

Efficient Treatment of Olive Mill Wastewater by Magnetic Olive Mill Seed Cakes

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ABSTRACT

The consumption and medicinal use of olive oil in the Mediterranean region is growing at alarming rate. However, olive mill wastewater threatens both aquatic organisms and human beings. Hence, there is urgent need to develop affordable treatment technology. In the present research, olive mill wastewater (OW) was collected from a three-phase olive production system located in the Karpaz region of Northern Cyprus. The collected OW was preserved and characterized before subjected to treatment. The chemical oxygen demand (COD) and phenolic content of the OW falls in the ranged of reported OW.

Pre-treated olive oil solid cake (OC) and fabricated magnetically-responsive olive oil seed cake (MOC) were applied as adsorbents for treatment of OW by batch and column systems. The physico-chemical characteristics of the OC and MOC were evaluated and reported. The COD and colour of the OW were reduced using both OC and MOC under varying experimental conditions.

The results herein, showed that MOC comparatively exhibited excellent performance and easy separation after use. Under optimum conditions in a batch and column systems, MOC reduces the COD to 6.5–8.9% and colour to 11.5–15.4%, while OC reduced the COD to 14.5–21.3% and colour to 27.6–33.5%. The MOC was reused severally with no significant loss in performance, suggesting that proposed treatment is technically and economically efficient.

Keywords: Magnetic olive seed cake; olive mill wastewater, COD removal

ÖZ

Akdeniz bölgesinde zeytinyağının tüketimi ve tıbbi amaçla kullanımı alarm verecek orana ulaşmıştır. Her nasılsa, zeytin atıksuyu, sudaki organizmaların yaşamını ve insan hayatını tehdit ediyor. Bu nedenden dolayı, acil bir şekilde bu atıksuyu arıtacak teknolojinin geliştirilmesi gerekmektedir. Bu tezde yapılan araştırmada, zeytin değirmeni atıksuyu (ZDA), üç faz sistemi kullanılarak zeytinyağı üreten Kuzey Kıbrıs'ın Karpaz bölgesindeki fabrikalardan toplanmıştır. Toplanan ZDA arıtılmadan önce, korunmuş ve karakterizasyonu yapılmıştır. ZDA'daki kimyasal oksijen ihtiyacı (KOİ) ve fenol içeriği daha önce yapılan çalışmaların tespit ettiği aralıkta bulunmuştur.

Pirina, zeytin çekirdeği ve posasından oluşmaktadır. Arıtma öncesi pirina (PR) ve yapay olarak hazırlanmış magnetik duyarlı pirina (MDPR) absorbent olarak, batch ve kolon sistemi kullanılarak ZDA'nın arıtılmasında kullanılmıştır. PR ve MDPR'nin fiziko-kimyasal karakterizasyonu değerlendirilip raporlandı. KOİ ve ZDA'nın rengi, PR ve MDPR, her ikisinin değişik deney koşullarında kullanımı azaldığı kaydedilmiştir.

Bu tezdeki sonuçlar göstermiştir ki MDPR'nin kullanımının çok iyi bir performans gösterdiği ve kolayca ayrıştırdığını gösteriyor. Uygun koşullar altında batch ve kolon sistemleri ile MDPR, KOİ %6.5-%8.9 aralığında azaltmaktadır ve rengini ise %11.5-%15.4 azaltmaktadır; PR ise KOİ %14.5-%21.3 aralığında azaltmaktadır, rengini ise %27.6-%33.5 oranında azaltmaktadır. MDPR'nin defalarca kullanımı performansını

düşürmemekte, bu da amaçlanan arıtma tekniđi olarak kullanılması ve ekonomik olarak verimliliđinden söz edebiliriz.

Anahtar kelimeler: magnetik duyarlı pirina, zeytin değirmi atıksuyu, KOİ uzaklaştırma

DEDICATION

I dedicate my dissertation work to my family and many friends. A special feeling of gratitude to my loving parents, My dear father Mohsen and my mother whose words of encouragement and push for tenacity ring in my ears. My brother Younis, Sad and Ahmed, To My sisters, My fiancée and My uncle Salih have never left my side and are very special. I also dedicate this dissertation to my many friends who have supported me throughout the process. I will always appreciate all they have done, especially My best friends Dilshad Zubair, Salam & Zeyad Qwlmny and Mohammed Qasim.

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Chapter 1

INTRODUCTION

1.1 General Background on Olive Oil Wastewater

Currently, water resources are becoming inadequate to fulfil the increasing demand of fresh water globally. The concerted development of industry worldwide is a major factor causing fresh water scarcity and deterioration of the environmental quality of the available water resources ([Zagklis et al., 2015](#)). Similarly, the discharges of untreated domestic and industrial effluents into the environment have deteriorating effects on the soil and groundwater; thus, making the groundwater and soil undesirable for use ([Azbar et al., 2004](#)). The growing interest in the consumption of olive oil in the Mediterranean region has enhanced the significance of the olive oil sector recently. However, it is not new that the waters produced by the olive oil sectors contain toxic components that severely affect the environment negatively ([Ntougias et al., 2013](#)).

The olive oil is obtained from the olive fruit via various techniques (traditional, two-phase and three-phase techniques) under controlled conditions. The olive oil production process includes a collection of fruits, adequate washing, crushing the fruits, and malaxation of the olive paste, centrifugation of resultant oil, filtration and storage ([Daâssi et al., 2014](#)). In the two-phase system, the oil is separated from the solid mass leaving behind a pasty residue which is difficult to process. On the other hand, water is added to improve oil separation and recovery in the three-phase

system. Thus, vegetation and oil waters are separated from the solid phase, while the olive oil is separated from OW by decantation. Therefore, the three-phase system generates large quantities of waste and by-products including, olive pomace, filter cake, olive wastewaters (OW) and liquid by-products (Frankel et al., 2013).

The olive wastewater (OW) is the most abundant amongst these wastes; approximately thirty million litres of OW are produced yearly in the Mediterranean countries (Daâssi et al., 2014). The generated OW is characterized by a strong irritating odor, an intense dark brown to black color, high phenolic content (0.5–24 g/L), pH of 2–6, high chemical oxygen demand (COD: 40–1200 g/L) and high biochemical oxygen demand (BOD: 35– 250 g/L) (Daâssi et al., 2014; Zagklis et al., 2015). These parameters are responsible for the toxicity of the OW and severe environmental issues since the OW are routinely disposed to the soil or aqueous receptors either untreated or inefficiently treated (Paraskeva et al., 2007).

1.2 Olive Oil Wastewater Regulation in Mediterranean Regions

The European Union Waste Framework Directive (2008-98-EC) regulates the olive mill wastewater and requires members to recycle at least half of the effluents by 2020 before discharge (Komnitsas and Zaharaki, 2012). Recently, some of the Mediterranean countries have implemented strict regulation aimed at exploiting the olive oil wastes, either through the promotion of sustainable management or the conversion into useful products such as natural antioxidants, animal feed and biofuel (Kalogerakis et al., 2013).

For instance, the Italian government allows spreading of olive wastewater on agricultural soils. The Spanish government prohibits the discharge of olive wastewater

into receiving waters; however, implemented two-phase extraction technology to reduce OW. There is no specific regulation regarding OW discharge in Greece, but Italy and Greece implemented the three-phase system (Azbar et al., 2004). The three-phase technique produces pomace and OW separately while the two-phase system generates a mixture of solid-liquid waste (pomace-OW).

Azbar et al., (2004) reported that the two-phase technique could save 80% water usage as compared with the three-phase system. The common practice for the management of OW in Cyprus includes direct discharge of solids into the environment (e.g., landfills, sea or soil) or the use of evaporation ponds (Anastasiou et al., 2011). The evaporation technique results in the loss of large amounts of water, which is a limited resource in Cyprus. Likewise, the evaporation ponds create a strong and unpleasant odour to the areas due to aerobic digestion in the open air system.

1.3 Environmental Effect of Olive Mill Wastewater

Various studies have reported the environmental effect of olive mill wastewater, which extends to affect the atmosphere, soil, and water. These environmental effects are ascribed to the toxicity, high pollution load and low biodegradation of the olive mill wastewater. The environmental effects are summarised as follows:

1.3.1 Effect on Water and Aquatic Life

A significant effect of the disposal of olive mill wastewater in aquatic systems has been reported via extensive toxicity bioassays. Olive mill wastes are toxic to both aquatic organisms and microorganisms. The OWs from traditional processing mills are more toxic than those from continuous extraction (two- and three-phase) systems since their effluents are more concentrated (Ntougias et al., 2013). The olive mill

wastewater has a discolouring impact on water bodies; ascribed to the polymerization and oxidation of tannins resulting in darkly polyphenols colour. The high amount of reduced sugar in OW results in low dissolved oxygen in the water, and, a subsequent imbalance in the whole ecosystem (Ntougias et al., 2013). Similarly, the phosphates and high reducing sugars concentrations could result in eutrophication and pathogens' growth. Obied et al. (2007) reported that the phenolic components of the OW exhibit strong inhibitory effects on aquatic biota.

1.3.2 Effect on Soil and Atmosphere

After soil pollution with olive mill wastewater, a significant enhancement in soil microbial activity is noticed. The OW applications in soils (loamy) can influence the bacterial community, due to the significant amount of OW phenolics in the loamy soil (Rousidou et al., 2010). Additionally, the mineral acids in OW can inhibit the cation exchange capacity of the soil, affect the soil aggregation properties and reduce its porosity (Cox et al., 1997). Gallardo-Lara et al. (2000) reported that the introduction of olive mill wastewater to the soil reduces the concentration of magnesium in the plant, and enhances of the availability of manganese in the soil. According to Bejarano and Madrid (1992), OW application to the soil enhances the release of heavy metals to the environment.

Reports have shown that fermentation occurs when olive mill wastewater is stored in open evaporation ponds, during this process methane and other pungent gases escape from the evaporation pond, and then pollute soil and water. Furthermore, due to the suspended solid contents of OW and its high acidity, the olive mill wastewater may be highly corrosive to sewer pipes. The suspended solid contents of OW could settle into the sewer system, cause clogging and subsequent enhancement in the acidity of

the discharged wastewater due to the anaerobic fermentation of the clogged solid contents (Niaounakis et al., 2004).

1.3.3 Phytotoxicity and Genotoxicity of OW on Plants and Animals

The genotoxic, phytotoxic and antimicrobial effects of olive oil mill wastewater are attributed to its high phenolic content and some organic acids (i.e., formic acids and acetic acids) produced during storage. The OW inhibits plant growth, causes fruit and leaf abscission (Della et al., 2001; Niaounakis et al., 2004). As reported, the exposure of hamster embryo cells to catechol and phenol induced gene mutations, cell transformation, chromosomal aberrations, chromatid exchange and unscheduled DNA synthesis (El-Hajjouji et al., 2007). Similarly, phenol and catechol present in OW notably enhanced the number of kinetochore-positive micronuclei and influenced the formation of micronucleated cells in human lymphocytes during *In vitro* studies (El-Hajjouji et al., 2007).

