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Biosorption of Cationic Dyes onto Cork Stopper Particles by Inverse Fluidized Bed

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Abstract— In this study cork stopper particles is used as a low cost biosorbent to remove the cationic dyes (Methylene blue (MB), Malachite green (MG), and Methyl violet (MV)) from simulated wastewater. Continuous experiments were studied in a laboratory scale in inverse fluidized-bed packed with cork stopper particles for removal these dyes. A set of continuous mode experiments was carried out in inverse fluidized bed column to study the effect of flow rate (10, 15, 20 l/h), bed depth (5, 10, 15 cm), and influent concentration (10, 20, 30 mg/l) on the performance of biosorption process onto cork stopper particles. The minimum inverse fluidized velocity was calculated and it was found to be 8 ×10-5 m/s. The results indicate that cork adsorbs dyes efficiently and can be used as a low-cost alternative for the removal of cationic dyes in wastewater treatment.

Keywords— Dyes, Continuous mode, Fluidization, Inverse fluidized bed, cork stopper particles, Methylene blue, Malachite green, Methyl violet.

1. Introduction

Surface water pollution by contaminates is common in highly industrialized countries due to direct discharge of industrial effluents water bodies or by precipitation of air borne contaminates into surface waters.""Of the pollutants released along with industrial effluents, dyes are the most easily detected since dyes are inherently highly visible, meaning that concentrations as low as 0.005 mg/l will capture the attention of the public and the authorities [24].""Away from the aesthetic problems caused by dyes, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water, which interferes with the growth of bacteria to levels insufficient to biologically degrade impurities in the water"[3]. "Colored effluents can cause problems in many ways: dyes can have acute and chronic effects on exposed organisms depending on the exposure time, and dye concentration; dyes absorb and reflects sunlight entering water and thus can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants [31].""The vast majority of these dyes are synthetic in nature and are usually composed of aromatic rings in their structures, making them carcinogenic and mutagenic [21], inactive and non-biodegradable when discharged in to waste streams [16]." Major research has been undertaken to develop new promising materials for dye removal. Malachite green ($C_{23}H_{25}ClN_2$, 364.91 g/mole, 614 nm) is a green crystal powder with lustre, highly soluble in water. "It acts as a respiratory enzyme poisoning fish. It decreases food intake, causes damage to liver, kidney and is infectious to skin, eyes and bones." Methylene blue ($C_{16}H_{18}ClN_3S.3H_2o$, 373.90 g/mole, 668 nm) is a dark green powder causes nausea, hypertension, haemolysis and respiratory distress [30]. "Methyl violet ($C_{24}H_{28}ClN_3$, 393.95 g/mole, 590 nm) may cause irritation to the respiratory tracks, vomiting, diarrhea, pain, headaches and dizziness. Long term exposure may cause damage to the mucous membranes and gastrointestinal tract [13]."Various techniques, such as adsorption [1,20], membrane process [18], coagulation [22], flocculation [35], photodecomposition [14], electrochemical oxidation [28], etc., have been used for the removal of dyes from waste water."Among these techniques, adsorption has been proven to be the most potential one due to its flexibility, simplicity of design, high efficiency and ability to separate wide range of chemical compounds"[7]. Optimization of adsorption methods should be carried out, first of all, by choosing or developing inexpensive adsorbents selective to the contaminants to be removed. "There are many factors that affect the decision of choosing an adsorbent for removal of pollutants from water such as: economical factor (cost of the adsorbent), abundance, availability, and effectiveness of the adsorbent [29].”“Various types of materials have been used as adsorbents, such as activated carbon, manganese oxide, silica gel, fly ash, wollastonite, lignite, peat, soil, alumina, rutil, geothite, hematit, bentonit, sphalerit, anatase, red mud, mica, illite, kaolinite, and clays”[2]. Cork “is the phellem layer of bark tissue that is harvested for commercial use, primarily from the cork oak. Because of its peculiar morphological structure and chemical composition, cork presents unique properties, like hydrophobicity, low density, low thermal conductivity, acoustic insulation, chemical stability, and durability”[5][12][19]. It is mainly used for stoppers in juice industry because of impermeable and compressible properties. “Cork is also used as insulation material in building and space vehicles due to its low thermal conductivity [23].” Cork also used in shoes insole and adsorption of pollutants as an adsorbent [25]. “The interaction of cork with organic pollutants, which are essentially hydrophobic, can be explained by its structure, especially its aromatic domain of suberin and lignin.”Being hydrophobic itself, cork has an advantage of affinity over other natural materials for the removal of organic pollutants [10]. Cork oak represents the advantages of being "the only tree whose bark can regenerate after harvesting, making cork a true eco-friendly material, as it is a renewable resource [11]. The aim of this research was to study the biosorption removal of MB, MG, and MV dyes from simulated wastewater by using cork stopper particles as in the continuous inverse fluidized bed.

