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Investigation of the removal of malachite green and copper ions by dual system using natural and biochar pea shells

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Abstract: This study aims to investigate the simultaneous removal of natural and thermally modified (biochar) pea shells, malachite green dye and copper heavy metal. Here, the removal of dye and heavy metal ions at the same time, depending on different adsorption parameters, was studied by using a dual biological system. Adsorption parameters were selected as different contact times (1-120 min), different pollutant initial concentrations (30-400 mg/L) and different adsorbent dosages (0.4-12 g/L). Also, adsorption experiments were applied to different isotherm models to reveal the structure of adsorption better. As a result of all these studies, natural pea shells have a removal efficiency 70% for copper ions and 94% for malachite green ions, while biochar pea shells have a removal efficiency 85% for copper ions and 99% for malachite green ions. Also, natural and biochar adsorbents have adapted to the Freundlich isotherm model. These results showed that pea shells could be an effective and inexpensive adsorbent for dye and heavy metal removal.

Keywords: Adsorption; biochar; copper removal; dye removal; pea shell.

1 Introduction Industrial developments in recent years have left their impression on the environmental society. The dye and heavy metals are two principal concomitant pollutants derived from many industries such as dyestuff, textile, leather, printing, paper and plastic, which continually bring about a severe environmental issue due to their high toxicity to human health (Mohan et al. 2007). Therefore it is essential to verify the water quality, significantly when even just 1.0mg/L of dye concentration in drinking water could significantly impact color and heavy metals, making it unfit for human consumption (Malik et al. 2007). Furthermore, dyes and heavy metals can affect aquatic plants because they reduce sunlight transmission through water. Also, dyes may impart toxicity to aquatic life and maybe mutagenic, carcinogenic. They may cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system (Kadirvelu et al. 2003; Shen et al. 2009). The removal of color and heavy metals from waste effluents becomes environmentally crucial because even a small quantity of dye in water can be toxic and highly visible (Chiou et al. 2004). The wastewaters containing dyes and heavy metals can be diminished; the level wanted with the physical, biological and chemical methods. Moreover, different physiochemical properties of dyes and heavy metals make the disposal of co-polluted effluent more challenging. Therefore, it is urgent to develop novel approaches to eliminate these harmful pollutants simultaneously. However, they have their inherent limitations, such as generating a large amount of sludge, less efficiency, sensitive operating conditions and costly disposal. Thus, the adsorption method is a relatively new process emerging as a potential alternative for removing heavy metals (Agarwal et al. 2017). Various efficient adsorbents, including carbon-based materials, biomass or biomaterials, minerals, polymers and metal-organic frameworks such as peat, wood, barley, rice husk, plant straw, rice bran, peanut shell, almond shell, hazelnut shell, algal biomass, fruit stones, plum kernels, banana pith, soybean, cottonseed hulls, humic acids, pea shell, corn stalk, tree bark, sugar beet pulp, leaves, green algae, activated carbon fibers and coconut have been widely employed to alleviate the ever-increasing reluctant effluent pollution.

Therefore there is a constant need to have an active process that can efficiently remove these dyes and heavy metals (Lee et al. 2006). Adsorption by agricultural by-products used recently as an economical and realistic method for removing different pollutants has proved to be efficient at removing many pollutants such as heavy metals and dyes (Adegoke and Bello 2015). As a significant class of carbon-based materials, the biomass-derived carbonaceous adsorbent is a promising adsorbing material for effective wastewater treatment due to its low-cost and easy access.

In this paper, a study of simultaneous adsorption of mixture copper (Cu) and malachite green (MG) dyes in a binary system was done using natural and biochar pea shells. The effects of the influential parameters such as contact time, initial metal and dye ions concentration and adsorbent dosages on natural pea shells' adsorption process.

2 Materials and Method

2.1 Materials Pea shells were used in the experiments. These were cut into small pieces (1-2 cm) before use. The pea shells were rinsed thrice with hot water, thrice with cold water, and dried in an oven at 105 °C for 24 hours to remove moisture content. After, they were ground and sieved for a particle size of 0.2–2.0mm.