1.4 General Treatment Processes of Olive Mill Wastewater

The OWs represent a significant environmental concern due to their bad smell, high toxicity, and notably high COD content. For these reasons, researchers need to proffer efficient, environmentally-friendly and economic treatment technologies to deal with olive mill wastes. Several treatment methodologies and management plans for oil mill wastes were proposed as briefly described and shown in [Figure 1](#).

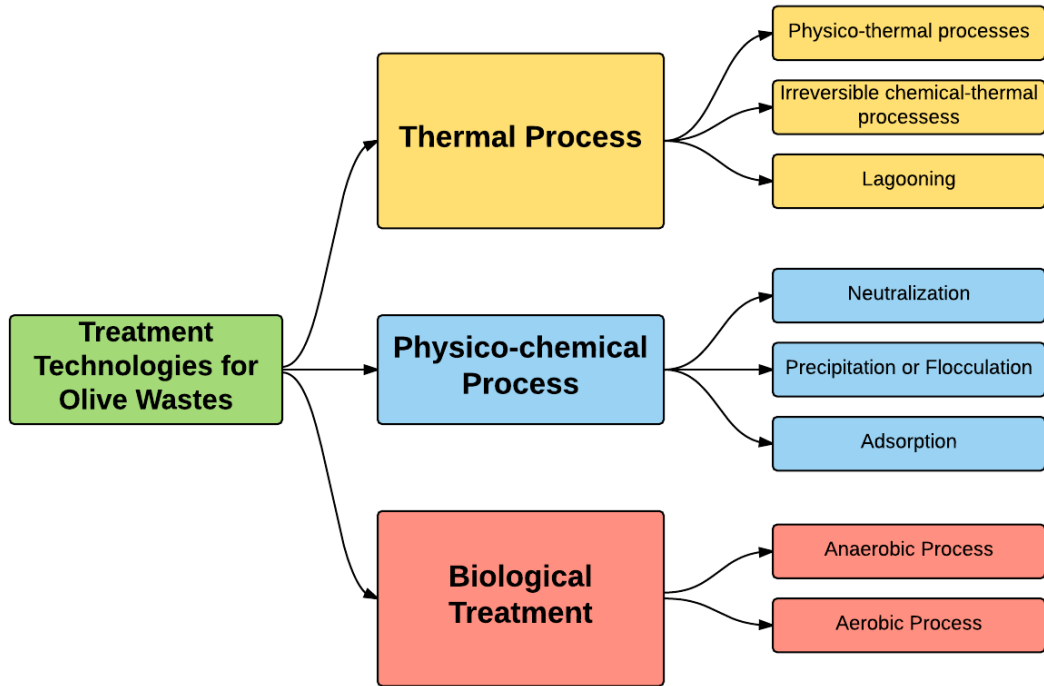


Figure 1: Broad classification of olive wastes treatment technologies

Different combinations of treatment technologies have been applied either as a pretreatment step for olive mill wastes before further treatment procedures or as a complete treatment process. The combination of processes aims at cleaning the olive mill wastes to ease the subsequent safe disposal or reuse.

1.4.1 Biological Treatment Process

The biological process is majorly based on the use of microorganism through series of microbiological procedures for the disintegration of the organic loads present in the OW. The biological treatment includes anaerobic and aerobic processes. The anaerobic process converts organic compounds present in the OW into carbon dioxide and methane. Energetically, the anaerobic process is suitable for the decontamination of OW containing high organic loads, due to the generation of methane and less sludge. However, the economic viability of the process is hindered because the anaerobic process requires further treatment, leading to additional costs.

Also, the presence of lipid inhibitors decelerates the process and hinders the complete removal of COD of the OW (Nogueira et al., 2015).

The aerobic process relies on bacteria that flourish under aerobic conditions. The aerobic processes are less attractive and produce lowly acceptable results for the treatment of OW. This may be attributed to the complexity of processes, large space requirement, high energy demand, large amounts of nutrients and excessive bio-solids generated (Niaounakis et al., 2004). Hence, the use of aerobic process commercially to attain high treatment efficiency is limited due to the aforementioned factors. However, the aerobic process can be combined with low-cost and environmentally-friendly technologies for the direct and efficient treatment of the OW.

1.4.2 Thermal Treatment Processes

There are numerous treatment techniques grouped under thermal process and these techniques all apply thermal energy (manmade heat source or by a natural source) to manage olive mill wastes. The commonly applied methods under the thermal process are lagooning, physico-thermal (evaporation and distillation) and irreversible chemical-thermal (combustion and pyrolysis) processes.

In the physico-thermal processes, concentrated solution, volatile stream (water and vapour) and volatile substances are generated. A large reduction in BOD₅ and COD is obtained via this process, and the remaining residue can be utilized as fertiliser or animal food if it is not concentrated. High energy consumption limits this process; odour issues and the low pH of the distillate that cannot be released into the environment nor reused to wash the olives before further treatment equally hampered the physico-chemical processes (Niaounakis et al., 2004). The irreversible chemical–

thermal processes are regarded as destructive techniques that limit further reuse of olive wastes. It is an effective technique, but the emission of toxic gaseous substances during the combustion and pyrolysis, the high energy demand, and expensive facilities reduces its efficiency.

1.4.3 Physico-chemical Process

This involves the use of chemical reagents to destabilise the colloidal and suspended matter of the OW and turned into an insoluble solid which will be removed easily from the waste oil. Hence, the removal of suspended solids, COD, BOD and decolorization of the OW is achieved. Among the physico-chemical processes, adsorption technique is frequently used due to its flexibility, simplicity of design, and insensitivity to toxic pollutants (Oladipo and Gazi, 2015). Hence, it is considered effective, low cost and suitable for the removal of phenolic compounds. This involves the attachment of dissolved substances (sorbate) in the polluted water to the surface of a solid material (sorbent). Various sorbent materials have been reported, and activated carbon is one of the most widely employed adsorbents.

The widely employed adsorbent for treatment of olive mill wastewater is activated carbon (Achak et al., 2009). Meanwhile, the relatively high cost and expensive regeneration system limit the use of activated carbon as economically viable adsorbent (Ozkaya, 2006). However, low cost activated carbon have been derived from various abundant and cheaply obtained bio-wastes, hence making adsorption an attractive technique for the removal of organic contents from heavily polluted wastewater (Oladipo et al., 2015).

1.5 Research Hypothesis

The research is based on the hypothesis that solid wastes generated from olive processing can be efficiently converted to magnetic materials, with high sorption capacity for discoloration and total phenol detoxification of olive mill wastewater.

1.6 Research Objectives

As mentioned, the olive mill wastewater causes severe environmental retrogressions including alteration of soil quality, discolouring of natural waters, odour nuisance and phytotoxicity. Thus, this research aims to minimise the negative environmental effects of OW in North Cyprus. The goals of this research are to:

- a) Characterise the olive mill wastewater obtained from a three-phase system in the Karpaz region of North Cyprus
- b) Prepare efficient magnetic adsorbent materials from the olive solid wastes
- c) Investigate the feasibility of the prepared magnetic adsorbents for the treatment of raw and micro-filtered olive mill wastewater by batch and column sorption systems.
- d) Establish the sorption mechanism and kinetic behaviour of the as-prepared magnetic adsorbents.

Chapter 2

EXPERIMENTAL

2.1 Reagents

A 99% (w/w) sodium hydroxide (NaOH) and hydrochloric acid (HCl) purchased from Sigma-Aldrich (Germany) were used for pH adjustment at concentration of 0.1 M. Potassium dichromate, ferric sulphate and ferrous ammonium sulphate purchased from Riedel-de Haen (Germany), were used in the preparation of magnetic adsorbent and COD calibration curve. 3,4 dihydroxy benzoic acid (97%) and 99% KOH purchased from Sigma-Aldrich (Germany) were used for total phenols and BOD determination tests.

2.2 Olive Mill Wastewater Collection and Characterization

Fresh OW was collected towards the end of 2015 from the olive mill processing plant, which is located in the Karpaz region of North Cyprus. At this mill, olive oil is produced using a three-phase system. The OW samples were collected in pre-washed tightly capped 2.0 L plastic containers, transported immediately to the Polymeric Materials Research Laboratory at the Eastern Mediterranean University and stored at approximately 5°C before analysis. The OW analyses were performed to assess its quality. The chemical oxygen demand (COD), electrical conductivity (EC), total phenolic compounds, total dissolved solids (TDS), pH, biological oxygen demand (BOD), density and total suspended solids (SS) were measured following standard methods ([Greenberg et al., 1992](#)) and presented in [Table 1](#).

Table 1: Characteristics of raw and filtered OW sample obtained

Parameter	Raw	Filtered
COD (mg/L)	7895±0.23	7456±0.88
TSS (mg/L)	898±0.77	353±0.32
EC (mS/cm)	10.52±0.45	9.91±0.23
Density (kg/m ³)	452±0.33	473±0.11
TDS (mg/L)	1753±0.64	1650±0.65
Ph	4.95±0.35	4.88±0.56
BOD (mg/L)	5671±0.22	5568±0.42
TOC (mg/L)	8956±0.45	8867±0.34
Salinity	9.7±0.65	11.1±0.81
Total phenolic (mg/L)	654±0.44	652±0.99

2.3 Preparation of Adsorbents for Treatment of OMWW

2.3.1 Preparation of Raw Olive-waste Cakes as Adsorbent

Exhausted olive-waste cakes obtained from an olive mill located in Karpaz region of North Cyprus were used as raw material for the treatment of olive mill wastewater. The olive-waste cakes (Fig.2) were washed severally with distilled water, dried at 100 °C overnight, crushed and sieved into various size fractions. The resulting material was labelled OC and used with no further treatment in the adsorption experiments.

2.3.2 Preparation of Magnetic Olive-waste Cakes as Adsorbent

The magnetic olive-cake adsorbent was prepared by chemical co-precipitation of Fe²⁺ and Fe³⁺ ions as described in our previous report (Oladipo and Gazi, 2015). Briefly, a quantity of OC (10g) was added to a freshly prepared solution of FeSO₄·7H₂O (0.25 M) and Fe₂(SO₄)₃ (0.75 M) in a 500 mL flask and continuously stirred at 30 °C for 20 min. Then, 0.2 M of NaOH was added to the mixture in a drop wise manner until a black precipitate was obtained. The precipitate was separated by filtration using an external magnet, washed severally with distilled water and dried at

100 °C in an oven overnight. The resulting magnetic material (MOC) was ground in a mill, sieved and applied for both batch and fixed-bed adsorption experiments.