2. Materials and Methods

2.1 Preparation of cork stopper particles

“The cork stopper particles used in this study was obtained from local markets. The collected biomaterial was extensively washed with tap water to remove soil and dust. Distilled water was used to wash the cork stoppers and dried in an oven (Type BBDE; S/N 20-601148, Korea) at 80°C for 10 hours.”Dry biomass was cracked and grinded. The product was sieved through a 150 and 75 µm diameter mesh.”The geometric mean diameter “is given by d_gm=(d_1 d_2)^(1/2) where d1: is the diameter of lower sieve on which the particles are retained and d2: is the diameter of the upper sieve through which the particles pass [4].”Fig.1 shows the pictures of natural biosorbent (cork stoppers) that used in this study, (a) before and, (b) after grinded and sieved to 110 µm diameter.


(a) Before grinding (b) After grinding and sieving

Figure 1: A sample of natural and grinded cork stopper particles.

2.2 Stock solution preparation

Stock solution of three cationic dyes (Methylene Blue, Malachite Green, Methyl Violet) were prepared by dissolving accurately weighed dye powder in distilled water at a concentration of 1g/l and left overnight to make the dye powder fully dissolved. Dye solution then diluted to the desired solution concentration that used for the continuous experiments.

2.3 Inverse Fluidized Bed

When the density of the particles is smaller than that of the liquid and the liquid in the continuous mode, fluidization can be attained by down flow of liquid, it named Inverse Fluidization. Considering a bed of solid particles floating on a fluid surface, when a liquid or a gas is passed at a very low velocity down through the bed of particles, the particles start to move and there is a pressure drop. Increasing the fluid velocity steadily, the pressure drop and the drag on the individual particles increases and finally the particles being more actively and get suspended in the fluid. The particles float or sink based on their density relative to the fluid/suspensions [6]. The use of low-density particles has some advantages and overcomes the problem, which occurs during conventional fluidization. Low-density particles require low fluid velocity for their expansion and hence low power requirement [17]. The advantages of using inverse fluidization as compared to a more simple packed bed of particles are a low and constant pressure drop when operating above the minimum fluidization velocity, excellent mixing between the solid particles and the liquid, high heat and mass transfer rates and an adjustable void age of the fluidized bed by changing the fluid velocity [32].

2.3.1 Applications of inverse fluidized beds"

The different applications of inverse fluidized bed are:

1. The application of inverse fluidized bed (IFB) technique in biotechnologies is one of the quite significant zones in bioreactor engineering. The different advantages of IFB lead to its application in wastewater treatments. IFB has been a powerful instrument in the treatment of

wastewater from different juice, sugar and distillery industries [6].

2. Inverse fluidization gets main application in environmental engineering for wastewater treatment and in biochemical processes like ferrous iron oxidation and aerobic and anaerobic biological wastewater treatment like treatment of juice distillery wastewater [34].