2.2 Reagent Copper ion solutions used in the experiment were prepared by dissolving the appropriate amount of $CuCl_2.6H_2O$ in distilled water according to Standard Methods 27. All chemicals used were analytical grade reagents of the highest quality available and deionized water was used. The solutions' pH was adjusted with HCl or NaOH solutions using a WTW 330 pH-meter with a combined pH electrode.

The basic dye, malachite green ($C_{23}H_{26}ClN_2$), was selected for adsorption studies. The stock solution of 1000 mg/L was prepared by dissolving accurately weighed amounts of malachite green in 1000 mL distilled water. The initial pH of solutions was adjusted to the required value by using NaOH or HCl solutions. All experiments were conducted in duplicate and the average values were used for data analysis.

2.3 Production of biochar pea shell The sieved pea shells were passed through pyrolysis using a steel reactor under nitrogen gas flow. The pyrolysis conditions; 600°C temperature, 5°C/min slow pyrolysis speed, 1 hour standby time and under 100 mL/min nitrogen gas flow. Pyrolysis conditions were determined by testing similar pyrolysis studies in the literature and selecting average values (Qiu et al. 2018; Demiral and Şamdan 2016; Georgieva et al. 2020; Kaya et al. 2020). From placing in the reactor at 25 g natural pea shell, 6 g of biochar pea shell were obtained as dry granules.

2.4 Adsorption experiments in dye-metal binary mixtures The batch tecnique conducted the experiments in 150 ml Erlenmeyer flasks containing 25 mL of distilled water at the desired level of heavy metal ions and dye. Batch adsorption procedure was used to determine the effect of various operating conditions on the adsorption process. This was performed by the addition of 0.01-0.3 g of pea shells to 25 mL of the binary metal-dye solution at room temperature. The effects of the contact time (1–240 min), adsorbent dosages (0.4-12 g/L) and initial concentration of Cu(II) and dye ions (30-400 mg/L) were investigated. The aqueous media containing desired combinations of heavy metal ions and the dye were prepared by diluting stock solutions of Cu(II) and malachite green dye and mixing them in an aqueous solution. Before analysis, the samples were centrifuged at 8000 rpm for 10 min using a centrifuge and the supernatant fractions were analyzed for the remaining heavy metal ions and dye. All of the biosorption experiments were repeated twice to confirm the results. After adsorption, malachite green concentration was measured with a Thermo brand Aquamate model UV spectrophotometer at 620 nm wavelength. An ATI-UNICAM 929 model Atomic Absorption Spectrophotometer (AAS) was used to determine Cu(II) ions. Concentration values were read with a hollow copper cathode lamp in acetylene flame using the direct aspiration technique. The device gives the concentration value in mg/L.

According to the contact time, the removal efficiency values, adsorbent dosage and initial pollutant concentration after adsorption were calculated with the following Equation 1;

$$E\ (\%) = \frac{(C_0 - C_e)}{C_0}\ x\ 100 \qquad (1)$$

Where; E (%) is removal efficiency, C_0 (mg/L) is initial concentration, C_e (mg/L) is concentration after adsorption. Also, adsorption capacities (qe) for the adsorbents were calculated. Adsorption capacity is the amount of milligram adsorbate held per gram adsorbent and is expressed in mg/g unit.

Besides, adsorption capacities were calculated in all adsorption studies. Adsorption capacity is the amount of adsorbate that the adsorbent's unit mass (or volume) can adsorb. The adsorption capacity (qe) is formulated in Equation 2;

$$qe(mg/g) = \frac{C_0 - C_e}{m} xV \qquad (2)$$

Where; C_0 and C_e (mg/L) are the initial concentration and equilibrium concentration of dye solution, respectively, V (L) is the volume of dye solution and m (g) is the mass of adsorbent.