Figure 2: Exhausted olive-waste cakes

2.4 Characterization of the Adsorbents

2.4.1 Bulk Density, Specific Surface Area and Magnetic Saturation

Bulk densities of the adsorbents were determined using a graduated flat-bottom container. The containers were filled with the samples, tapped severally until constant volume obtained and then weighted. The bulk densities were calculated as the ratio of the samples weights to volume and expressed in g/cm^3 . The specific surface area of the adsorbents was evaluated through nitrogen adsorption and calculated using the Brunauer–Emmet and Teller equation (Oladipo and Gazi, 2016). The magnetic saturation was determined using vibrating sample magnetometer.

2.4.2 Surface groups and Point of Zero Charge Determination

The basic and acidic groups available on the adsorbents surface were determined by Boehm titration experiments following a modified procedure in our report (Oladipo and Gazi, 2015). The basic sites were neutralized by HCl solution (0.1 N) and the total acidic sites by 0.1 N alkaline solutions (Na_2CO_3 , NaHCO_3 and NaOH) in the

presence of 1.0 g of adsorbents in 200 mL flasks. The reaction flasks were agitated at 25°C temperature for 48 h. Then, 15 mL of each suspension was withdrawn and titrated with NaOH/HCl solutions to quantify the acidic-basic sites. The pH point zero charge (pH_{pzc}) determination was performed (Oladipo et al., 2015). The experiments were performed in conical flasks (100 mL) containing 25 mL of KCl solution (0.1 M). The initial solution pH (pH_i) in each flask was adjusted (2–12) using either 0.1 M HCl or 0.1 M NaOH. Then, 0.1 g of the adsorbents was added to each flask and agitated for 24 h and allowed to equilibrate for another 3 h. The difference between the values of final pH (pH_f) and initial solution pH (pH_i) was plotted versus the pH_i . The point of intersection of the curves gave the pH_{pzc} .

2.5 Batch Adsorption Studies

A calibration curve of UV–vis absorbance at 254 nm against the COD concentration of the OW was established as shown in Fig.3. Batch adsorption experiments for COD and colour removal at various adsorbents doses (2–6g); contact time (1–24 h) and varying initial solution pH (3.0–12) at 200 rpm were performed. At pre-defined period, the adsorbents were separated via filtration or external magnet, and the residual COD concentration from the clear supernatant was analysed. Triplicate experiments performed, and average results were recorded. For isotherm experiments, 0.1g of adsorbents was added to six sets of 10 mL beakers containing a different initial COD concentration of OW at pH 5. The mixture was agitated for 24 h. The COD and colour removal efficiency R (%) by batch mode was calculated as follows:

$$R(\%) = 100 \times \frac{C_0 - C_e}{C_0} \quad (1)$$

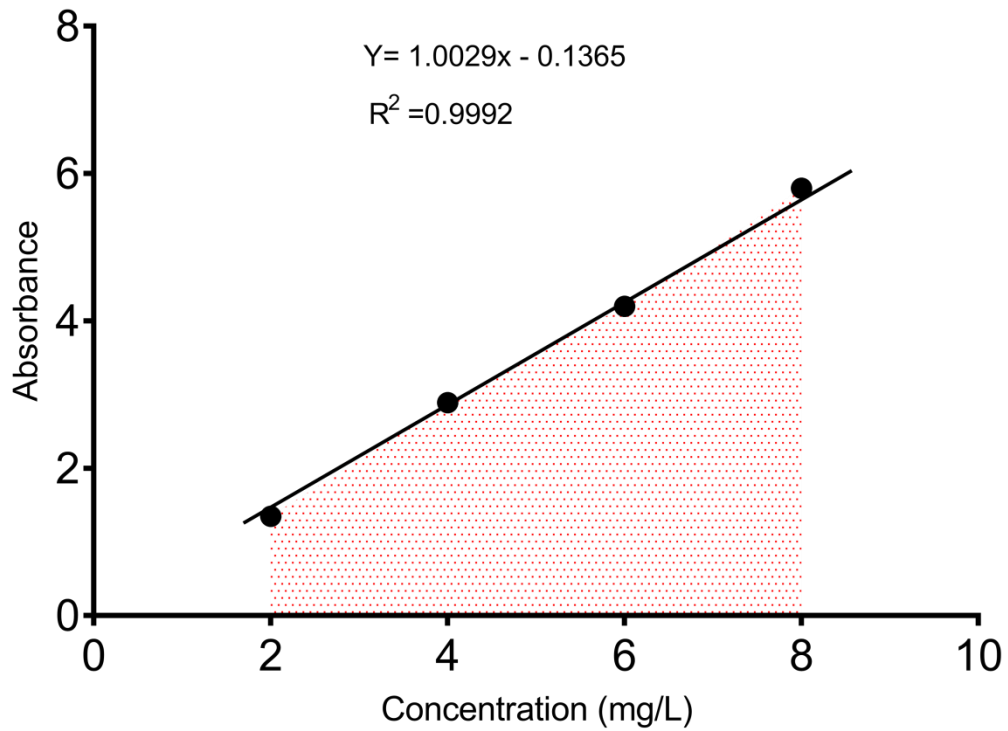


Figure 3: Calibration curve for COD and color removal

2.6 Fixed-bed Column Adsorption Studies

The continuous decolourization and COD removal of OW was achieved by fixed-bed passage made of modified injection tube of 1.5 cm inner diameter and 20 cm height. A layer of cotton of 0.3 cm was placed at the bottom of the tube to prevent adsorbents from escaping out of the tubes. Approximately 2.0 – 6.0 g of the adsorbent materials was packed in the tubes to yield the desired bed depth (2–6cm). The OW solution of pH 5 and 7456 mg/L COD concentration at room temperature was passed through the tubes at varying flow rate of 1–8mL/min. The treated OW solutions were collected at fixed time intervals, the color of treated solutions was observed and the concentration measured at the specified wavelength ($\lambda_{\max} = 254$ nm) by a spectrophotometer. The total amount of COD removed is obtained according to equation (2):

$$q_{\text{tot}} = \frac{F}{1000} \int_{t=0}^{t=\text{tot}} C_{\text{ad}} \times 100 \quad (2)$$

The colour removal efficiency is obtained according to equation (3):

$$R(\%) = \frac{q_{\text{tot}}}{M_{\text{tot}}} \times 100 \quad (3)$$

Where F is the flow rate of the OW solution (mL/min), C_{ad} is adsorbed concentration, t_{tot} is total time (min) R(%) colour removal efficiency.

2.7 Elution-Desorption and Reuse Experiments

The regeneration and reuse of the proposed adsorbents is necessary for economic and environmental benefits. Based on the fixed-bed and batch evaluations, the magnetic olive cake (MOC) is concluded to be more efficient, high sorptive capacity and easily separated after spent as compared to the non-magnetic olive cake. Hence, the desorption experiments to regenerate the MOC were performed using distilled water, 0.2 M HCl and 0.2 M NaOH. Then, the reusability of MOC was investigated by six cycles of alternating adsorption–desorption experiments with fresh OW solutions. The breakthrough curves were obtained using 1 mL/min flow rate and bed depth of 6 cm at pH 5.

Chapter 3

RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

The results of the pH_{pzc} and the Boehm titrations elucidate the surface chemistry of the adsorbents. Both OC and MOC appear to have less basic sites on their surface, and therefore considered to be acidic. Specifically, the total acidic sites present in OC and MOC were 1.15–1.56 meq/g (phenolic: 0.68–0.89 meq/g, carboxylic: 0.33–0.49 meq/g, lactonic: 0.14–0.18 meq/g) while, basic sites were 0.37–0.49 meq/g, respectively. The pH_{pzc} measurements of OC and MOC support the above finding as both adsorbents surfaces are positively charged at the acidic domain (pH below 5). The physical characteristics of the OC and MOC prepared under optimal conditions are shown in [Table 2](#).

Table 2: Physico–chemical characteristics of the adsorbents

Parameters	Values	
	OC	MOC
Ash content (%)	11.106	8.16
Bulk density (g/cm^3)	0.738	0.635
Saturation Magnetization(emu/g)	0.00	38.34
Moisture content (%)	8.67	6.33
BET surface area (m^2/g)	329.11	345.89
Micro-pore volume (cm^3/g)	0.318	0.218
pH_{pzc}	4.3	5.2

3.2 Effect of Operating Variables in Batch System

The COD is a valuable measure for assessing the organic matter in wastewater and high COD level reduce the quantity of dissolved oxygen in aquatic environments. Hence, the reduction of COD is necessary. Also, the colouring agent of OW is majorly attributed to the phenolic compounds (viz., polyphenols and phenol) present in the OW solutions (Ugurlu and Kula, 2007). Thus, various operating parameters affecting the COD and colour removal of the OW are investigated and described below.

3.2.1 Effect of Adsorbent Dosage

As the OC dosage increases from 2.0 to 4.0g, the COD removal efficiency increases from 44.5% to 55.8%; however, no significant COD removal efficiency was noticed as the OC dosage increased from 4.0 to 6.0 g. A similar trend was observed when MOC dosage increased from 2.0 to 6.0 g as shown in Fig. 4, the COD removal efficiency increased from 65% to 93%. Interestingly, about 35% increases in removal efficiency were recorded when MOC was used instead of OC. The higher COD removal efficiency noticed in MOC may be attributed to the availability of more active sites and the presence of a magnetic moiety (Fe_3O_4) on its surface as compared with non-magnetic OC (Nassar et al., 2014).

The reason for non-significant increases in COD removal when the adsorbents dosage increased from 4.0 to 6.0 g may be ascribed to the decreasing surface activities (Anandkumar and Mandal, 2012). At the same time, the colour removal efficiency increased rapidly to 83% when 2.0 g of MOC was used, then followed by slower colour removal efficiency from 90% to 96% as the MOC dose increased from 4.0 to 6.0g. The slower rate of colour removal efficiency of MOC from 4.0 to 6.0g is

probably due to adsorbent–adsorbent interactions, hence, masking the MOC active sites for further colour removal (Anandkumar and Mandal, 2012).