2.3.2 Minimum inverse fluidization velocity

‘The minimum fluidization velocity Umf is "an important hydrodynamic Parameter involved in the design of this type of system’. “It is defined as the lowest superficial velocity at which the downward weight of the particle because the "downward flow of the liquid just counters the upward buoyancy force of the solid particles, i.e., the net upward force is equal to the net downward force [9].” A classical well-known correlation for predicting U_{mf} in a conventional fluidized bed was introduced by [33].

$$Re_{mf}=\sqrt{33.7^2+0.0408Ar}-33.7 \qquad (1)$$
$$\text{for} \quad 0.4 < Re < 500$$

$$Ar=d^3_p\,(\rho_l-\rho_p)\,\rho g\,/\,\mu^2 \qquad (2)$$

Where:

$$Re_{mf} = U_{mf}\rho d_P/\mu \qquad (3)$$

Where: Re_{mf} is Reynolds No. at $U = U_{mf}$, U_{mf} is the minimum fluidized velocity (m/s), d_p is the particle diameter (m), g "the gravitational acceleration (9.81 m/s^2)", ρ_l"the density of liquid (kg/m^3)", ρ_p "the density of solid (kg/m^3)", Ar "the Archimedes number and μ_l is the liquid viscosity (Pa.s)".

2.3.3 Continuous inverse fluidized bed experiments

“A schematic representation of experimental equipment is shown in figure (2).” The schematic representation consisted of a fluidization column, valves and piping, flow meter, water pump, and distributer.

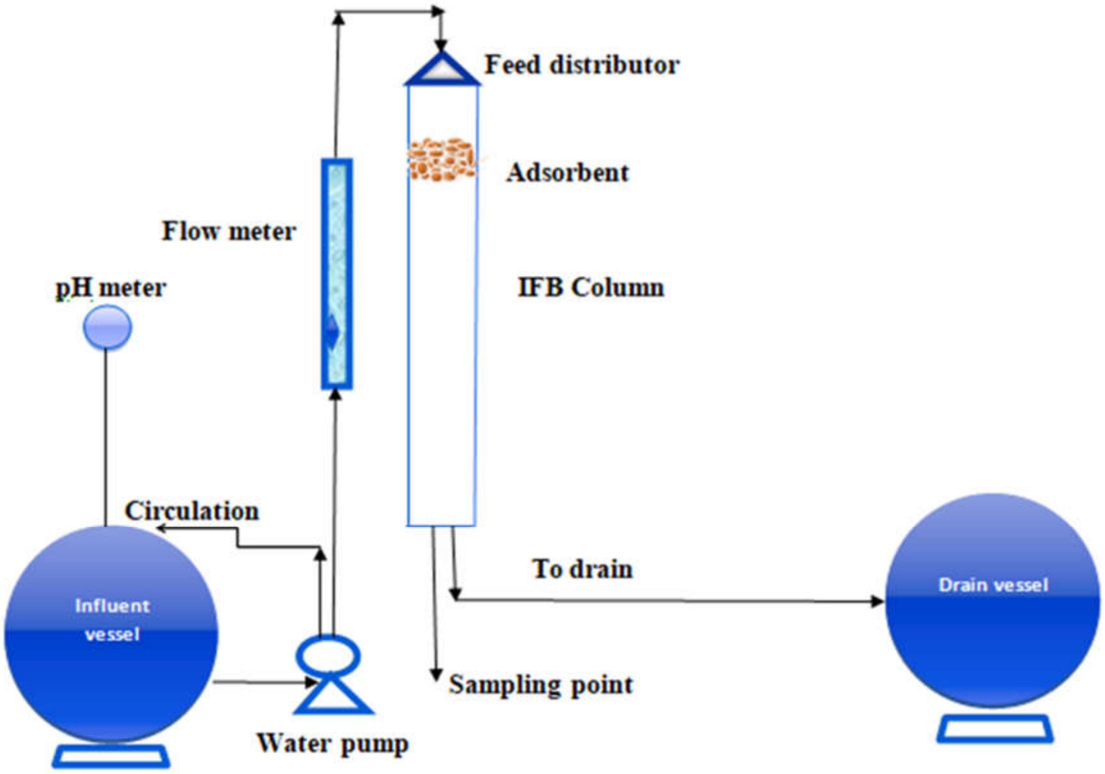


Figure 2: Schematic diagram of the experimental setup of inverse fluidized bed.

