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AGRICULTURAL WASTES DERIVED ACTIVATED CARBON FOR THE REMOVAL OF IRON FROM CAR-WASH WASTEWATER

Abstract: Over the past few decades, car-washing centres have increased due to the increase in the number of vehicles. Car-wash effluents are highly polluted with non-biodegradable, toxic, and carcinogenic heavy metals, including iron, lead, chrome, cadmium, and zinc. The focus in this study is on iron removal from car-wash wastewater due to its toxicity to the food chain, health, and environment. In comparison with the costly wastewater treatment technologies, adsorption is a widespread, simple, and cheap method that has been applied for the metal removal from car-wash wastewater. Since the conversion of agricultural waste into valuable sorbents is a renewable and eco-friendly approach, activated carbon was used in this research to assess iron removal performance from car-wash wastewater applying the adsorption technique. The impact of the following parameters: contact time (0 min to 120 min), iron concentration (8 mg/L to 14 mg/L), dose of adsorbent (0.2 g to 1 g per 25 mL wastewater), and pH (4 to 10) on the adsorption efficiency of activated carbon was studied. Fe was efficiently removed (98 %) at the optimum values of contact time 120 min, concentration 12 mg/L, dose 1 g, and pH 8, respectively. The investigated parameters (particularly dose of adsorbent and pH) need to be studied in a broader range as they did not show a potential difference in terms of iron removal efficiencies. Turbidity, TDS, and TSS were removed from car-wash wastewater after 2 hours of contact time, with removal efficiencies of 88 %, 75 %, and 55 % respectively. Effluent characteristics of car-wash stations are usually variable due to the differences in the amount of dirt from vehicles, size and number of washed vehicles, and type of used detergents.

Keywords: activated carbon, adsorption, car-wash, wastewater, iron

Introduction

The predominant effluents generated from car-wash stations are: heavy metals, grease and oil, detergents, polycyclic aromatic hydrocarbons (PAH's), and volatile organic compounds (VOC's) [1]. There can be problems associated with the discharge of metal-loaded wastewater into water bodies without treatment. These problems are: decline in the oxygen level, an imbalance in microbial activity, and death of waterborne organisms. Furthermore, the subsequent flow of metals into the sea is toxic to aquatic life, since they may accumulate at the base of the aquatic food chain, reaching later to human beings [2]. Ghaly et al. [3] reported that the iron levels from stream receiving carwash effluent were slightly high (3.21 mg/L - 3.27 mg/L), above the recommended permissible levels for drinking water. Abagale et al. [4] found that the iron concentrations were in the range of

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1.1 mg/L to 8.9 mg/L in wastewater samples collected from three different car washing bays, which were also above the allowable limits for crop irrigation purposes.

Recently, efforts have focused on the treatment of car-wash wastewater by adapting different treatment alternatives such as flotation, ultra-filtration, coagulation-flocculation, and membrane reactors [5]. For the particular removal of metals from car-wash effluent, various treatment technologies have been applied, such as ion-exchange (target metal was copper 0.018 mg/L to 0.2 mg/L) [6], reverse osmosis (target metal was zinc 0.132 mg/L to 2 mg/L) [7], and phytoremediation (target metals were cadmium 0.002 mg/L to 0.01 mg/L, lead 0.0209 mg/L to 5 mg/L) [8]. However, methods of ion exchange and reverse osmosis require high operation and maintenance costs, as well as generating toxic sludge that requires proper disposal, while phytoremediation is a slow and seasonally effective treatment method [9]. The cost of implementation, operation and maintenance, along with treatment efficiency, are important criteria for the right choice of any treatment technique. Nowadays, space is an essential criterion, as it directly affects the construction cost of treatment plants, particularly for small-scale car-wash centres, where reduced space has been adapted. For the purpose of improving effluent from the car-washing process, high effluent quality has also been regarded [10]. To comply with the current stringent regulations and to restore a safe environment, there has been an urgent need for the treatment of car wash effluent in a sustainable manner [11]. Adsorption is a surface phenomenon by which a solution of adsorbate adsorbs onto the surfaces of an adsorbent, which is highly efficient, inexpensive, and sustainable [9, 12].