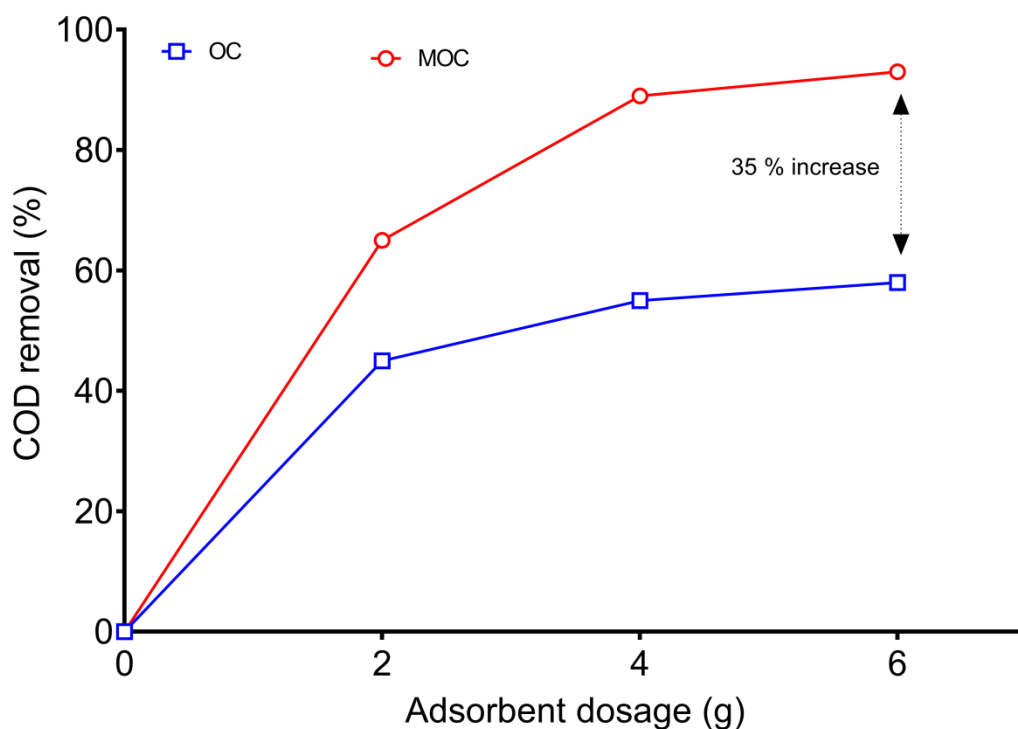


Figure 4: Effect of dosage on COD removal by OC and MOC

As seen in Fig.4, the colour removal efficiency of OC was higher than that of MOC when 2.0 g dosage was introduced into the treatment medium containing the OW effluent. Meanwhile, a significant decrease in the colour removal efficiency was noticed for OC when the dose increased from 2.0 g to 6.0g as compared with MOC. At the initial stage, some active sites were present on the OC, but these sites decrease with the increase in the adsorbent dosage probably due to masking of the already utilised site which results in a decrease in the colour removal efficiency of OC. Hence, it is concluded that 2.0g of OC is sufficient to reduce the OW effluent to about 95% while 6.0g of MOC is required to achieve same colour reduction efficiency.

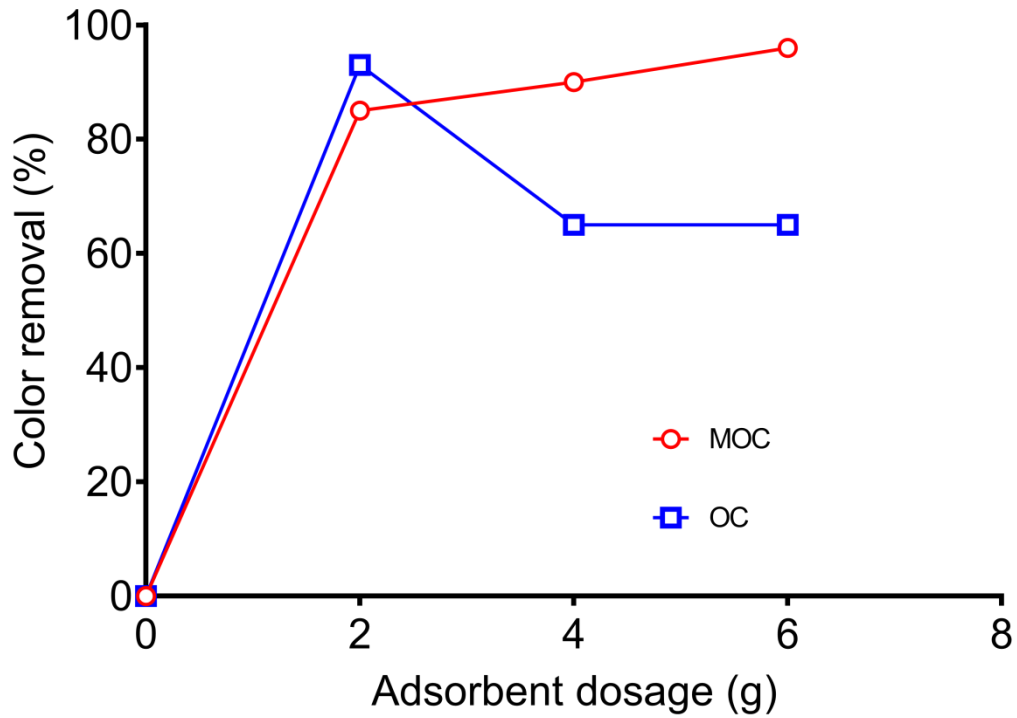


Figure 5: Effect of dosage on colour removal by OC and MOC

3.2.2 Influence of Treatment Time

The influence of treatment period on the COD and colour removal efficiency by OC and MOC are shown in Fig. 6-7. At the beginning, rapid increases in the COD removal rate was observed in the first 90 min, and then a slower rate until equilibrium was established at 120 min. The rapid COD removal in the beginning stage of the treatment process is mainly due to the presence of a large number of active sites are available for interacting with the organic ions present in OC (Nassar et al., 2014; Muthusamy et al., 2013). However, as the sorption progressed, the organic content present in the OW solution increasingly covered the adsorbent surface. Hence, after 90 min, plateauing occurs, and the adsorbents reached equilibrium within 120 min of treatment time.

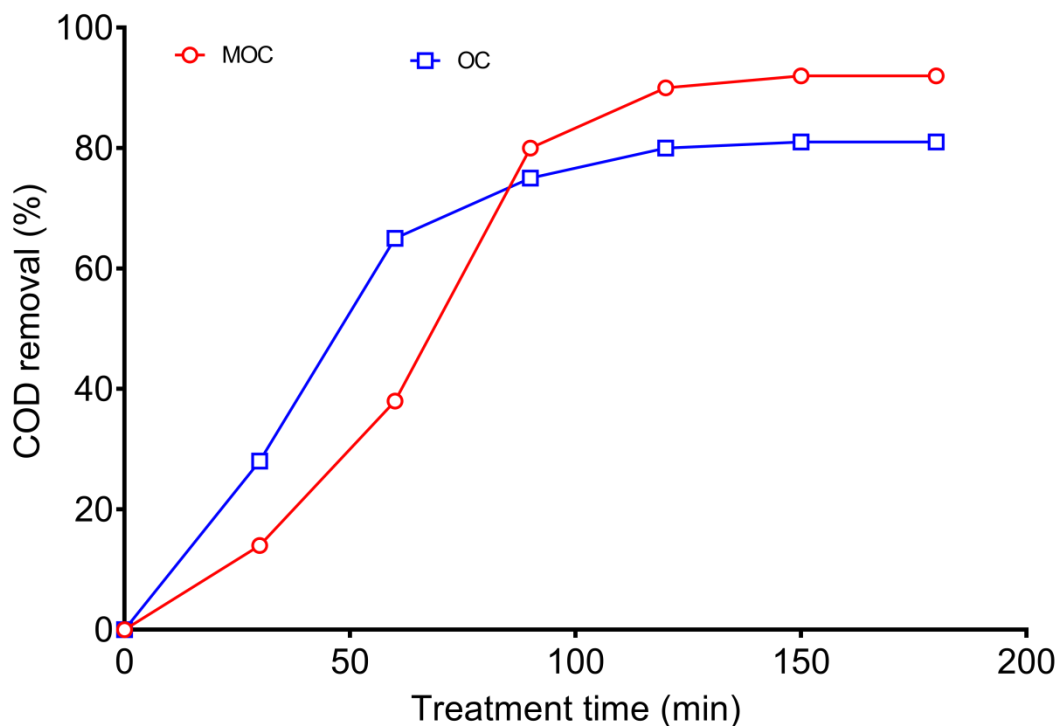


Figure 6: Effect of treatment time for COD removal using OC and MOC

It is important to stress that 65% COD removal efficiency was recorded when OC was used while only 38% COD removal was observed with MOC in the first 60 min. The COD removal rate of OC decreases with time and becomes slower compare with MOC. This simply means faster consumption of active sites of OC at the initial stage as compared with MOC. As shown in Fig. 7, rapid colour removal rates were recorded for both OC and MOC within the first 50 min and equilibrium was established just after 60 min. After 180 min, 45% colour removal efficiency was recorded for OC and increased to 95% when MOC was used in same time frame. This observation also confirmed that MOC is more robust, efficient and suitable for both colour and COD reduction in highly organic polluted effluents in addition to its magnetic separability.

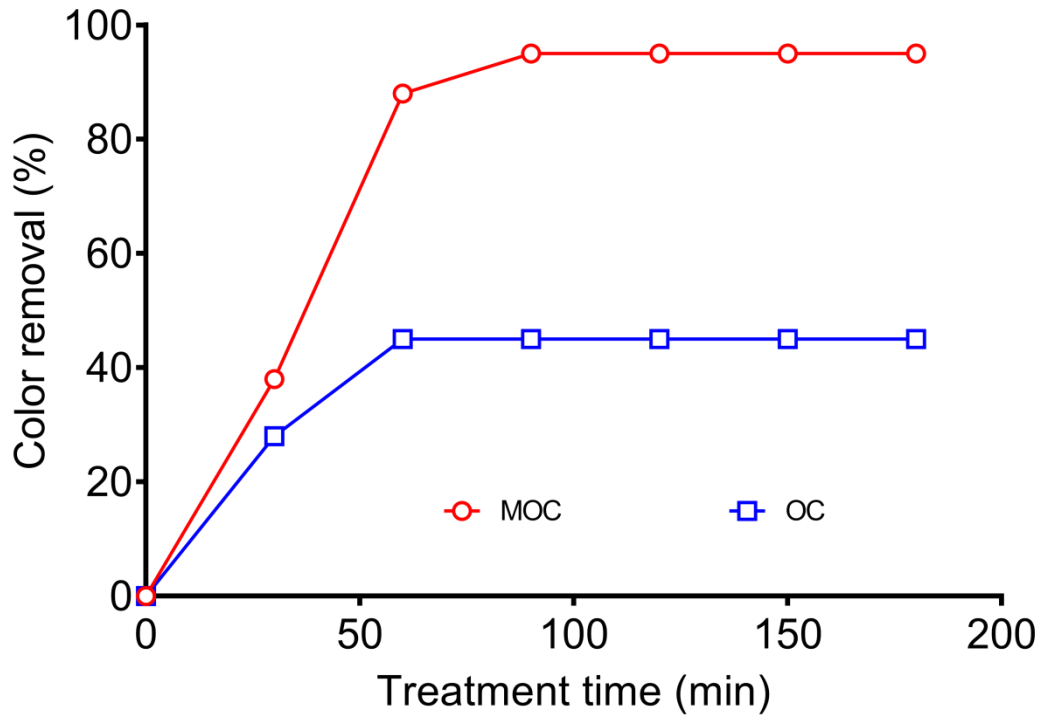


Figure 7: Effect of treatment time for colour removal using OC and MOC

3.2.3 Effect of Solution pH

The pH of the solution has considerable effects on the treatment process. Alteration in pollutants chemistry, degradation of adsorbents and protonation–deprotonation of functional groups of the adsorbents are some of the effects of solution pH (Yipmantin et al., 2011). The COD reduction by OC and MOC was observed by varying pH from 3 to 12 as shown in Fig. 8. At pH 3 (acidic domain), the COD removal for both OC and MOC was negligible. The pH_{pzc} of OC and MOC are 4.3 and 5.2, respectively. At pH below pH_{pzc} , the surfaces of the adsorbents are predominantly positive and suitable for the attraction of negatively charged phenolate ions but protons competitively dominate the race to occupy OC and MOC surfaces (Ngwabebhoh et al., 2016).