2.4 Adsorption isotherms In this research, to determine the mechanism of dye and metal biosorption on the natural and biochar pea shells, the experimental data were applied to the Langmuir and Freundlich isotherm equations. The Langmuir sorption isotherm is the best known of all isotherms describing sorption and it has been successfully applied to many sorption processes. Langmuir isotherm is used to describe the single-layer adsorption characteristics of the clinoptilolite. The Freundlich isotherm is an empirical model that is based on adsorption on the heterogeneous surface area.

3 Result and Discussion

3.1 Effect of contact time on dye and metal removal The contact time study was carried out in periods ranging from 1-240 minutes. Removal efficiencies of natural and biochar pea shells are shown on separate charts for malachite green and copper. Also, qe (mg/g) value, expressed as the adsorption capacity for all contact time periods, was also calculated. Figure 1 shows the removal results of malachite green dye. Accordingly, it is seen that natural and biochar pea shells provide similar removal values. Besides, the adsorption reached equilibrium very quickly with a yield of over 90%

starting from the 15th minute. In the malachite green removal study conducted by Khan et al. (2014) using activated pea shell against contact time, adsorption reached equilibrium in a concise time. They quickly achieved 80% removal efficiency at the beginning of the contact time period.

In the graph of the relationship between adsorption and contact time, the increase in percentage removal efficiency seen at the beginning occurs as a result of the high surface area available at the beginning, and it is seen that the dye and metal absorption rate starts to decrease due to the decreasing surface as the time increases. With the occurrence of saturation in the adsorbent, adsorption begins to be held inside instead of the outer surface. Due to the smaller inner surface area, the increased contact time causes the efficiency to decrease or remain constant (Yu et al. 2000).

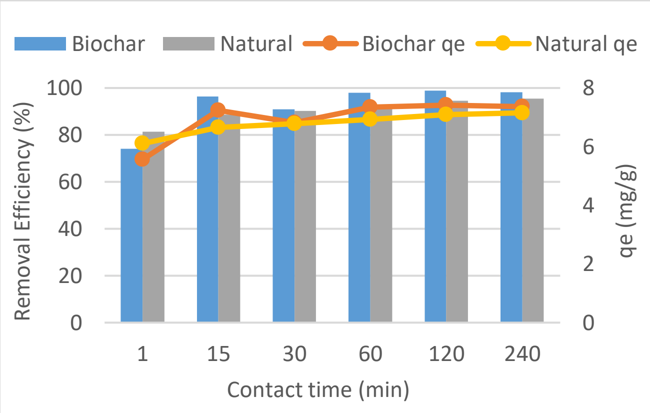

Fig. 1 Effect of contact time on malachite green removal

Figure 2 shows the copper removal results. Biochar pea shell removal efficiency is 5-17% higher than natural pea shell. The highest removal efficiency was achieved as 85% in the 30th minute with the biochar. Haq et al. (2020) obtained the equilibrium at 30 min in the contact time study in which zinc removal with the activated pea shell. After 30 minutes of up to 80 minutes, the efficiency of the removal remained around 70%. Küçükgül and Kutlu (2006), in their copper removal study against the contact time with biochar oak wood, the removal efficiency, which was around 40% at the beginning, reached the balance by increasing to 90% in the 180th minute.

