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Adsorption of Malachite Green and Methyl Green on Cow bone

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Abstract

The animal bone meal prepared from the Cow bone has been investigated as a low cost solid adsorbent used for the removal of the hazardous Malachite Green (MG) and Methyl Green (MeG) from wastewater. It was proved that the concentration used was 200ppm as adsorption of MG and MeG dyes. The study was carried out in a batch system to optimize operation variables: working temperature, time and pH for the same adsorbent quantity of bone ash dye solution. This procedure is particularly suitable and has low cost system for purification of wastewater from MG and MeG at relatively short period of time.

Keywords: wastewater, Animal (Cow) Bone, Malachite Green, Methyl Green, Spectrophotometer.

1. Introduction:

The major point sources of pollution originate from the collection and discharge of domestic wastewaters, industrial wastes (Deborah Chapman 1996). The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals (Zongping Wang *et al.* 2011). Wastewater management is one of the challenging issues in the world. The traditional aim of wastewater treatment is to enable wastewater to be disposed safely. Increasingly another important aim of wastewater treatment is to recover energy, nutrients, water and other valuable resources from wastewater (Dr. Michael R. Templeton; Prof. David Butler 2011).

Malachite green (MG), is the Triphenylmethane dyes it is related to some of the oldest synthetic cationic dyes, it is still used in large quantities for coloring tin-weighted silk, wool, and paper, while methyl green, (MeG), is the nitro derivative of methylene blue, is an interesting dye, also it is used chiefly for producing black shades on silk, in combination with logwood-iron mordants and also with tin phosphate.(Klaus Hunger 2003 & H. E. Fiera *et al.* 1949).

Many materials, like fly ash and walnut shell activated carbon silicates and porous glass, etc, where used as adsorbents for adsorb wastewater contaminants (A.A. Nazari Moghaddam *et al.* 2010 & Y.C. Sharmai *et al.*2009).

Literatures were also shows that MG can be eliminated using another different techniques, like; ultrasound irradiation (C. Berberidou et al.2007 & Hazrat Ali et al.2009),, Biosorption using (bacterial cellulose) (Ali Ashjaran1 et al 2012), Enteromorpha carbon and Hydrilla verticillata biomass i ((Yijie Chen et al 2012, R.Jayaraj§ et al 2011, Rajesh Kannan, R. et al 2010, C.Parvathi et al 2011, B. Cheknane et al 2010, Hajira Tahir et al 2010, A. Bennani Karim et al 2011, Seema Singh et al 2013, P T Godbole and A D Sawant 2006, R. Rajeshkannan et al 2010, Rais Ahmad and Rajeev Kumar 2010, Mi-Hwa Baek et al 2010 & Xiangliang Pan, Daoyong Zhang 2009).

Among the above, bone reflects a remarkable affinity for pollutants. These pollutants become bound up in the adsorbent through the process of adsorption (R. Slimani *et al* 2011 & M. El Haddad *et al* 2012).

In the present work, a cow bone was chosen as a cheap material for the purpose of elimination of one of the two types of dyes which are Malachite Green and Methyl Green

2. Materials and Experiments:

Bones ash sample was taken from Animal (Cow), was cleaned from the residual meat and muscles and finally grinded then combusted at 800 oC for 3 hours in the muffle furnace. The bone ash was cooled in a dissector and crashed with sieving; choosing the mesh size of 63µm. Purified MG and MeG (99.99%) were used as standards.

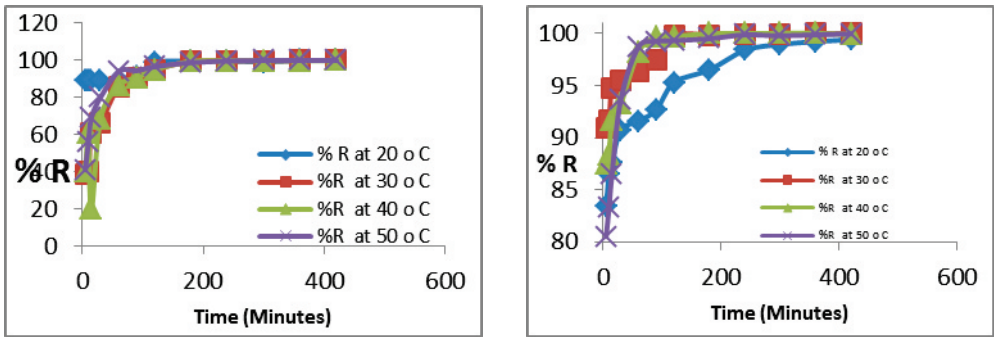
Uv-vis spectra were recorded using TU-1800S UV-Vis spectrophotometer. The pH of the solutions was adjusted above 4 for MG and for MeG between 5-7. The calibration curve of MG and MeG was obtained using series standard solutions of MG and MeG, and the absorbance of both was measured at 617nm and 630nm respectively.