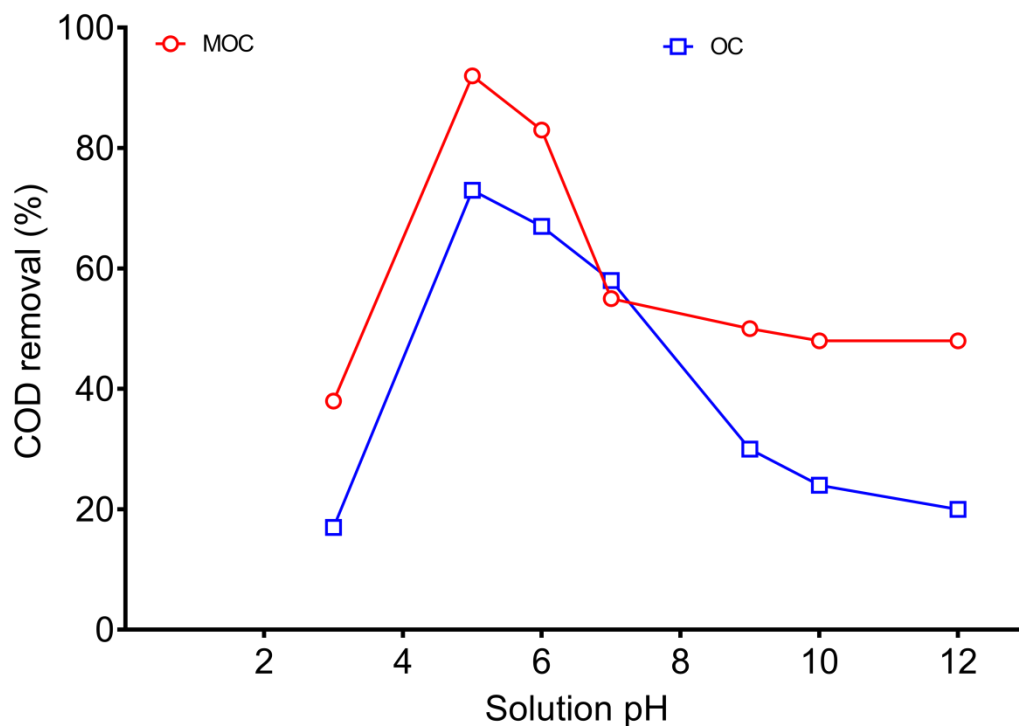


Figure 8: Effect of solution pH for COD removal using OC and MOC

A progressive increase in COD removal was noticed from pH 3 to optimum pH 5. The increase in pH between 3 and 5 lowers the electrostatic repulsion between the adsorbents surface and H^+ . Hence, an increase in COD removal was recorded. When the solution pH decreased from 5 to 8, the COD removal efficiencies decreased from 69% and 95% to 30% and 50% in the presence of OC and MOC, respectively. The reduction in COD removal efficiency is due to competition between the negatively charged adsorbents surface and the negatively charged phenolate anion (Khan et al., 2012). Similarly, 75% colour removal was observed at pH 5 in the presence of MOC while only 50% colour was removed when OC was applied as an adsorbent in the treatment of OW effluent. Beyond pH 5 (Fig. 9), negligible colour removal was recorded. Thus all other experiments were performed at pH 5.

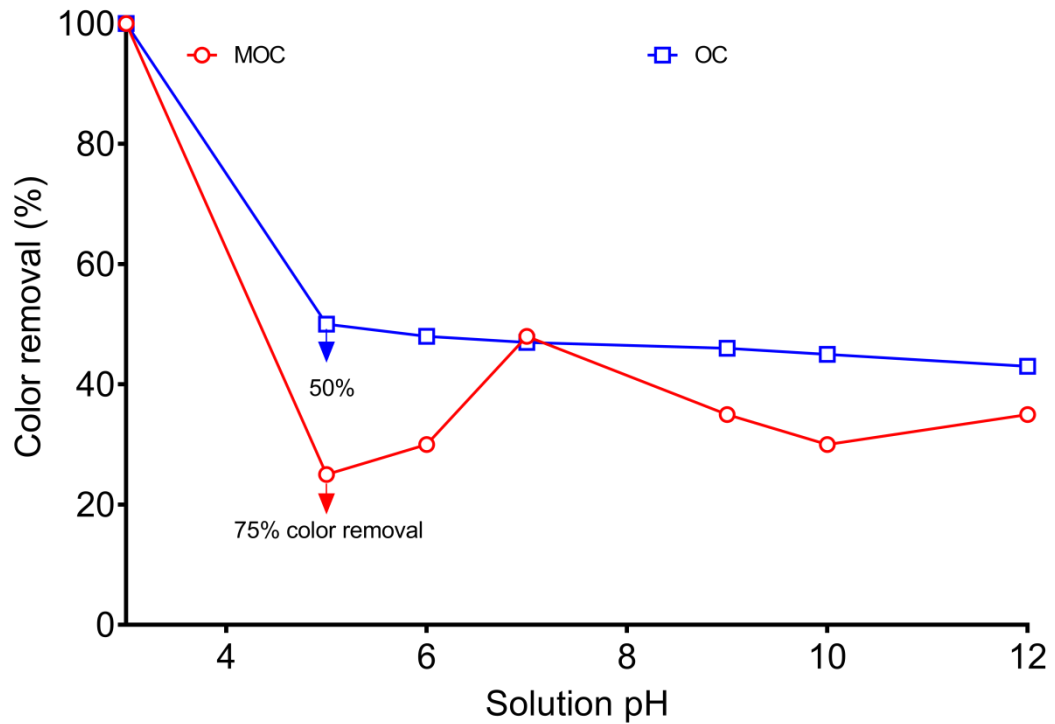


Figure 9: Effect of solution pH for colour removal using OC and MOC

3.2.4 Effect of Effluent Concentration

The OC and MOC removal efficiency as a function of initial COD concentration (100–3000 mg/L) was investigated. The COD removal rate increases with increase in initial concentration (Fig.10). The higher initial COD concentration provides a driving force to overcome the mass transfer gradient of the loaded organic ions in the OW between the medium and adsorbent phases, thus increasing COD removal (Ngwabebhoh et al., 2016).

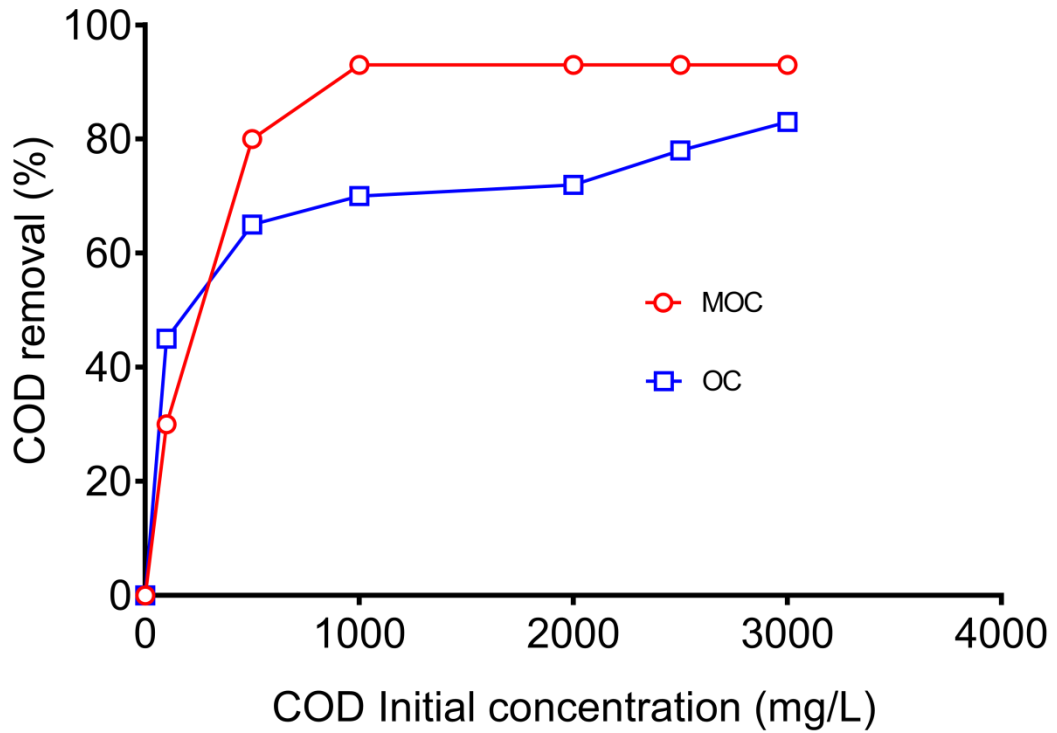


Figure 10: Effect of feed concentration for COD removal using OC and MOC

A similar trend is noticed in Fig.11; the colour removal efficiency increased rapidly as the COD concentration increased from 100 to 1000 mg/L. A further increase in COD concentration beyond 1000 mg/L showed no appreciable increase in colour removal in the presence of MOC while; the colour removal efficiency reached equilibrium at COD concentration of 500 mg/L in the presence of OC. Hence, it is concluded that MOC can be applied to treat highly polluted organic-laden effluent as compared with OC.