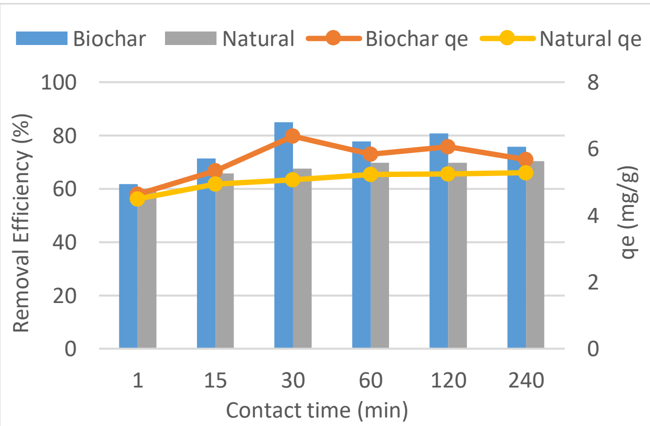

Fig. 2 Effect of contact time on copper removal

3.2 Effect of adsorbent dosage on dye and metal removal

A dosage study was carried out at adsorbent dosages ranging from 0.4 to 12 g/L. Removal efficiencies and qe values are shown in separate figures for malachite green and copper. Figure 3 shows the malachite green removal efficiency graph. According to the graph, it can be said that biochar is more effective in removal. It was observed that the removal efficiency was partially increased with the increasing adsorbent dosages. Similarly, Khan et al. (2014), in their malachite green removal study, which they performed against the adsorbent dosage using activated pea shell, showed that the removal efficiency increased from 76% to 96% with the increasing adsorbent dosage.

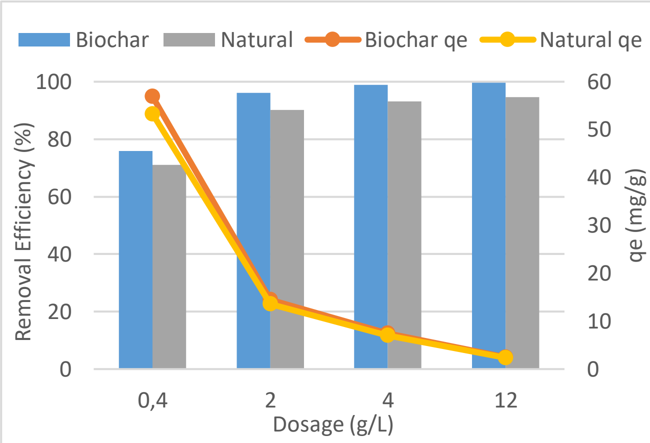

Fig. 3 Effect of contact time on malachite green removal

Figure 4 shows the copper removal graph. Here, the highest yield was seen around 80% with biochar adsorbent at 2 and 4g/L dosage. It can be said that with increasing adsorbent dosage, the removal efficiency begins to decrease. Also, it was observed that the adsorption capacity value above 50mg/g at 0,4g/L dosage for both pollutants decreased to 1-2mg/g at the dosage of 12g/L.

The study of the adsorbent dosage in which Haq et al. (2020) performed zinc removal with activated pea shell increased the removal efficiency from 41% to 64% with the increased adsorbent dosage.

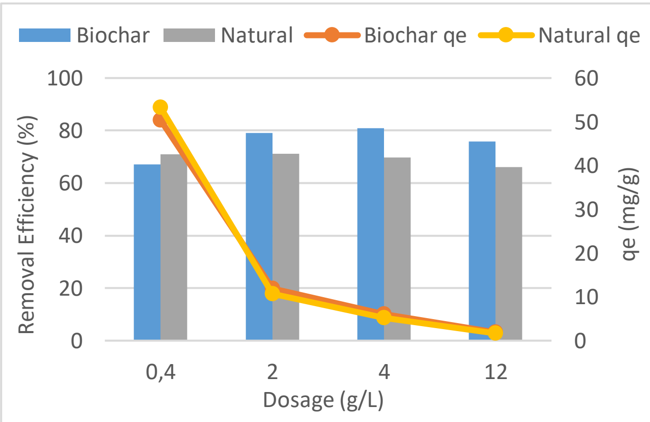

Fig. 4 Effect of adsorbent dosage on copper removal

3.3 Effect of initial metal and dye ion concentrations Studies carried out at concentrations of 30-400mg/L to investigate the effect of the initial pollutant concentration on adsorption are given in two separate graphs.

