

The adsorption of methylene blue from aqueous solution by using waste potato peels; equilibrium and kinetic studies

Yalçın Aþkn ktem^{1*}, Selda G. Pozan Soyulu² and Nevin Aytan¹

¹Istanbul University, Engineering Faculty, Department of Environmental Engineering, 34320, Istanbul, Turkey

²Istanbul University, Engineering Faculty, Department of Chemical Engineering, 34320, Istanbul, Turkey

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This study examined the adsorption of methylene blue from aqueous solutions using waste material potato peels. After one hour, the maximum adsorption yield in methylene blue solution was determined as 33.87 mg/g at pH 8. Among the equilibrium isotherms with two or three parameters (Langmuir, Freundlich, Temkin, Sips, etc.) applied the acquired data, Langmuir isotherms had the highest correlation (0.99 %) and the maximum adsorption capacity of methylene blue was calculated as Q_{max} ; 33.55 mg/g. In kinetic assessments, a pseudo-second order constant best defined the rate of adsorption. It is thought that the development of adsorption depends on the loads of various functional groups, which form adsorbent, hydroxyl and carboxylic groups in the potato peels, play a significant role in methylene blue adsorption.

Keywords: Waste, Potato peels, Methylene blue, Adsorption, Isotherms, Kinetics

Introduction

Dyes are used extensively in sectors such as food, drug, cosmetics, textile, ink, toner, press and automotive industries for coloration purposes. Synthetic dyes and pigments has been significant pollutants of aquatic environments. Colored wastewaters critically affect the balance of aquatic life in ecosystems (ie, light transmittance and photosynthesis). In addition to negative environmental effects, dyes may also have toxic, mutagenic and carcinogenic effects¹. Treatment processes such as adsorption, filtration, oxidation are used for removal of dyes from wastewaters. Many recent adsorption studies have focused on biomasses and the use of wastes. Wastes are very cheap and easily available materials in production of adsorbent. Production of adsorbent from different wastes not only achieves the removal of pollutants in harmless forms but also has environmental effects of reducing waste. In many studies have employed many substances such as biomass, olive stone, seaweed, fungal species and bentonite²⁻⁶. Potato peels is disposed as a waste in many countries. However, potato peel can be used as adsorbent to remove most of pollutants in aqueous solutions. The high adsorption ability

of Methylene Blue (MB) makes it a dye commonly used in various industrial applications, especially the textile industry. MB is frequently used, within the literature, in determination of adsorption mechanism. Many studies have examined various absorbents such as chrome waste sludge, clay minerals, bottom ash, sawdust, various agricultural wastes, and corn tassel⁷⁻¹³. In this research paper, potato peels has been used to study adsorption performance of methylene blue from aqueous solutions.

Experimental

Methylene Blue and Equipment

The present study used analytical grade ($C_{16}H_{18}ClN_3S \cdot 3H_2O$) Sigma- Aldrich MB as adsorbent. MB, T60U PG Instrument Ltd. branded UV-vis spectrometer was used in calibration curve and experimental measurements. Molecular bond characterizations of organic and inorganic groups contained in potato peels were determined using a Thermo Nicolet 380 branded Fourier Transform Infrared Spectrometer (FT-IR). A particle size analyzer (Brookhaven 90 Plus) was used for distribution size of the adsorbent. Surface area was determined by using N_2 adsorption at low temperature by means of a Costech Sorptometer 1042 branded appliance. All studies were performed as duplicate and average values were used for statistical analysis.