It is of great importance to apply inexpensive and sustainable adsorbents, which could be afforded by using waste derived from agricultural products [13]. The use of natural adsorbents has recently been emphasised in terms of the economy, society, and the environment [14]. Activated carbon (AC) is a byproduct of agricultural waste that is derived from natural materials, and is abundant, renewable, and biodegradable. This could tackle the environmental issues regarding the direct discharge of car-wash effluents into water bodies [15-17]. Many researchers have worked with the adsorption process to remove different arrays of heavy metals from car-wash effluent using AC that is derived from agricultural byproduct wastes such as wood sawdust, hazelnut, and coconut shells (target metal was Cr) [18, 19], Eucalyptus bark and pomegranate peel (target metals were Cu and Pb) [20, 21], and granulated and powdered AC (target metals were Ni, Cd, and Zn) [22, 23]. However, an adsorption study regarding the removal of iron from car-wash wastewater using agricultural waste-derived AC has not been highlighted yet.

In this research, a batch adsorption experiment was carried out using a laboratory prepared AC as an adsorbent seeking the removal of iron from car-wash wastewater. The effects of adsorbent dosage, contact time, initial concentrations, and initial pH on the iron adsorption rate were investigated. Optimising the adsorption performance was accomplished by monitoring the influence of each factor independently, while the others were maintained at a constant level. The properties of car-wash wastewater in terms of turbidity, suspended, and dissolved solids were also evaluated.

Materials and methods

Sieve analysis

Sieving analysis of AC was performed (based on particle size) at Al-Esraa University/ laboratory of soil, according to soil classification system/ British standards (BS 5930: site Investigation). Figure 1 represents the distribution of AC grain size.

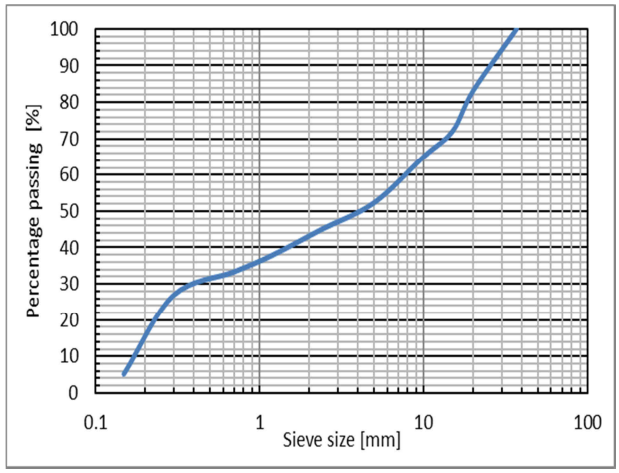

Fig. 1. Sieve analysis of AC

Adsorbent preparation

Rathi and Kumar [24] reported that utilising a mixture of adsorbents resulted in better adsorption rates than a single material adsorbent. Therefore, a mixture of waste materials (coconut shell, banana peel, eggshell, and rice husk) was used in this experiment. The mixture was obtained and washed using tap water. Then, the mixture was dried under the sun for 5 - 7 days and crushed to obtain a net weight of 300 g. The sample of the mixture was next carbonised in a furnace (LMF-G12-Labtron) at 400 °C for about 30 min and then cooled by a desiccator. The last step was drying the sample in an oven (TR4.BL-Sermac) at 105 °C for about 24 hours and re-cooling it with a desiccator. The sample of the waste-derived AC was preserved until use.

Characterisation methods of physical properties of activated carbon

The porosity of AC was estimated using the saturation method based on the amount of water added to AC divided by the total volume of the AC sample. Bulk density was determined on the basis of dry weight divided by volume of media. Both tests were performed using the Standard Test Methods for Laboratory Determination [25].

d_{60} is the diameter of AC grains, which corresponds to 60 % (by mass) of grain sizes that are smaller and 40 % that are larger. d_{10} has the grain diameters of 10 % (by mass) that are smaller and 90 % that are larger. This test was conducted according to the Standard

Practice for Classification of Soils [26]. The physical properties of AC are shown in Table 1.

Table 1

Physical properties of AC porous media

Properties	Test results
Porosity [%]	70
Bulk density [kg/m^3]	1553
Effective size d_{10} [mm]	0.18
Mean grain size d_{60} [mm]	4

Collecting and characterisation of wastewater

300 mL of six wastewater samples were collected from the top of the settling tank in a car-wash installation situated in Baghdad at different times during this study. The wastewater samples were preserved in polypropylene bottles, shipped cold, and kept at 4 °C before use. All the collected wastewater samples were analysed (Table 2) for the determination of pH, Fe, turbidity, TSS, and TDS. However, for examining the impact of initial Fe concentrations on the adsorption performance, only four samples were selected (8, 10, 12, and 14) mg/L (Fig. 3).