Figure 5 shows the malachite green removal efficiencies graph. Accordingly, it can be said that initial concentration does not have a significant effect on the removal of malachite green and similar yields are obtained. It was observed that the adsorption capacity increased only with increasing concentration. Çoruh and Gürkan (2018) carried out malachite green removal studies with waste foundry sand at initial malachite green concentrations varying between 25-400 mg/L. Removal efficiency, which was around 95% up to 150mg/L, dropped to 50% at 400mg/L.

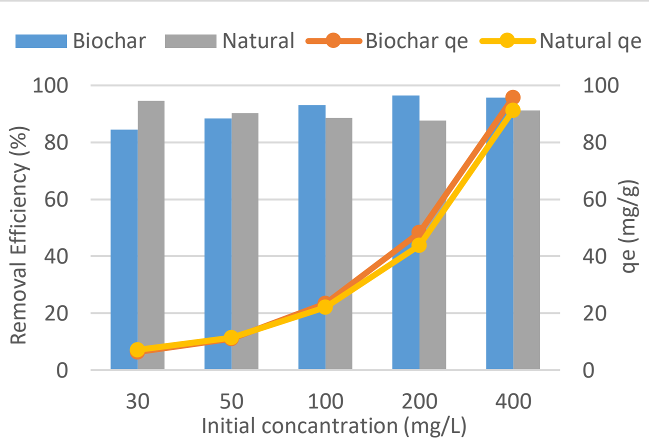

Fig. 5 Effect of initial concentration on malachite green removal

In Figure 6, copper removal efficiencies are given. The biochar has been shown to have higher yields in copper removal. It was observed that the efficiency decreased for both adsorbents at the highest starting concentration. Küçükgül and Kutlu (2006) made a copper removal study with biochar oak wood against the initial copper concentration. While copper concentration has 90% removal efficiency at low initial concentrations, removal efficiency has decreased to 20% at high initial concentrations.

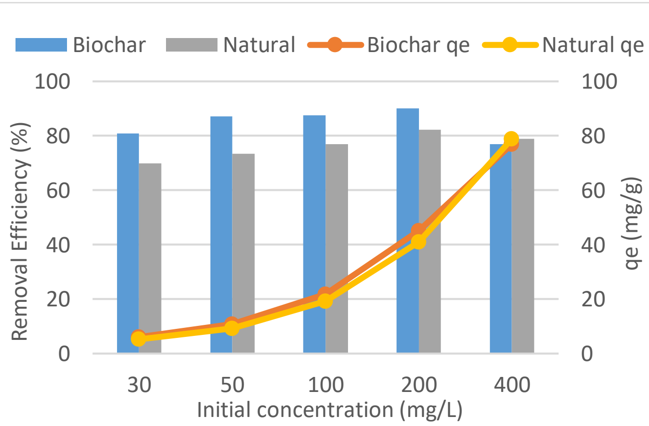

Fig. 6 Effect of initial concentration on copper removal

Malik et al. (2007) achieved a maximum 94% removal efficiency due to their studies of malachite green removal with activated nutshell. Azaman et al. obtained a maximum removal efficiency of 89% due to their studies of malachite green removal with biochar coconut shell under different adsorption conditions. Ali et al. (2020) obtained a maximum removal rate of 91.46% using the modeling method in their malachite green removal studies with active peanut husk. Abdelhadi et al. (2017) achieved a maximum 90% copper removal in their copper removal studies with biochar olive mill. They also achieved 74% copper removal with commercial activated carbon under the same adsorption conditions. As shown in these examples, paint and heavy metal removals are generally considered separately in the literature. When looking at the examples, the removal efficiencies obtained from the same adsorbent or same pollutant removal studies; It is close to or lower than the removal efficiencies obtained in this study.

3.4 Comparison of adsorption isotherms Adsorption isotherms or capacity studies are of fundamental importance in the design of adsorption and ion-exchange systems since they indicate how the metal and dye ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of increasing metal and dye concentrations.