*Author for correspondence
E-mail: oktemy@istanbul.edu.tr

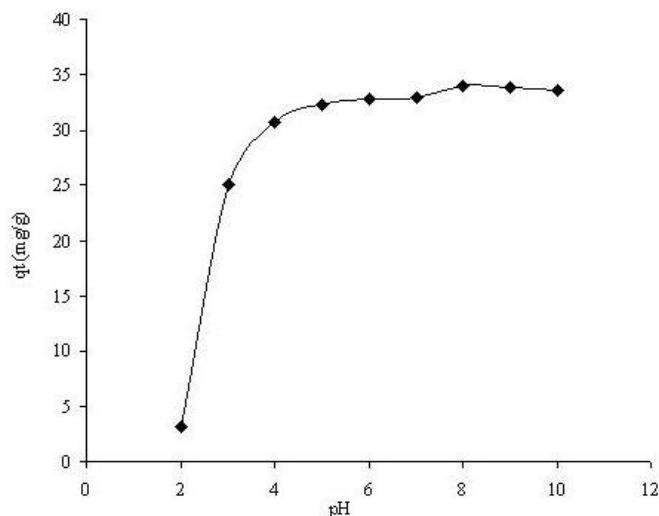


Fig. 1—The effect of pH on MB adsorption potato peels (? q_t adsorption capacity (mg/g))

Adsorbent Preparation

Waste potato peels were collected from a local restaurant garbage. After separating the potato peels from the waste, they were washed with hot water. Peels were left in to the distilled water to remove of the soil for one day. After the sample was washed with distilled water, it was dried at 40° C in order to gradually reduce the water content in the oven. The dried material was grinded to the required sizes with a commercial mill. The average particle size was in range between 10-50 μ_m . The weighted average of the values was determined as 20 μ_m . The prepared adsorbent was kept in an impermeable cup prior to use. before this study, It was not applied any chemical or physical pretreatment to adsorbent. Specific surface area of the adsorbents was determined as 3 m²/g

Batch experiments

All testing sets were carried out at 20±1°C to prevent structural degradation by temperature of the organic groups found in potato peels. Tests were carried out batch while determining the adsorption capacity of potato peels. Adsorption experiments was studied in a 100 ml erlenmeyer containing various amounts of adsorbent (0.1-10 g) and 50 ml MB at various concentrations (ranging between 25 and 400 mg/l), between pH (2) and pH (12), agitation speed (200 rpm). Following termination of the adsorption process, adsorbent was separated from fluid phase for 15 minutes at room temperature (at 4 ± 1°C) using a centrifuge (9000 rpm) and the supernatant was taken to residue analysis.

The adsorption of dye by the potato peels was calculated using the mass balance (Eq. 1) shown below.

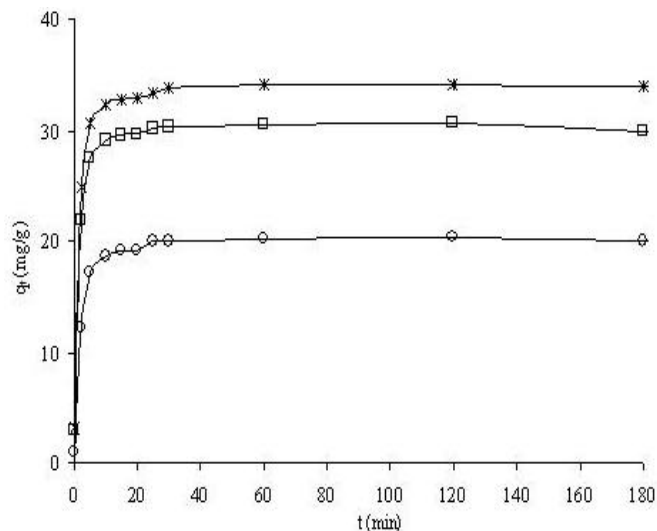


Fig. 2—The effect of contact time on adsorption amount at different MB concentrations (? 25 mg/l, □ 50 mg/l, * 100 mg/l)

$$q = \frac{C_i - C_f}{m} \times V \quad \dots(1)$$

In this equation, q denotes the amount of dye adsorbed per unit potato peels (mg/g); V denotes the solution volume (l); m denotes the amount of potato peels (g); C_{initial} (mg/l) denotes the initial dye concentration; and C_{final} (mg/l) denotes the residual dye concentration.