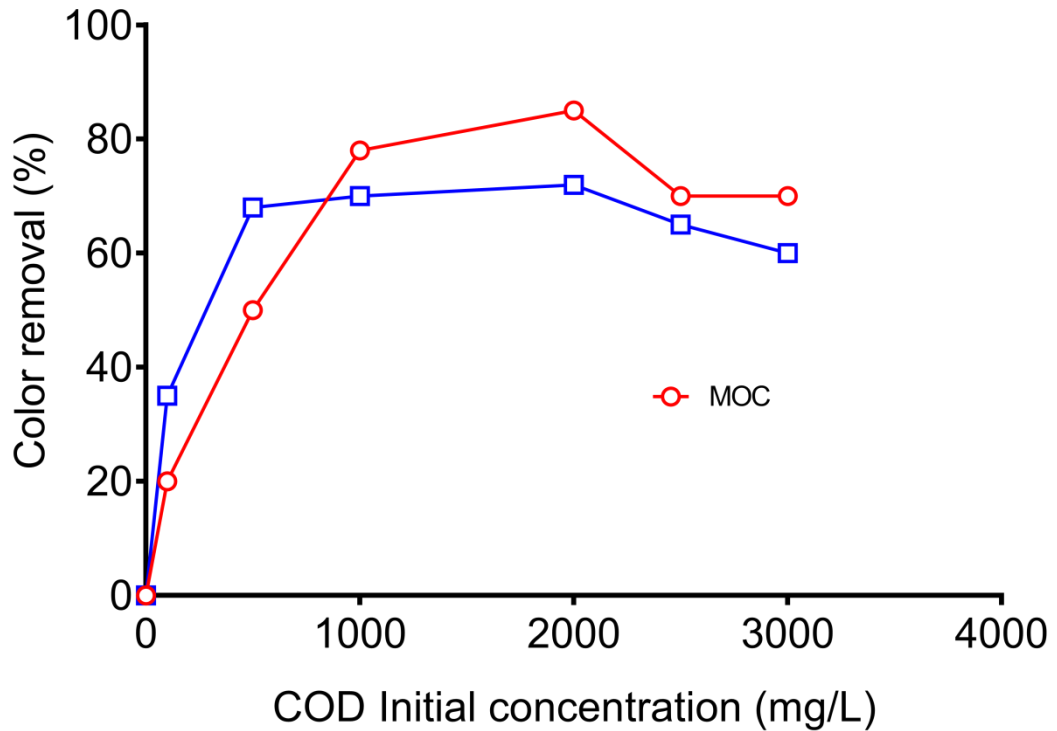


Figure 11: Effect of feed concentration for colour removal using OC and MOC

3.3 Effects of Operating Variables in Fixed-bed System

3.3.1 Effect of Bed Depth

The breakthrough curves obtained with the bed depth of 2–6 cm for COD removal are shown in Fig.12–13, while other parameters were kept constant. As observed, steeper breakthrough curves and shorter breakthrough time were obtained as the bed height increased. Moreover, longer breakthrough and exhaustion time were achieved by MOC with the increase in the bed depth as compared with OC. For instance, the breakthrough time (at $C_e/C_o = 0.15$) of MOC was 190, 60, and 27 min while that of OC was 240, 150 and 60 min for 6, 4 and 2 cm bed height, respectively. Similarly, the exhaustion time (at $C_e/C_o = 85\%$) of OC reduced from 155 to 136 min at bed height of 2 cm when MOC was used. The COD removal efficiency by OC and MOC was 77 and 83% for the bed height of 4 cm, respectively.

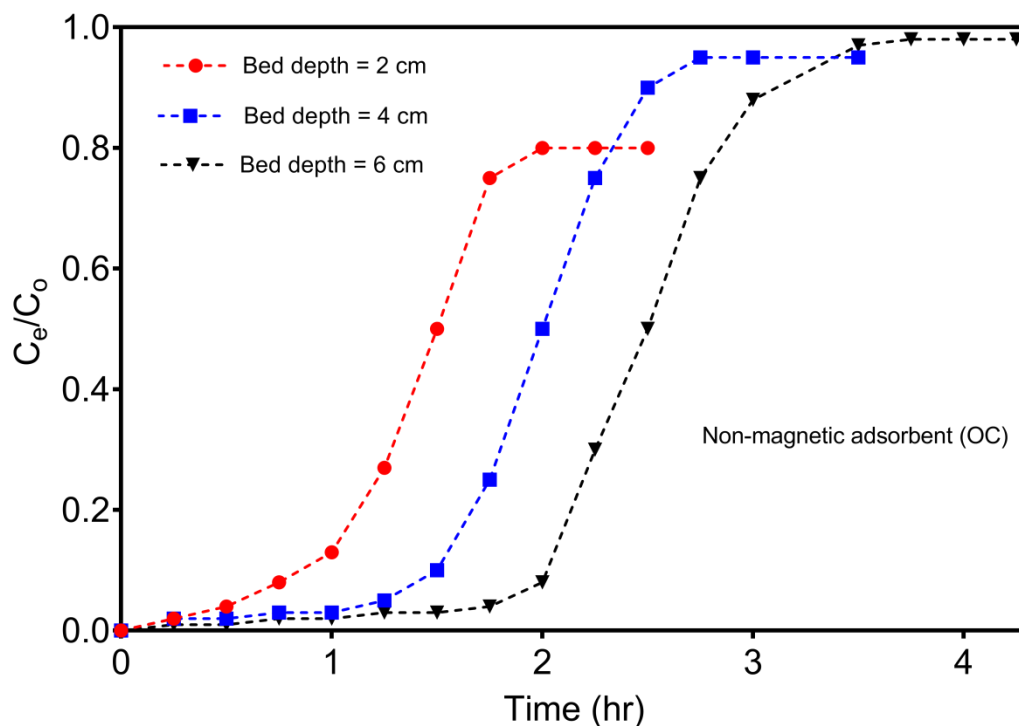


Figure 12: The influence of bed height on the COD removal breakthrough curves using OC (Flow rate; 1 mL/min, pH; 5 and room temperature)

The result suggested that the organic pollutant in the OW have enough time to interact and get transported through the MOC pores as compared with OC; hence, MOC resulted in higher COD removal. Also, the higher COD removal observed at higher bed depth is attributed to the higher adsorption sites at increased bed height. That is increases in the surface area of the adsorbents with increasing bed depths results to increased functional groups for COD reduction (Jang and Lee, 2016).

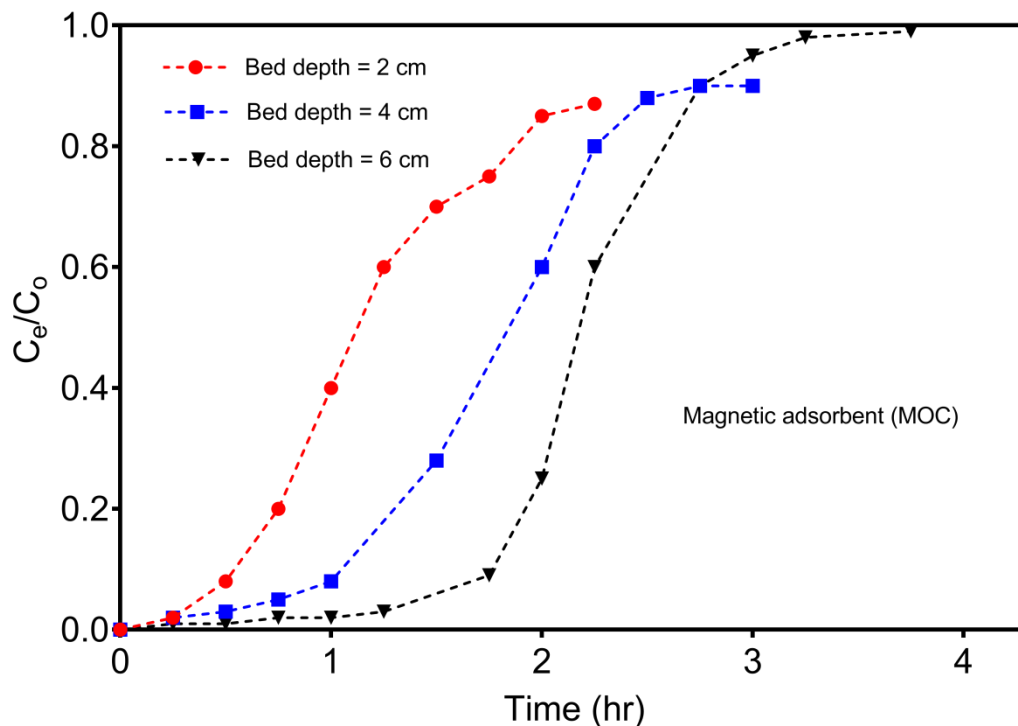


Figure 13: Influence of bed height on COD removal breakthrough curves using MOC

3.3.2 Flow Rate Effect

The influence of flow rate on the performance of MOC and OC for COD removal with a bed depth of 6 cm was evaluated. The flow rate was varied between 1 mL/min and 8 mL/min at a constant initial COD concentration of 1000 mg/L. From the OC breakthrough curves (Fig. 14), it was observed that less processing time was needed to reach the breakthrough for high flow rate. The breakthrough times were observed to be 15, 43 and 60 min for a flow rate of 8, 5 and 1 mL/min, respectively. The results showed that an increase in flow rate led to the less effective diffusion of organic ions in the OW solution through the pores of the MOC. Hence, lower COD removal efficiency was obtained (Nguyen et al., 2015).

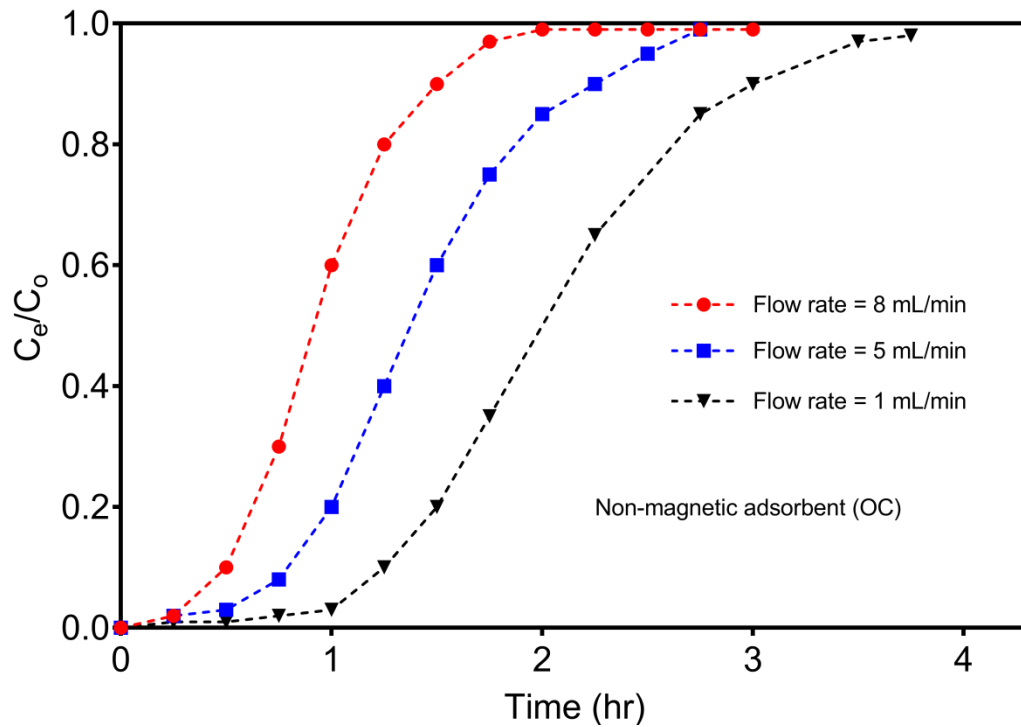


Figure 14: The influence of flow rate on the COD removal breakthrough curves using OC (Bed Depth: 6 cm, pH; 5 and room temperature)

Similarly, steeper breakthrough curves were noticed with increasing flow rate when MOC was used. This behaviour can be explained based on the fact that the organic ions in the column have less residence time to reach equilibrium at higher flow rate. Thus, the lower flow rate is beneficial for COD removal in MOC column.