Freundlich isotherm may be expressed as Equation 3:

$$\log q_{e=\,\log K_F} + \frac{1}{n}\log C_e \qquad (3)$$

Where; qe(mg/g) stands for sorption capacity, K_F(mg/g) indicates relative sorption capacity, while n represents affinity between sorbate molecules and sorbent. Usually, the magnitude of n for physical sorption is more significant than that for chemical sorption; its magnitude is less than one (Dönmez and Aksu 2002).

Langmuir isotherm may be expressed as Equation 4:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 x K_L} + \frac{1}{Q_0} C_e \qquad (4)$$

Where; Q_0 and K_L are the constant parameters that indicate the sorption capacity (mg/g) and sorption rate (L/mg), respectively (Rangabhashiyam et al. 2018).

In this study, the Langmuir and Freundlich isotherms for copper and malachite green dye ions removal using natural and biochar pea shells. The calculated results of the Langmuir and Freundlich isotherm correlation coefficient are given in Table 1. The data obtained were well fitted with the Freundlich equation as compared to the Langmuir equation under the different concentrations studied for both natural and biochar pea shells. Freundlich's R^2 values are calculated to be 0.8671 and 0.7895 for copper and malachite green with biochar pea shell, respectively. The R^2 values for Freundlich are calculated to be 0.9785 and 0.9419 for copper and malachite green with natural pea shells, respectively.

Values of qm, which is defined as the maximum capacity of sorbent, have been calculated from the Langmuir plots. The greatest equilibrium sorption capacity qm for copper and malachite green dye ions were obtained for 163.93mg/g and 277.77 mg/g, respectively.

Table 1 Correlation coefficients of isotherm models

Isotherm	Parameter	Biochar MG	Biochar Cu	Natural MG	Natural Cu
Freundlich	**k_F (L/g)**	2.106	2.131	3.892	2.665
	n	0.511	1.17	1.255	0.804
	R^2	0.7895	0.8671	0.9419	0.9785
Langmuir	**q_{max} (mg/g)**	33.783	163.93	277.77	147.05
	K_L (L/mg)	0.047	0.01	0.009	0.004
	R^2	0.3564	0.5135	0.1503	0.3798

4 Conclusion

In this study, malachite green and copper removal efficiency was investigated with pea shell, a natural waste material. The pea shell selected as a natural adsorbent has been used in adsorption with both natural and thermally treated biochar form. Optimum adsorption conditions; 4g/L adsorbent dosage, 2 hour contact time, 150rpm shaking speed and 25mL volume were determined. In general, higher yields were obtained in the removal of copper than the natural pea shell with the biochar pea shell. Malachite green gave similar removal efficiency values in both adsorbents. While the highest yield in malachite green removal was 94.57% with a natural pea shell, it increased to 99.65% with a biochar pea shell. In copper removal, the highest yield with natural pea shell was 69.84%, while the biochar was increased to 85.03% with pea shell. In the literature, dye and heavy metal removals are generally considered alone. In this study, measurements were taken for two parameters simultaneously after adsorption in a single sample. However, very high pollutant removal efficiencies were obtained for both parameters. Also, both adsorbents adapted to the Freundlich adsorption isotherm model for malachite green and copper adsorption. According to these results, the pea shell is an effective adsorbent used for malachite green and copper removal. The malachite green and copper removal efficiencies of natural and biochar pea shell adsorbents are close. This situation may make the thermal treatment of pea shells seem an unnecessary step. However, in the purified sample obtained after the adsorption with a natural pea shell, the natural pea shell leaves a little yellow-green color and causes turbidity. This situation requires a separate treatment step and causes extra cost and time loss. Thermally treated biochar pea shell has high dye and heavy metal removal efficiencies without causing any adverse changes in the sample structure.

Authors' contributions: Sevda Esma Darama was interested in performing the experiments, calculating the results, interpreting the data and arranging them according to the format. Semra Coruh was interested in organizing the study.

Conflict of interest disclosure: Our work has not been carried out with any organization or employees.

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