Results and discussion

Effect of pH

The pH of the dye solution is important in all adsorption processes, as it has a significant effect on adsorption capacity¹⁴. The pH effect during adsorption can be seen in (Fig.1). Minimum adsorption capacity in pH 2 was determined as 3.18 mg/g. Methylene blue is a cationic dye. At the pH 2 in solution, hydrogen ions are dominated. Adsorbent functional groups with negative charge are occupied by hydrogen ions. Therefore, the lowest adsorption occurs at this pH conditions. At pH 3, adsorption capacity was reached about to 25 mg/g by increasing approximately eight times. Finally, at pH 8, maximum adsorption capacity was raised up to 33.87 mg/g. The MB adsorption capacity of the adsorbent increased steadily from 3.18 mg/g to 34 mg/g with increased in pH up to 2.0–8.0, respectively. Therefore, all the adsorption experiments were carried out at pH 8.0.

Effect of agitation time

The relationship between agitation time and adsorption in different concentrations (25-100 mg/l) was shown in (Fig.2). Fig. 2, shows that the amount of the

Table 1—Langmuir and Freundlich isotherm parameters

Isotherm	Langmuir			Freundlich		
	Q_m (mg/g)	a_L (L/mg)	R^2	n	K_f	R^2
potato peels	33.55	0.116	0.99	4.25	9.61	0.79

sorbed MB into adsorbent was increased with time. The agitation time necessary to reach equilibrium was determined as 60 min. The adsorption capacities were calculated to 30.69, 34.18, and 20.36 mg/g for methylene blue solutions having initial concentration of 25, 50, and 100 mg/l, respectively. The equilibrium uptake in the case of potato peels occurred after 60 min. The results showed that % 80 of absorption has occurred within the first ten minutes.

Adsorption isotherms

Two fundamental models, namely the Langmuir isotherms¹⁵ and the Freundlich isotherm¹⁶ were used to fit the experimental data. The Langmuir method can be written in the linear form shown in (Eq. 2), below:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad \dots(2)$$

Here, C_e is the equilibrium concentration (mg/l); q_e is the amount of adsorbed dye (mg/g); Q_0 is the maximum dye per gram of adsorbent; and b was the adsorption equilibrium constant (l/mg). The Freundlich isotherm can be written below as linear form;

$$\text{Log} q_e = \text{Log} K_F + \frac{1}{n} \text{Log} C_e \quad \dots(3)$$

K_F and $1/n$ Freundlich are the model constants, indicating the relative adsorption capacity of the adsorbent (mg/g) and the adsorption density, respectively. The present study used Langmuir, Freundlich and Temkin isotherms in the estimation of adsorption constants and the highest correlation coefficients are shown in (Table 1).

The highest regression correlation coefficient was observed in the Langmuir model (0.99), followed by the Freundlich model (0.79) (Fig.3 and Fig.4). It is clear that the best model to define methylene blue adsorption is the Langmuir model. According to Langmuir isotherm results, the maximum adsorption capacity (Q_0) of potato peels was 33.55 mg/g (1.04×10^{-4} mol/g), which is comparable to other adsorbents of natural origin¹⁷. It is possible that the adsorption capacity of potato peels may

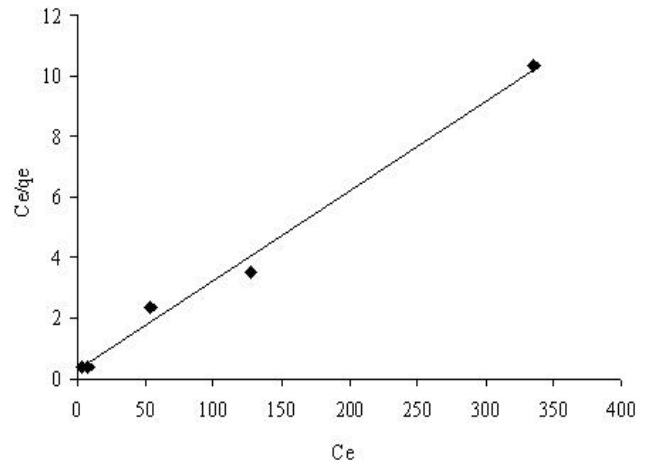


Fig. 3—Langmuir isotherm for MB adsorption (— Langmuir isotherm).