The fluidization column was made of Perspex with an internal diameter (ID) of 0.05 m and column length of 0.5 m. P.V.C flanges, and pipes were used. A distributor was fitted at the top of the fluidized bed to ensure unified distribution. The flow of effluent water was adjusted by ball valves, and flow readings were measured by Q.V.F. glass flow meter type NIHONTOKUSHU KEIKI SEISAKUSHO for the range between 6 and 90 l/h. Centrifugal pump type NO.0904 (Model SMKF/1) of 40 l/min was used to feed the influent solution from feed container to the adsorption column. A solution was circulated to the feed container to achieve constant through up.

3. Experimental procedure

Column experiments were achieved to measure the break through curves for MB, MG and MV. Experiments were carried out at various initial concentrations (Co), flow rates (Q), and bed depths (L). The experimental conditions were summarized in Table (1). The experimental procedures for column system experiments were as follows:

- Cork stopper particles were placed in the adsorption column for the desired bed length.
- Synthetic wastewater at the desired concentrations was prepared in the feed vessel, using distilled water.
- pH value of the solutions was adjusted in the feed container and continuously measured. The solution was circulated via the centrifugal pump to achieve homogeneous solution.
- Synthetic wastewater was pumped to the adsorption column through the flow meter at the required flow rates.
- Samples were taken at constant time intervals, to measure the remaining concentrations of dyes.
- Breakthrough curves were plotted for effluent concentration (Ce/Co) versus time (t).

Table 1: Experimental conditions in continuous system.

Biosorbent	Cork stopper particles
Adsorbate	MB,MG,MV
Bed Depth, cm	5, 10, 15
Flow rate, (l/h)	10, 15, 20
Initial Concentration(mg/l)	10, 20, 30
Particle size, mm	0.11

4. Result and discussion

4.1 Breakthrough curves for MB, MG and MV dyes using inverse fluidized bed

Breakthrough curves for the biosorptions of MB, MG, and MV onto cork stopper particles"in inverse fluidized bed were obtained. The biosorption process was conducted at different flow rates, bed depths, and initial concentrations.

4.1.1 Minimum fluidized velocity

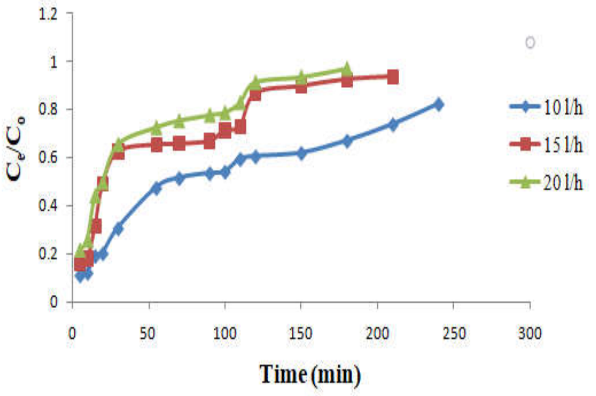
"Minimum fluidized velocity in continuous experiments was determined using equation (3) and it was 8*10-5 m/s (minimum flow rate = 0.576 l/h). The minimum fluidization velocity (Umf) depends upon the density of particles. As the particle density decrease, the upward buoyancy force increase and a higher downward force (that is liquid flow rate) is required to reach the conditions of onset of fluidization [15]."