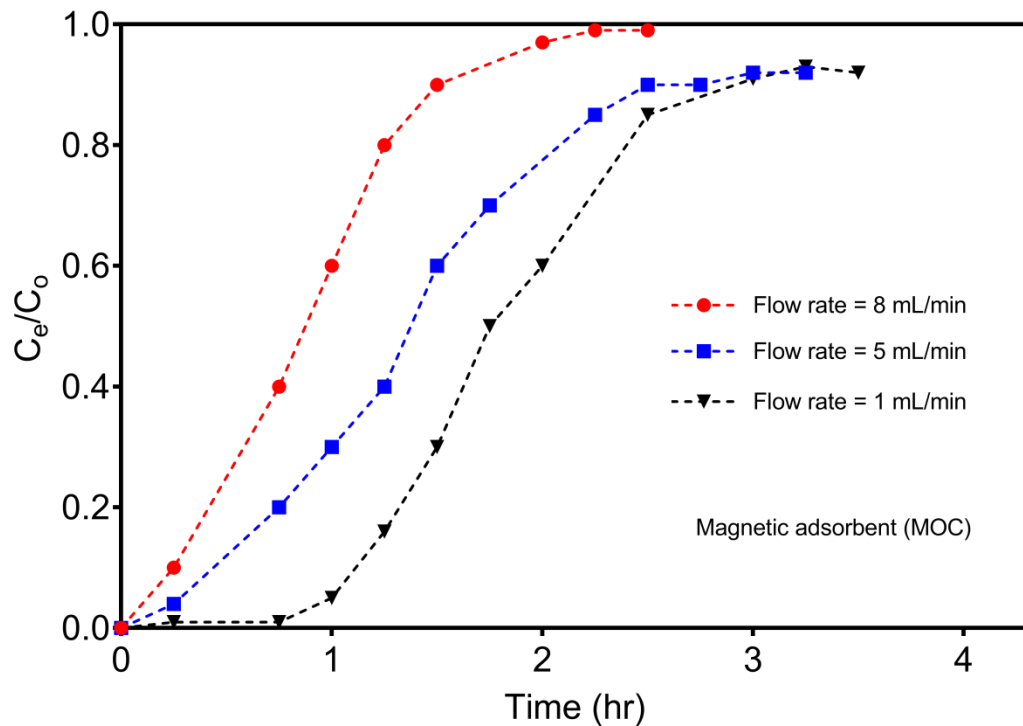


Figure 15: The influence of flow rate on the COD removal breakthrough curves using MOC (Bed depth; 6 cm, pH; 5 and room temperature)

3.3.3 Effect of Influent Concentration

The inlet concentration results to a certain gradient which provides the mass transfer driving force. Hence, to investigate the driving force, the initial COD feed concentrations were varied from 500 to 3000 mg/L using MOC or OC of 6cm bed height and feed flow rate of 1 mL/min.

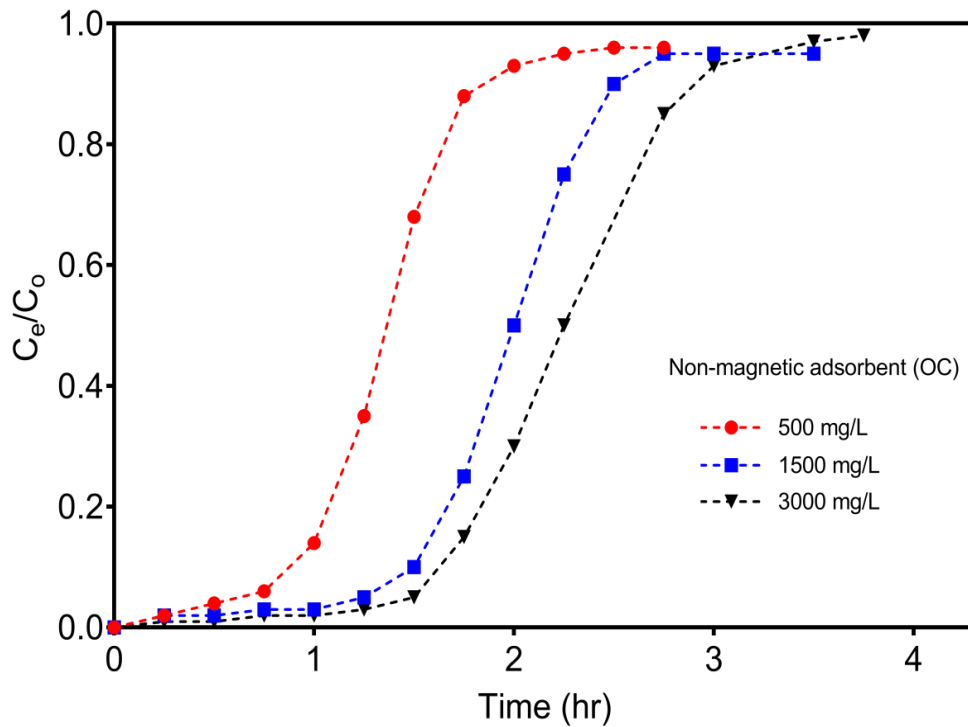


Figure 16: The breakthrough curves using OC at various COD concentration (Bed depth; 6 cm, pH; 5 and Flow rate; 5 mL/min)

As shown in Fig. 16, rapid breakthrough time was noticed at higher initial COD feed concentration. This is attributed to increased driving force of the organic ions in OW solution to overcome the mass transfer resistance in the aqueous phase. Hence, the available active sites are occupied rapidly at a higher initial COD concentration (Song et al., 2016). Conversely, a lower COD concentration results in a decreased diffusion of organic ions from the film layer to the surface of the adsorbents. Thus it can be concluded that higher COD removal was achieved with increased feed concentration for MOC and OC. However, COD removal by MOC exceedingly higher to that of OC as the feed concentration increased.

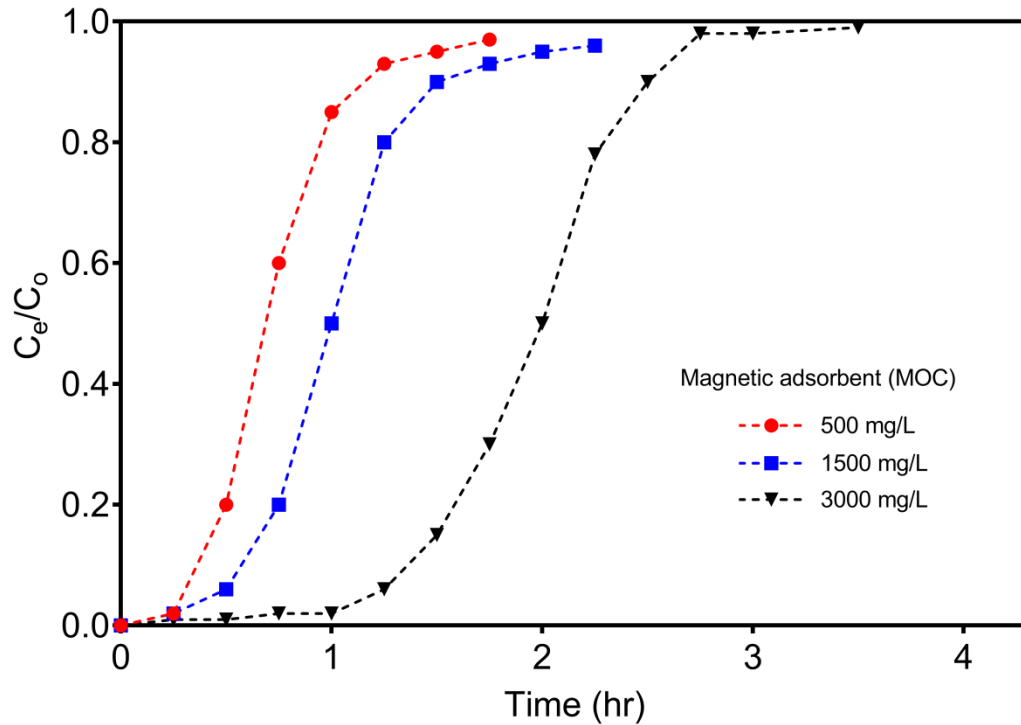


Figure 17: The breakthrough curves using MOC at various COD concentration (Bed depth; 8 cm, pH; 5 and Flow rate; 5 mL/min)

3.4 Adsorption Kinetics and Isotherms Modeling

To determine the COD and colour removal rate by OC and MOC, pseudo-first-order and pseudo-second-order model were employed to characterise the experimental data. The kinetic rate constants were obtained by the plots of $\ln(q_e - q_t)$ versus time and t/q_t against time. As tabulated (Table 3), the R^2 values of the pseudo-first-order kinetics for COD removal confirmed that this model failed to describe the sorptive process (Gupta and Babu, 2009). Meanwhile, the R^2 values of the pseudo-second-order were greater than 0.96 for both OC and MOC, and the theoretical $R_e(\%)$ agreed with the experimental values. The trend suggested that valence forces are involved in the overall rate either by exchange or sharing of electrons between the organic ions and adsorbent surfaces (Ho, 2006). Also, it is noticed that the rate constants decreased with an increase in the solution pH, which further confirmed electrostatic repulsion at higher pH.

Table 3: Pseudo-first and pseudo-second rate constants for COD removal

OC		Pseudo-first-order			Pseudo-second-order		
pH	R _e (%)	k ₁ (1/min)	R _{cal} (%)	R ²	k ₂ (g/mgmin)	R _{cal} (%)	R ²
3	18	0.031451	45	0.78	0.000866	23	0.99
5	78	0.040565	67	0.54	0.001038	80	1.00
10	20	0.053178	55	0.92	0.000637	23	1.00
MOC							
3	38	0.041652	30	0.88	0.000743	41	0.98
5	93	0.051069	76	0.91	0.001159	92	0.97
10	58	0.059579	54	0.67	0.000916	57	1.00

To gain insight into the mechanism of COD and colour removal, the experimental data are fitted into two isotherm models (Freundlich and Langmuir). The linearized isotherm equations (Song et al., 2016) are represented for Langmuir and Freundlich, respectively as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (4)$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (5)$$

Where q_e (mg/g) and C_e (mg/L) are the quantity of organic ions removed and equilibrium COD concentration at time t , respectively, and q_m (mg/g) is the maximum quantity of organic removed. K_L (L/mg) represents the Langmuir constant. The n in Freundlich equation represents the heterogeneity factor, and K_F (mg/g) is related to adsorption capacity.