Table 2

Characteristics of raw car-wash wastewater

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
pH [-]	6.7	7.1	7.3	7.5	7.8	7.9
Fe [mg/L]	8	10	11	12	13	14
Turbidity [NTU]	107	155	186	220	253	274
TSS [mg/L]	222	240	307	460	490	538
TDS [mg/L]	270	345	460	600	778	803

Study of adsorption

A series of 250 mL conical flasks were filled with 25 mL of car-wash effluent and AC doses (0.2, 0.4, 0.6, 0.8, 1.0) g. The samples were agitated by shaking at a speed of 200 rpm for 120 min. The contact time and other conditions (adsorbent dose, initial Fe concentration, and pH) were selected on the basis of preliminary experiments that demonstrated the equilibrium, which was established at 2 h contact time. After this period, the suspension was filtered using Whatman filter paper No. 1 in order to separate the sorbent from the aqueous solution. Thereafter, 10 mL of the filtered solution was obtained and analysed for Fe ions, which were measured following the procedure of the FerroVer method (10249, Powder Pillows) with a HACH (DR-6000) spectrophotometer at a wavelength of 510 nm.

The experiment was repeated at a constant AC dose (1 g per 25 mL of wastewater) under various initial Fe concentrations (8 - 14) mg/L, contact time (0 - 120) min, and pH (4 - 10). All sampling was done in triplicates.

The weight of iron adsorbed by the adsorbent (q_e) was computed using equation [27]:

$$q_e = \frac{C_i - C_e}{W} \cdot V \tag{1}$$

where C_i and C_e are initial and final concentrations of wastewater [mg/L]; V - solution volume [mL]; W - weight of adsorbents [g].

pH was measured using a pocket-sized pHep HI 98107 meter (HANNA instruments). Turbidity was measured using the nephelometric method (2130 B). TSS was measured using the drying method (2540 D). The difference in weight of paper with residue and weight of clean paper dried at 105 ºC represents the total suspended solids. TDS was measured using the drying method (2540 C) based on the difference between the weight of dish with residue and the weight of the clean evaporating dish at 180 ºC.

The mass balance equation is a determined tool for calculating the adsorbent efficiency [%] [27]:

$$Removal\ efficiency\ of\ absorbent\ (\%) = \frac{Initial\ Values - Final\ Values}{Initial\ Values} \cdot 100\% \quad (2)$$

Adsorption mechanism

Three main steps are generally incorporated into adsorption on solid surfaces: firstly, translocation of metal from an aqueous solution to the adsorbent surfaces; secondly, adsorption onto solid surfaces; and finally, binding of metal ions within the adsorbent particles. Basically, the electrostatic attraction reinforces adsorption of the charged metals on the adsorbent surfaces, since metals already have a strong affinity towards hydroxyl (OH^-) or negatively charged functional groups. Particle diffusion is often the rate-limiting factor in many adsorption processes. In addition, attractive forces such as van der Waal forces, hydrophobic functions, and hydrogen connection could be implied in the metal adsorption onto the sorbent surfaces [13].

Results and discussion

Effect of time

To determine the equilibrium time for the maximum uptake of iron, adsorption on AC was studied as a function of time under laboratory conditions of Fe concentration = 12 mg/L, speed = 200 rpm, AC dosage = 1 g, and pH = 8. Figure 2 indicates that the rate of iron uptake was rapid (> 60 %) at the beginning (the first 40 min of the experiment), followed by a slow adsorption until approaching an equilibrium state (88 % removal rate) within two hours of contact time.

Based on the literature, adsorption usually requires more than one hour for the adsorbent sites to be completely occupied. Therefore, more adsorbate particles take place within the unoccupied sites after the first hour of the adsorption mechanism. This eliminates pore spaces and helps adsorbent surfaces to approach the saturation status [28, 29].