4.2 Effect of flow rates

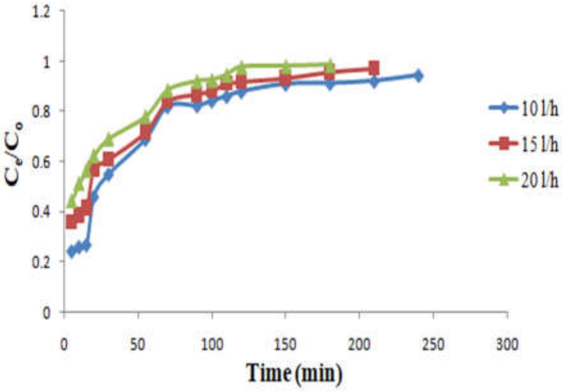
The effect of changing the volumetric flow rate was investigated. The experimental breakthrough curves are shown in figures 3 (a, b, and c) in term of Ce/Co versus time. Figure 3 (a, b, and c) show that, as the flow rates increases, the breakthrough curves become steeper. Increasing the flow rate will increase the volume treated until achieving the breakthrough point, therefore, the service time of the bed decreases. This is also, due to the decreased contact time between the solute and the biosorbent at higher flow rate. The experimental results showed that, by increasing the flow rate from 10 l/h to 20 l/h, the percentage of MB removal efficiency will decrease from 89% to 78.4% after 10 min, from 75.7% to 55.8% for MG, and from 87.8% to 64% for MV after the same time. Similar findings were obtained by [8]. "These results can be expressed as; at the Umf the expansion was homogenous and the porosity was not high, but when the flow rate increased, the porosity will increase then the surface area increase also. However, for higher flow rate the residence time will be more effective than the porosity, thus the pollutant removal will decrease. These results agree with that found by [27].

4.3 Effect of bed depth

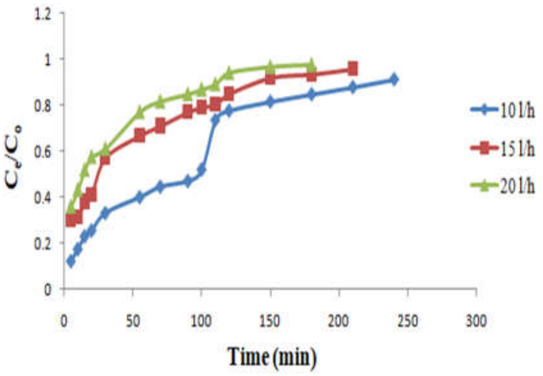
Figure 4 (a, b, and c) represents the breakthrough curves for biosorption of MB, MG, and MV respectively onto cork stopper particles at different bed depths. With increasing bed depth, the time at which an effluent concentration reached equilibrium increased. This is due to large contact time occurred between dye loaded solution and particles when the bed depth is increased. Smaller bed depths will be saturated in shorter time; this indicates that at smaller bed depth the effluent adsorbate concentration ratio increases more rapidly than that at larger bed depth. The same conclusion was obtained by [32]. In single system when the depth of the bed changed from 5 cm to15 cm the removal of MB increased from 89% to 94.84% after 5 min of operation, for MG the removal efficiency increased from 75.7% to 91.24% and from 87.8% to 94.3% for MV after the same time.



(a) Methylene blue (MB)

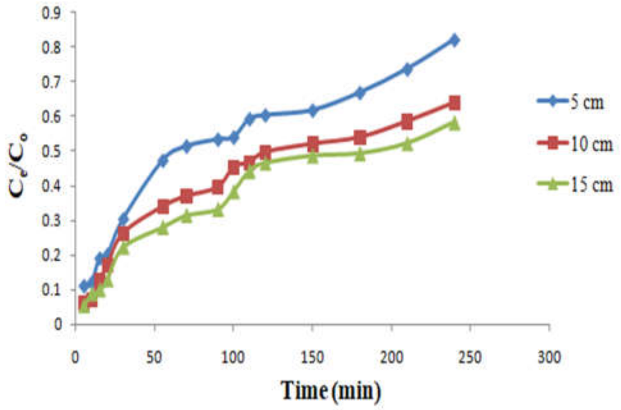


(b) Malachite green (MG)