Table 4: Isotherm parameters at various conditions for COD removal

Sorbent	Model	Bed height (cm)			Flow rate (mL/min)			Concentration (mg/L)		
		2	4	6	1	5	8	500	1500	3000
MOC	Langmuir									
	q_m (mg/g)	245	412	679	679	423	265	255	405	654
	K_L (L/mg)	0.19	0.22	0.35	0.43	0.25	0.15	0.38	0.22	0.12
	R^2	0.95	0.99	0.98	0.97	0.99	1.00	1.00	0.99	0.99
	Freundlich									
	K_F (mg/g)	42.5	65.6	81.9	63.8	45.6	28.3	76.3	33.9	23.9
	n	1.23	1.33	1.09	1.37	1.09	1.41	2.21	2.11	3.21
	R^2	0.95	0.96	0.99	0.96	0.98	0.98	0.99	0.97	0.99
	OC	Langmuir								
q_m (mg/g)		211	347	549	549	378	209	298	388	511
K_L (L/mg)		0.16	0.28	0.43	0.29	0.12	0.09	0.21	0.19	0.04
R^2		0.96	0.98	0.99	0.96	0.98	0.98	0.99	0.97	0.99
Freundlich										
K_F (mg/g)		32.2	55.3	68.4	71.3	34.3	11.8	89.3	53.7	9.81
n		0.89	0.99	1.78	1.45	0.96	1.33	0.71	3.23	4.45
R^2		0.65	0.76	0.84	0.88	0.76	0.91	0.83	0.75	0.84

The obtained isotherm parameters are shown in [Table 4](#). Interestingly, the treatment process follows a Langmuir type ($R^2 > 0.96$) monolayer interaction in all conditions when OC was applied. Contrastingly, the use of MOC in the removal of COD and colour from the OW solutions was described by both Langmuir and Freundlich isotherms ($R^2 > 0.95$ and $n > 1$). The good fittings of both isotherm models indicated that molecular layer and heterogeneous asymmetric interactions occurred on the MOC surface with the organic ions present in the OW solutions ([Song et al., 2016](#)). The treated samples via batch and column systems are shown in [Fig.18](#) below.

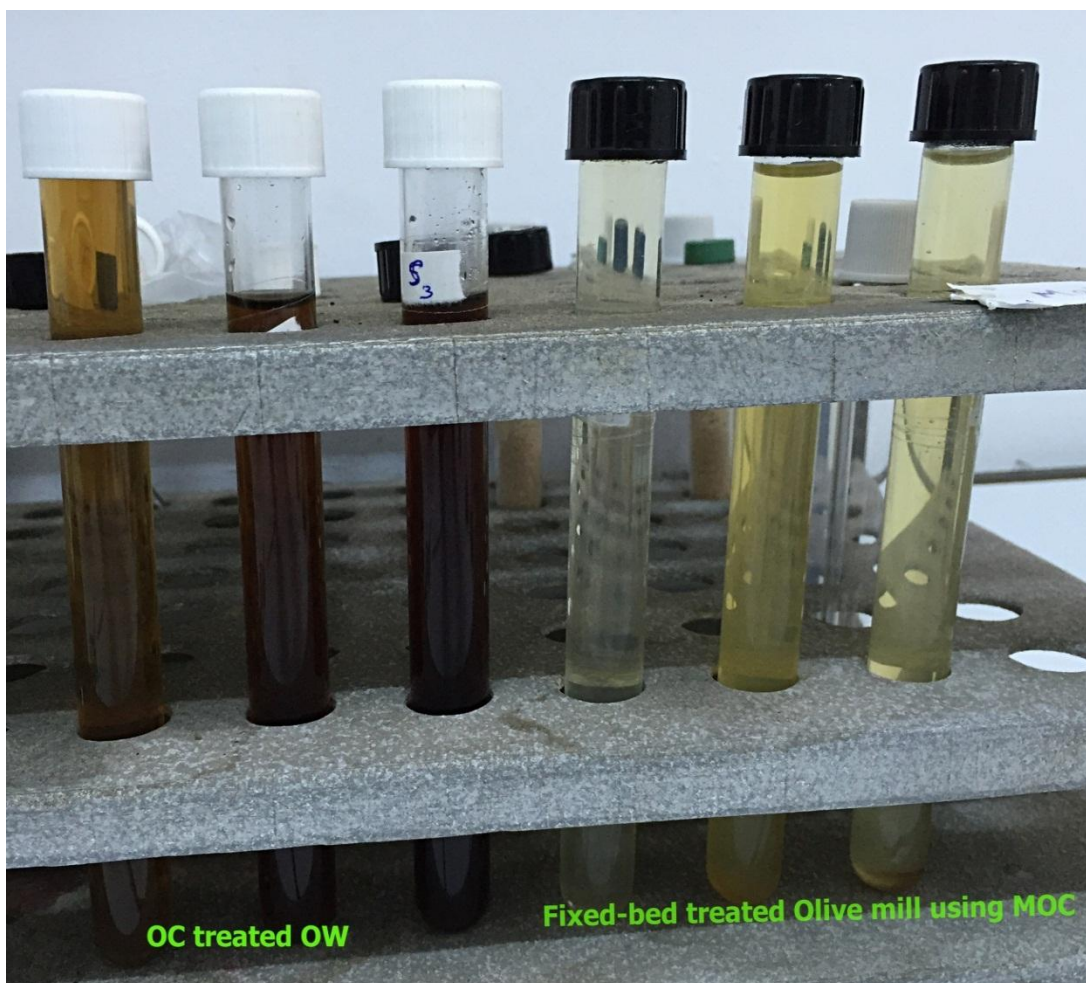


Figure 18: Fixed-bed treated olive wastewater using OC and MOC.

3.5 Desorption–Adsorption Cycles

The reusability of the adsorbents is important in practical and economic aspects. It is concluded that the MOC exhibited higher COD and colour removal than the OC according to both the batch and fixed-bed studies. Hence, the spent MOC was eluted using distilled water, 0.2 M of NaOH and HCl solutions for 12 h by keeping the bed height of 2 cm and flow rate of 5 mL/min in constant. About 83, 65 and 48% elution efficiencies were recorded with NaOH, H₂O and HCl, respectively. This may be attributed to electrostatic competition between the loaded phenolate ions and hydroxyl ions. Thus, NaOH was used for all other desorption experiments. After desorption of the organic ions, the desorbed MOC was dried at 100°C and loaded

into the pre-washed column. The regenerated MOC was then subjected to alternate desorption–adsorption cycles.

From the Fig. 19, six consecutive use-reuse experiments performed in the batch and fixed-bed modes. The COD removal rate for the first three consecutive cycles via column passage increases from 63.5% to 89.6%. The slight increase is probably due to reconfiguration and regeneration of active sites on the MOC surface by thermal treatment. However, the COD removal efficiency decreased after the third cycles. This may be due to deterioration of the adsorbent and consumption of its active sites (Oladipo and Gazi, 2014). It is important to point that desorption efficiency was comparatively higher by batch mode for the first three consecutive cycles. Afterwards, desorption was almost similar with a slight decrease from 83% to 56.4% for both batch and column mode.

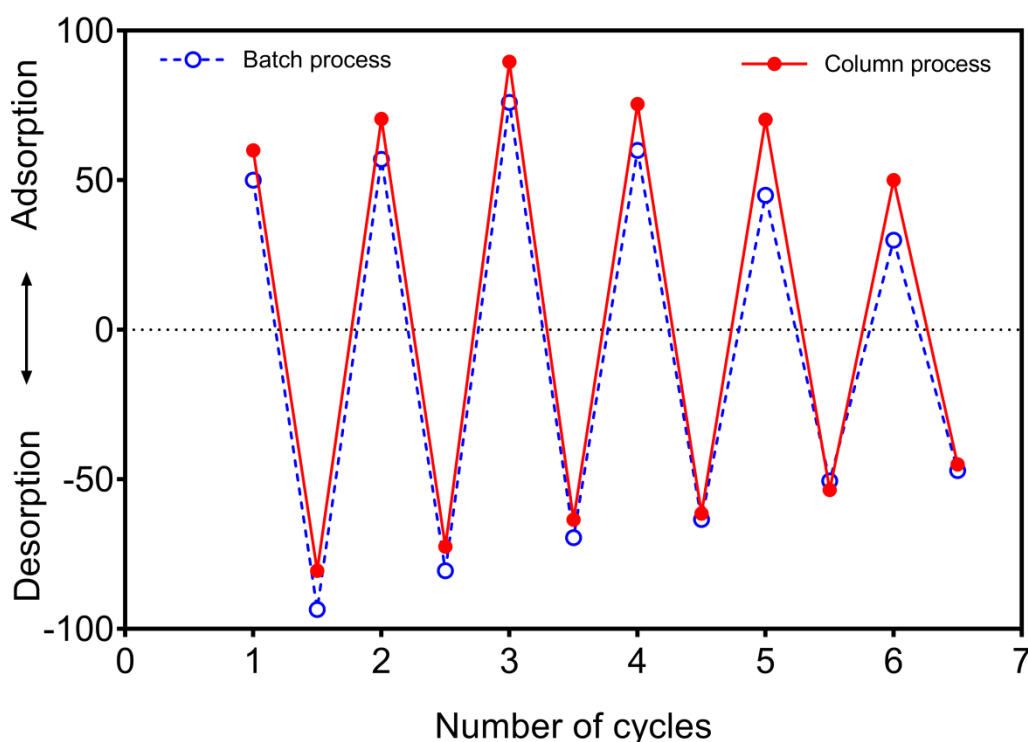


Figure 19: Desorption–adsorption studies using MOC

Chapter 4

CONCLUSION

From this research, the following major conclusions were drawn:

- Efficient magnetic responsive–olive mill solid cakes were successfully fabricated and characterised. Both magnetic (MOC) and non-magnetic–olive mill solid cakes (OC) were applied as adsorbents for COD and colour reduction from olive mill wastewater.
- The OC and MOC are efficient in a batch and column systems; however, MOC comparatively exhibited higher performance under all conditions investigated.
- The influential parameters for COD and colour removal efficiency were adsorbent dosage, pH, feed concentration, and flow rate and bed depth.
- Under optimum conditions in a batch and column systems, MOC reduces the COD to 6.5–8.9% and colour to 11.5–15.4%, while OC reduced the COD to 14.5–21.3% and colour to 27.6–33.5%.
- Langmuir isotherm suitably described the OC spontaneous adsorptive mechanism. The good fittings of both Freundlich and Langmuir isotherms in the presence of MOC indicated that monolayer and heterogeneous interactions occurred on the MOC–organic ions interphase.
- Conclusively, the fabricated MOC offers economic and environmental benefits for treatment of oily wastewaters.

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