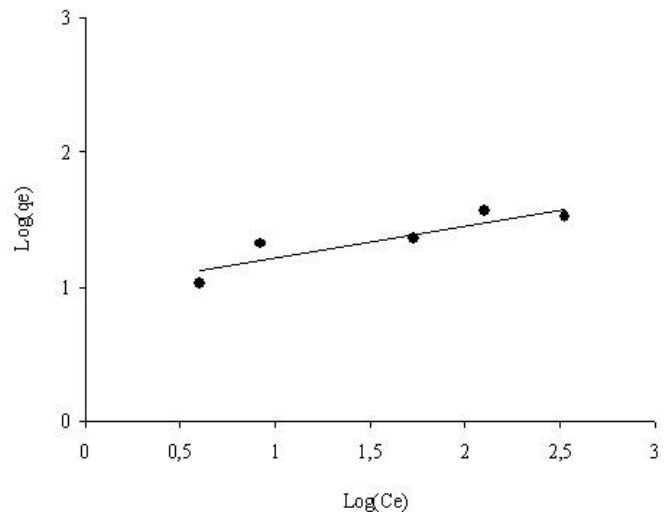


Fig. 4—Freundlich isotherm for MB adsorption (• Freundlich isotherm)

be increased by pre-processing (operation with acid-base, chemical substance additions etc.).

Adsorption kinetic

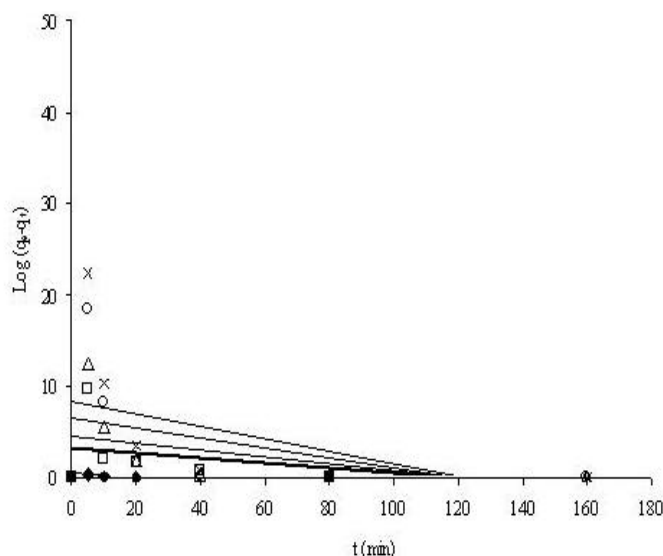
In estimating the rate of mechanism and reaction effective throughout this process, Lagergren pseudo-first-order and pseudo-second-order models were applied to experimental data. In our study, the kinetics of MB sorption on the potato peels were analyzed using different kinetics presented in Table 3 including; the Lagergren

Table 2—Kinetic parameters for MB adsorption in various concentrations

C_0 (mg/l)	$q_{e(\text{exp})}$	The pseudo-first-order			The pseudo-second-order		
		$q_{e(\text{Cal})}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e(\text{Cal})}$ (mg/g)	k_2 (g/mg.min)	R^2
25	10.5148267	0.939290652	0.0626416	0.80	10.6044539	0.0729	0.999
50	20.8178218	0.993893812	0.0061260	0.19	21.2765957	0.0225	0.997
100	23.1534653	0.917698454	0.0859019	0.20	23.6406619	0.0165	0.998
200	36.6700000	0.855460576	0.1561434	0.21	37.7358491	0.0079	0.998
400	33.7500000	0.883079925	0.1243623	0.19	34.4827586	0.0119	0.999

Table 3—FTIR spectra of potato peels before and after loaded MB

Group	Wavelength Range (cm^{-1})	Before Ads.	After Ads.	Difference
OH Stretching vibrations	3550-3200 (broad)	3405	3399	-6
CH Stretching vibrations	2780- 3340	2854	2850	-4
Carboxylic groups	1500-1640	1540	1513	-27
C-O Stretching of COOH	1300-1375	1382	1384	+2
C-O Stretching of COOH	1200-1275	1238	1230	-8
C-O-C Vibrations in Esters	1010-1275	1066	1060	-6
CH out-of-plane bending vibrations	750-995	838	840	+2