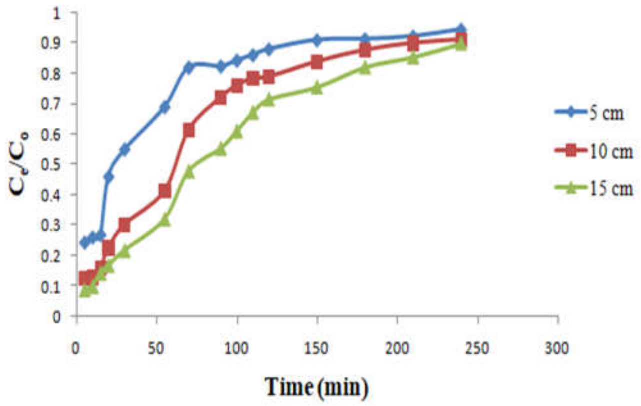


(c) Methyl violet (MV)

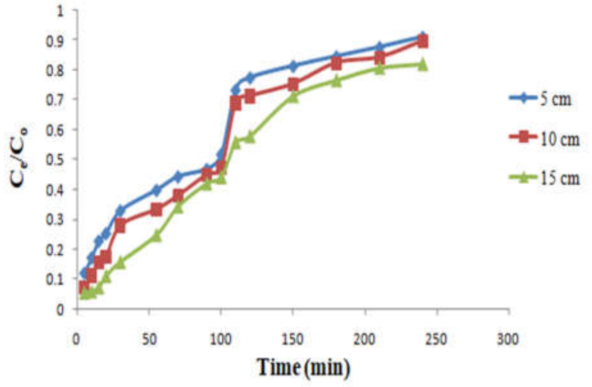
Figure 3: (a, b, and c): Experimental breakthrough curves for biosorption of MB, MG, and MV dyes respectively onto cork stopper particles at different flow rates (L= 5 cm, C_o= 10 mg/l , and pH =3).



(a) Methylene blue (MB)



(b) Malachite green (MG)

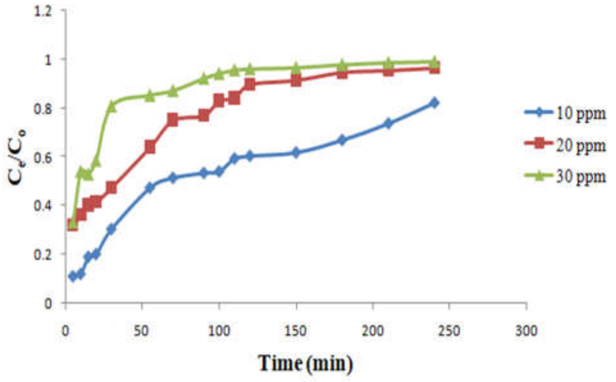


(c) Methyl violet (MV)

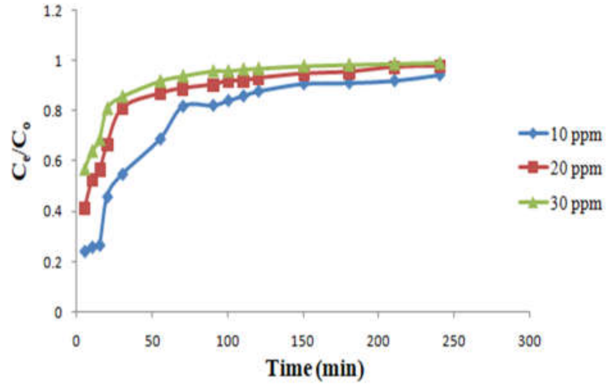
Figure 4: (a, b, and c): Experimental breakthrough curves for biosorption of MB, MG, and MV dyes respectively onto cork stopper particles at different bed depth (Q= 10 l/h, C_o= 10 mg/l and pH = 3).