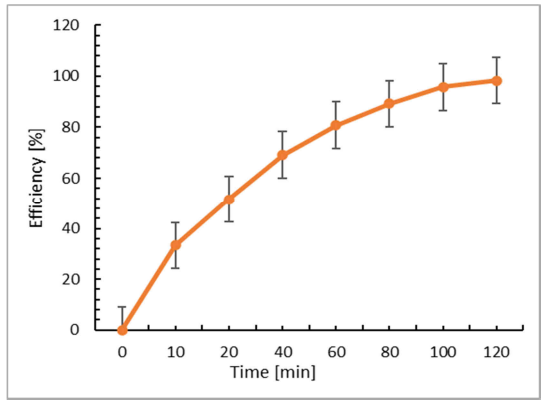

Fig. 2. Effect of time on the Fe^{+2} adsorption by AC from car wash wastewater

Effect of initial iron concentration

Iron concentrations in the raw wastewater samples ranged between 8 and 14 mg/L (Table 2). Figure 3 presents the influence of initial Fe^{+2} concentrations on the percentage removal of iron under laboratory conditions of contact time = 120 min; agitation speed = 200 rpm; AC dosage =1 g; and pH = 8. Generally, Fe adsorption efficiency (%) enhanced with increasing the initial concentrations, resulting in an adsorption capacity of (12.5, 17.5, 7.5, and 20) mg/g, respectively (Fig. 3). The reasons behind this are the expansion in the driving forces of mass transfer and the existence of unoccupied active sites [30]. However, the percentage removal of iron dropped by 14 % with the increment in the initial concentration from 12 mg/L to 14 mg/L. Agarry and Owabor [30] reported that adsorbents generally have a limited number of active sites, and at a certain concentration, the active sites become almost saturated. In this experiment, the active sites of adsorbents became nearly saturated at an initial Fe concentration of 12 mg/L, and hence the removal efficiency dropped when the iron concentration was raised to 14 mg/L. Figure 3 shows that the difference in the removal efficiency at concentrations ranging between 10 mg/L and 14 mg/L was unclear enough. Metal adsorption usually has its maximum energy sites at lower ratios of metal/ adsorbent, which sustains the adsorption capacity. Conversely, at a higher metal/ adsorbent ratio, the energy sites were almost saturated, which restricted the adsorption capacity [31].

The results also showed two-stage behaviour for the range of the studied concentrations. The preliminary stage was governed by a significant increase in the uptake efficiency owing to the accessibility of the available adsorption sites on the surface of AC, followed by the second stage, when the rate was almost constant, reflecting equilibrium at around 120 min by saturation of adsorption sites (Fig. 4).

Adsorption of iron implies the diffusion of iron molecules and their electrostatic attractions from the bulk of the solution into the solid phase (surfaces of AC). The electrostatic attractions between positively charged Fe ions and the negatively charged functional groups of AC strongly enhance the adsorption performance [28].

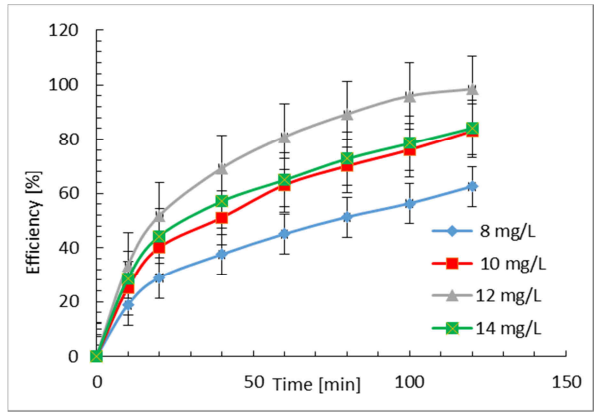

Fig. 3. Effect of Fe^{+2} concentration on removal efficiency

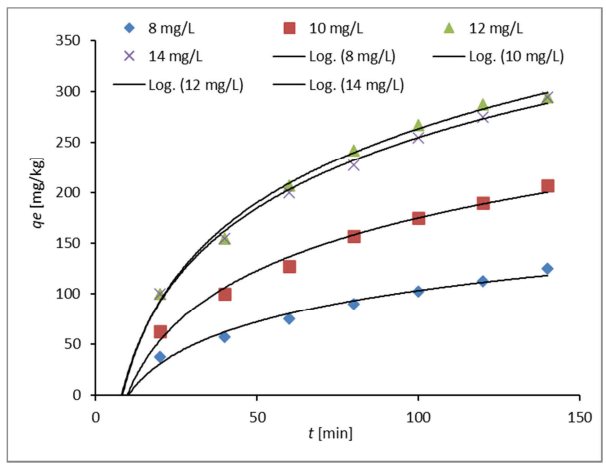

Fig. 4. Adsorption capacity over time at different initial concentrations. Regression relations are: q_e = 44.8 ln(t) – 103.1 (r^2 = 0.97) (*initial concentration* = 8 mg/L), q_e = 75.11 ln(t) – 170.78 (r^2 = 0.98) (initial concentration = 10 mg/L), q_e = 105.72 ln(t) – 223.3 (r^2 = 0.99) (initial concentration = 12 mg/L), q_e = 100.85 ln(t) – 209.58 (r^2 = 0.99) (initial concentration = 14 mg/L)