Fig. 5—Pseudo-first order kinetics for MB adsorption ($\circ$ 25 mg/l, $\square$ 50 mg/l, $\triangle$ 100 mg/l, $\times$ 200 mg/l, $\ast$ 400 mg/l)

pseudo-first order¹⁸, Types-1 pseudo-second order^{19,20}. The Lagergren pseudo-first-order rate equation is given below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \quad \dots(4)$$

Here, the amount of MB adsorbed on the adsorbent at a particular time t , q_t (mg/g), is the Lagergren

adsorption rate constant, k_1 (1/minute). The kinetic data was also studied using a further analysis method, the pseudo-second-order rate equation, shown below:

$$\frac{t}{q_t} = \left[\frac{1}{k_2 \cdot q_{eq}^2} \right] + \frac{1}{q_{eq}} \times t \quad \dots(5)$$

Here, k_2 the pseudo-second order adsorption rate constant (g/mg.minute) and the second order reaction rate equation have been used. The value of q_e is obtained from the slope of the line and k_2 is obtained from the intercept. The pseudo-first-order equation in linearized form applied to experimental data is shown in Fig.5. Correlation coefficients was calculated from 0.53 to 0.75 at different initial MB concentrations for pseudo-first-order kinetic model. The pseudo-first-order rate equation with low correlation at low concentrations becomes more uncertain at high concentrations. The pseudo-second order rate model has adapted to much better to the experimental data, with a value of $R^2 \approx 0.98$ (Fig.6.)

FTIR Spectra for adsorbent

Adsorbent includes carboxylic (hemicelluloses, pectin, lignin), phenolic (lignin, lipids, waxes) and some hydroxyl groups (cellulose, lignin, pectin) in its structure²¹. The FTIR spectra for potato peels before and after sorption for MB were almost similar. After the sorption, the

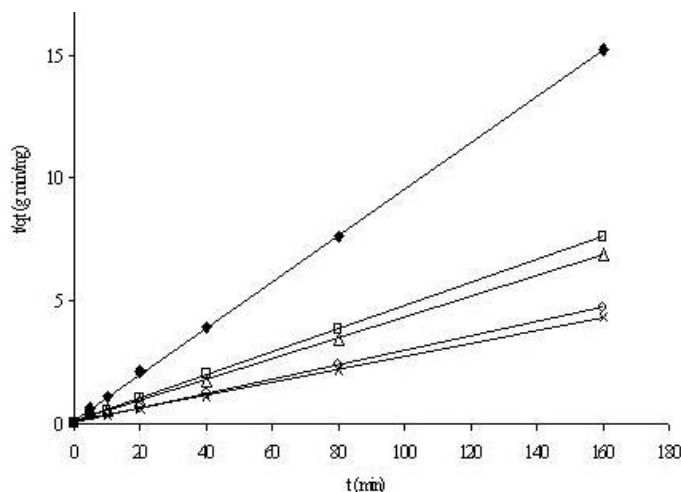


Fig. 6—Pseudo second order kinetics for MB adsorption
($\bullet$ 25 mg/l, $\square$ 50 mg/l, $\blacktriangle$ 100 mg/l, $\times$ 200 mg/l, $\circ$ 400 mg/l)

intensity of some bands changed and transmittance of peaks was relatively greater in the case of potato peels loaded with MB compared to the raw potato (Table 3).

Conclusion

The results demonstrate that potato peels can be used successfully as adsorbent for removal of MB in aqueous solutions. The sorption data of potato peels is fitted with Langmuir and Freundlich isotherms. Pseudo-second-order rate equation was determined as MB adsorption best rate equation. The effective group in MB adsorption is determined to be hydroxyl and carboxyl groups in functional groups of adsorbent.

Acknowledgments

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