4.4 Effect of initial concentration

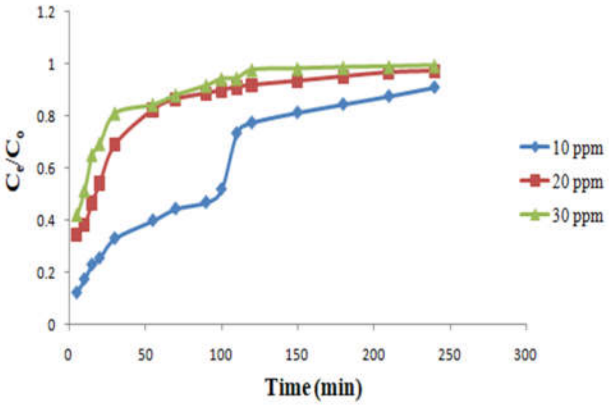
The breakpoints were associated inversely with the initial concentration , i.e. the time wanted to reach saturation reduces with increasing the inlet solutes concentration. This may be explained by the facts that since the rates of diffusion are controlled by the concentration gradient , it takes a longer contact time to reach saturation for the case of low values of initial solute concentration. The same conclusion was obtained by [26]. Figure 5 (a, b, and c) shows the breakthrough curves for biosorption of MB, MG, and MV respectively onto cork stopper particles at different initial concentrations. When the initial concentration of the dyes changed from 10 ppm to 30 ppm the removal of MB decreased from 89% to 66.5% after 5 min of operation, for MG the removal efficiency decreased from 75.7% to 43.3% and from 87.8% to 58.2% for MV after the same time.



(a) Methylene blue (MB)



(b) Malachite green (MG)



(c) Methyl violet (MV)

Figure 5: (a, b, and c): Experimental breakthrough curves for biosorption of MB, MG, and MV dyes respectively onto cork stopper particles at different initial concentrations (L= 5 cm, Q= 10 l/h and pH = 3).

5. Conclusion

In this study, cork stopper particles were used as a natural, economic, and abundant biosorbent to remove MB, MG, and MV from simulated wastewater by biosorption process. Continuous mode experiments were done in inverse fluidized bed column to study the effect of various bed depth (5, 10, 15 cm), flow rate (10, 15, 20 l/h), and influent concentration (10, 20, 30 mg/l) on the performance of biosorption process onto cork stopper particles. The experimental results showed that the breakpoint time decreases with increasing the flow rate, and it is decreased with the decreasing in bed height. The breakpoint was inversely related to the initial concentrations and the time required reaching saturation decreases with the increase of the inlet solute concentration. Minimum fluidized velocity in continuous experiments was determined and it was $8*10^{-5}$ m/s (minimum flow rate = 0.576 l/h).

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الامتزازالحيوي للأصباغ القاعدية باستخدام سدادات الفلين بواسطة عمود التمييع العكسي

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الخلاصة – يعرض هذا البحث إمكانية استخدام سدادات الفلين كمادة مازة لإزالة الاصباغ القاعدية (المثيلين الأزرق، الملكيت الأخضر، والمثيل البنفسجي) من المحاليل المائية. وأجريت تجارب الامتزاز للنظام المستمر في نطاق المختبر بواسطة عمود التمييع العكسي. تم القيام بسلسلة من التجارب في انبوب التميع العكسي لدراسة تأثير تغيير كل من معدل الجريان (20, 15, 10) لتر/ساعة، وارتفاع الحشوة (5,10,51) سم والتركيزالابتدائي للملوث (30, 20,10) ملغ/لترعلى كفاءة الازالة لعملية الامتزاز الحيوي وعلى نقطة الانفصال. تم حساب الحد الادنى لسرعة التمييع العكسية وكانت قيمتها 8× 10-5 م/ثانية النتائج اوضحت ان مادة الفلين كفؤة لأمتزاز الاصباغ القاعدية كما يمكن استخدامها كمادة ذات كلفة منخفضة لازالة الاصباغ القاعدية من المياه الملوثة.

الكلمات الرئيسية – أصباغ؛ النظام المستمر؛التمييع؛ عمود التمييع العكسي؛ دقائق سدادات الفلين؛ المثيل البنفسجي; الملكيت الأخضر ;المثيلين الأزرق.