Effect of pH

The range of pH for the raw wastewater samples was between 6.7 and 7.9 (Table 2). To evaluate the effect of solution pH on Fe adsorption, the initial pH levels were adjusted to the desired values (4 - 10) using 0.1 M solution NaOH or HCL. Overall, the percentages of Fe removal increased with increasing pH, as shown in Figure 5, with an optimal removal efficiency of 98 % at pH = 8.

Titchou et al. [32] confirmed that the pH of the solution had a significant impact on the surface charge of the adsorbent and degree of adsorbate ionisation. In addition, the chemical properties of the adsorbent surfaces and the affinity of the adsorbate molecules to the adsorbent depend on the state of both materials. High to moderate pH normally sustains the negative charges on the adsorbent surfaces, which in turn promotes the adsorption

capacity. Conversely, lower pH levels encourage the existence of positive charges on the adsorbent surfaces, improving the electrostatic appeal between ions and adsorbent surfaces and hence hindering the adsorption capacity [27].

Iron removal from an aqueous solution by adsorption is highly dependent on pH, which affects the surface charge of the adsorbent, degree of ionisation, and speciation of the adsorbate [33]. At high pH values, deprotonation starts causing an electrostatic attraction between the adsorbent (negatively charged) and iron ions (positively charged), and therefore adsorption of ions is promoted. In contrast, as pH decreases, the positively charged ions might repel with AC surfaces conveying an equal charge, restricting the adsorption [11].

However, there was generally no clear difference in terms of iron removal between the applied pH levels, as the trends of iron removal were close to each other.

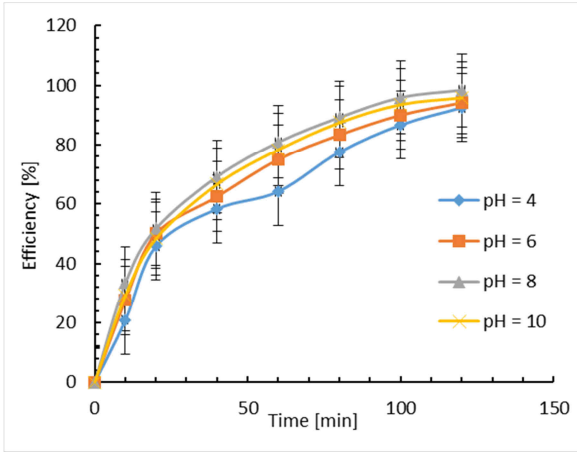

Fig. 5. Removal capacity of iron by AC at several solution pH

Effect of adsorbent dosage

Dose of the adsorbent is a key parameter for the capacity of the adsorbent to uptake the metal ions through the available binding sites [31]. In this study, the dosage of AC as an adsorbent ranged from 0.2 g to 1 g per 25 mL of wastewater at a shaking speed of 200 rpm, contact time of 2 h, and pH of 8. The percentage of iron removal increased with increasing the dose of AC, with an optimum result obtained using a dosage of 1 g per 25 mL of wastewater, where 100 % Fe was removed (Fig. 6). This is due to the accessibility of more adsorption sites, where the adsorbent dose was increased [33]. Hammood et al. [27] stated that rising the adsorbent loads created a high surface area (active sites of exchange) with greater water holding capacity and consequently sustained the adsorption efficiency. Furthermore, at the maximum adsorbent dose, ion exchange is fulfilled due to overlapping within the adsorption sites, thereby eliminating the spaces within the adsorbent surfaces for the uptake of iron and encouraging the diffusion affinity towards the adsorbent [31].

Overall, there was no clear difference in terms of iron removal between the applied AC dosages, particularly from 0.4 g per 25 mL of wastewater and up.

