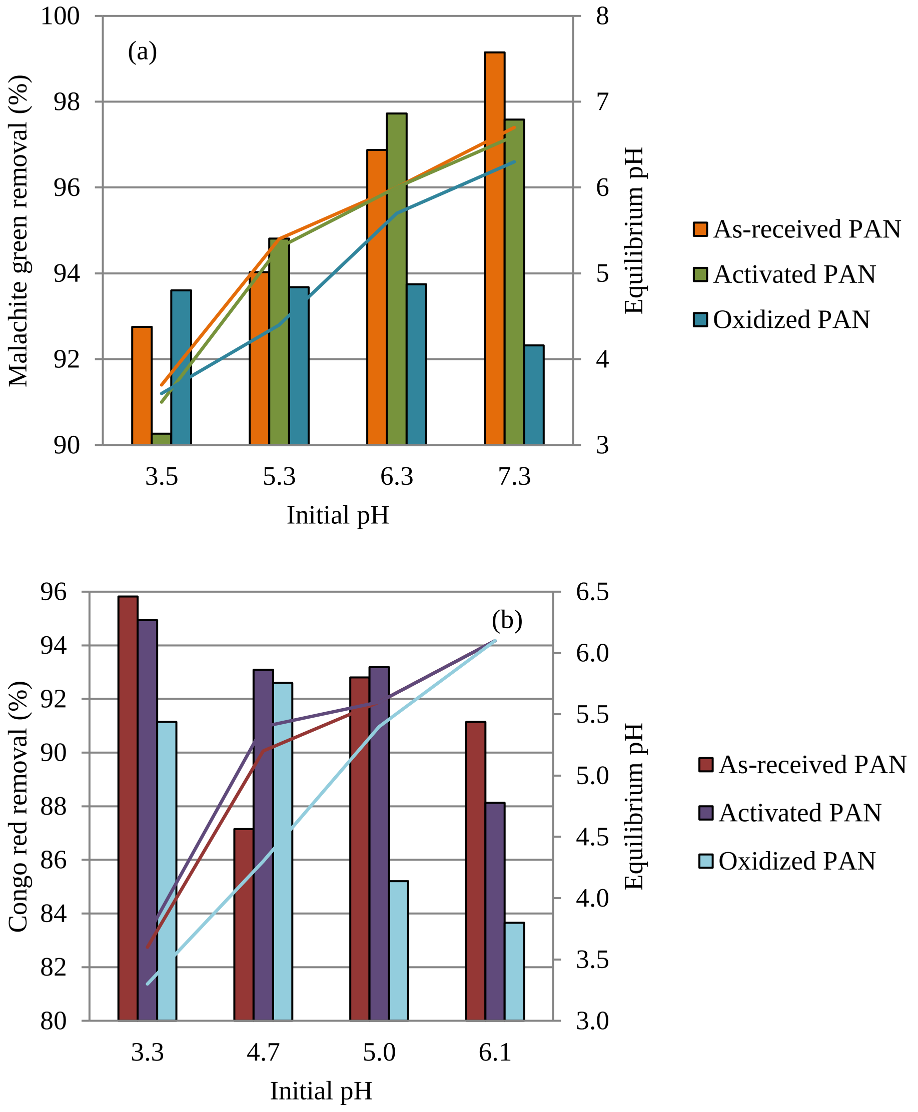


Figure 5: Effect of pH on dyes removal by sorbents (bar: removal performance; line: equilibrium pH), (a) malachite green adsorption (C_o = 15 mg/L), (b) congo red adsorption (C_o = 15 mg/L).

4.0 Conclusion

Sorbents were prepared from polyacrylonitrile carbon fibre at mild conditions for malachite green and congo red removal from water. The activated and oxidized sorbents recorded the surface area of 31.2 m^2/g and 14.9 m^2/g, respectively. All sorbents showed an increasing adsorption with increasing dyes concentration up until 20 mg/L. At this concentration, the activated sorbent displayed a higher malachite green removal of 18.8 mg/g (94 %), while both activated and oxidized sorbents endowed a 17.5 mg/g (87.5 %) of congo red removal. The equilibrium of adsorption by both dyes was attained almost instantly the moment the sorbents are in contact with the solutions. Different adsorption behaviours were observed at varying solution pH depending on the surface charge nature of dyes. Nevertheless, the sorbents are somewhat tolerable against pH conditions. In conclusion, through simple modifications, the materials could be sufficiently employed for dyes wastewater treatment.

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