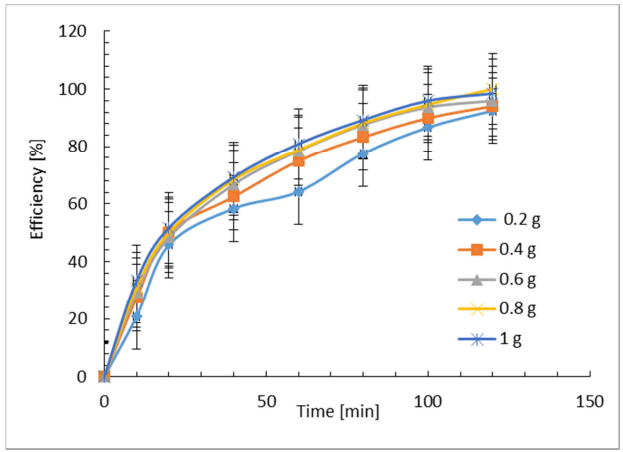

Fig. 6. Effect of AC dosage on removal efficiency of Fe^{+2}

Turbidity, total dissolved, and suspended solids

In this experiment, wastewater samples had additional tests of turbidity, total dissolved solids (TDS), and total suspended solids (TSS). Figures 7, 8, and 9 show the relationships of TDS, turbidity, and TSS respectively, with time under pH = 8, Fe^{+2} initial concentration = 12 mg/L, and AC dose = 1 g.

TDS is an indicator of the minerals and salt content in wastewater. The value of TDS is of great importance since the treated effluents are often used for irrigation purposes [34]. TDS was in the range of 270 mg/L to 803 mg/L for the raw wastewater samples. It can be seen from Figure 7 that the removal efficiency of TDS gradually increased with time, reaching 50 % during the first 40 minutes of the experiment and up to 75 % at the end of the experiment. This was in agreement with the findings reported by Baddor et al. [34], who treated oil and grease from car-wash wastewater (influent TDS = 1200 mg/L) in order to reduce sewer problems and avoid environmental pollution caused by the direct discharge of high load car-wash effluents into water bodies.

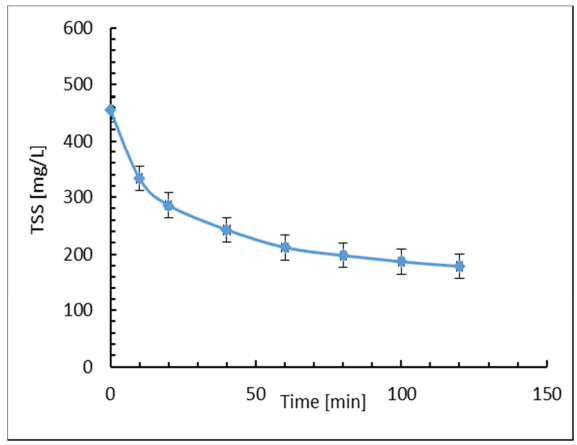

Fig. 7. Variation of total dissolved solids

In water bodies, monitoring the turbidity parameter is necessary, as it directly impedes light absorption and photosynthesis [35]. Moreover, turbidity is an indicator of the existence of suspended particles in the effluent. In this experiment, turbidity was measured to assess the removal of suspended matter. The turbidity values for the raw wastewater fall in the range of 107 NTU to 274 NTU (Table 2). It can be seen from Figure 8 that the removal efficiency of turbidity was 55 % during the first 20 min of the experiment, reaching 88 % at the end of the experimental time (Fig. 8). The high value of turbidity in the influent was due to the presence of dirt, mud, and brake particles in car-wash wastewater. These particles have a large molecule size in comparison with other pollutants, indicating that car-wash wastewater has a high concentration of total suspended solids [36].

Effluents from car-wash wastewater in Malaysia, Brazil, and Australia had a turbidity value of (275.1, 426, and 1000) NTU, respectively [11, 36, 37]. From the above data, it can be presumed that car-wash stations could have various effluent properties because of the difference in number and size of washed vehicles, amount of generated dirt on vehicles, and kind of used cleaning products.

Rubi-Juarez et al. [35] confirmed that the excess concentration of iron ions normally reacts with suspended matter to separate them from the aqueous phase over the course of adsorption.

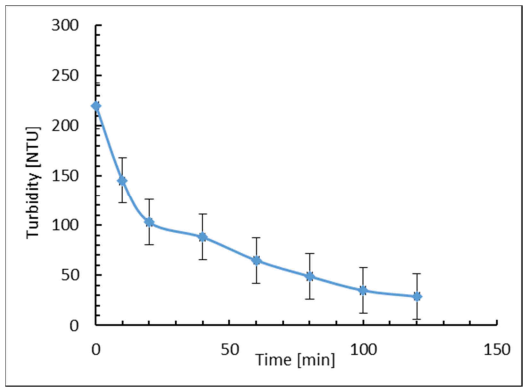

Fig. 8. Variation of turbidity

Table 3

Effluent characteristics of car-wash wastewater

Parameter [mg/ L]	Values
Fe	0.2
TDS	166
TSS	179

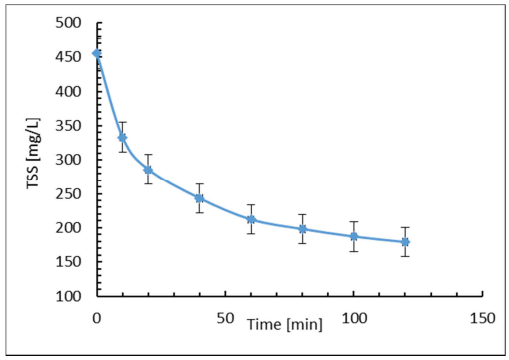

Fig. 9. Variation of total suspended solids

The range of TSS was from 222 mg/L to 538 mg/L in the samples of raw wastewater. About 45 % of TSS removal was accomplished during the first 40 minutes, approaching 55 % at the end of the experiment (Fig. 9). Similar TSS results concerning the removal of Fe from car-wash wastewater were obtained in a study conducted by Bazrafshan et al. [38], applying a combination of chemical and electrical coagulation processes to treat car-wash wastewater. TSS from vehicle-wash effluents in Malaysia and Australia were 826 mg/L and 307 mg/L, respectively [11, 37]. Table 3 shows the effluent characteristics of car-wash wastewater.

By considering three involved elements (suspended matter, adsorbent, and cations) in the TSS removal process, it can be assumed that two interaction modes are incorporated in this process: 1) cationic species react with adsorbent to capture suspended matter, causing precipitation; 2) adsorption of suspended matter onto AC (acted as nuclei or centres), creating a sweep floc mechanism and hence producing hydroxide species [35, 39].

Conclusion

The batch adsorption experiment for the removal of iron by AC (as a cost-effective and eco-friendly adsorbent) demonstrated that the process was affected by the following factors: contact time, pH, adsorbent dose, and initial concentration. 1 g per 25 mL of wastewater, 12 mg/L, 120 min, and 8, respectively, were the optimum values for approaching an equilibrium state, revealing the high affinity of AC for Fe ions.

Contact time plays a vital role since adsorption is a time-dependent process because it saves time and energy and would be beneficial in the design of an economical wastewater treatment system. Although the highest removal efficiency of iron was accomplished at the maximum value of the applied adsorbent dose, the difference in the iron removal efficiencies within the range of the applied adsorbent doses (particularly between 0.4 g and 1 g) was not clear enough. Therefore, broadening the range of the applied doses (lower and higher than the investigated range) is recommended. An initial Fe concentration of 12 mg/L ultimately sustained the iron removal rate; this effect was suppressed when the concentration was raised to 14 mg/L due to the complete saturation of the active sites of the adsorbent. Therefore, there is a need to expand the research undertaken in this study (particularly in the range of 10 mg/L - 14 mg/L) to better define the role of initial concentration in adsorption performance. A slight alkaline pH (8) was best for iron

adsorption onto surfaces of AC. However, as the influence of the studied pH range (particularly between 6 and 10) did not potentially show a difference, defining the role of pH on the iron adsorption performance requires further investigation.

Iron reacted effectively with suspended and dissolved materials for the purpose of separating them from car-wash wastewater through adsorption before disposal. Characteristics of effluents generated from car-wash centres may be vary, due to the differences in: number and size of washed vehicles, amount of dirt on vehicles, and type of utilised detergents.

Developing an economic and simple treatment option such as adsorption may offer many advantages, such as encouraging consumers and owners of car-wash stations to establish units for treatment and recycling purposes to reduce scarcity in the world and achieve the goals of sustainability. Future work on evaluating the potential of AC for treating car-wash effluents should also be considered by computing ecological and carbon footprints.

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