Batch adsorption experiments were performed using two sets of 100 ml flasks containing 0.3 gm of bone ash with 50 ml (200 ppm) for both dyes using different temperatures (20, 30, 40, 50 C) on shaking thermostat with constant speed of 150 rpm using thermostat water bath for the pre-determined period to reach equilibrium. At the end of predefined time interval the adsorbent bone was removed from aqueous solutions by centrifuging at 3000 rpm for 10 minutes. The progress of adsorption was monitored by determining the residual concentration of MG and/or MeG in supernatant following visible absorbancy at 617nm and 630nm respectively.

The pH values at optimum temp. of the dyes used were (2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12). Same protocol was applied for further experiments.

3. Results and Discussion

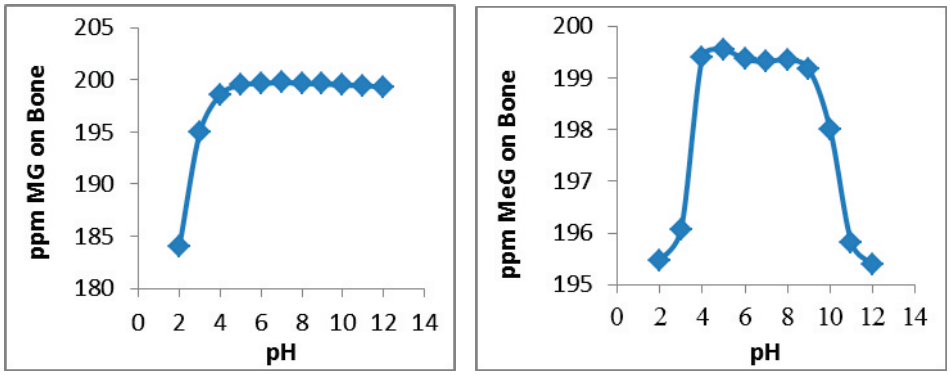
All of the adsorption conditions time, temperature and pH were optimized in order to achieve the best results of waste removal. Time and temperature were studied, using 50 ml of MG and/or MeG of 200 mg/L solutions over a period of time from 0 to 500 min. Figure 1 (a,b), shows the best elimination capacity as MG% and MeG% removal of the waste obtained at 250 min. Results reflects no effects of temperature on the efficiency of the adsorption by the bone adsorbent.



(a) (b)

Figure 1. Equilibrium time and Temperature – Optimization for Adsorption of (a) MG (b) MeG by Bone

Figure-2a, shows the optimum pH of MG and for MeG it was between 5-7 as indicated in fig (2b).



(a) (b)

Figure2 .pH – Optimization for (a) MG & (b) MeG

3.1. Kinetic studies

The kinetics of adsorption describes the rate of MG and MeG uptake on Bone Ash and this rate controls the equilibrium time. The kinetics of adsorbant uptake is required for selecting optimum operating conditions for the full-scale batch process.

The kinetic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes. The kinetics of the adsorption data was analyzed using different kinetic models such as pseudo-first-order and pseudo-second-order models.

3.2. Pseudo-first-order model

The kinetic data were treated with the Lagergren first-order model:

$$dq/dt = k1\ (qe-q)\ldots\ldots \qquad \ldots\ldots(1)$$

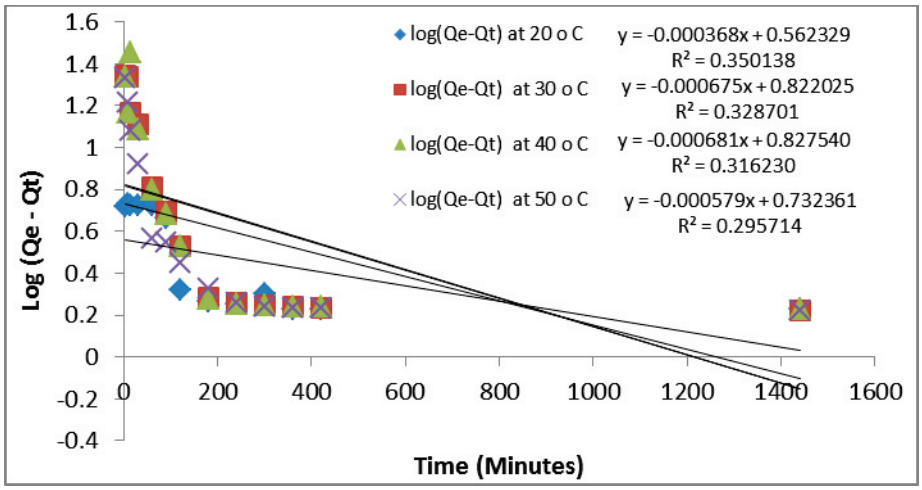
Integrating equation (1) with respect to integration conditions:

q = 0 to q = qt at t = 0 to t = t, the kinetic rate expression becomes:

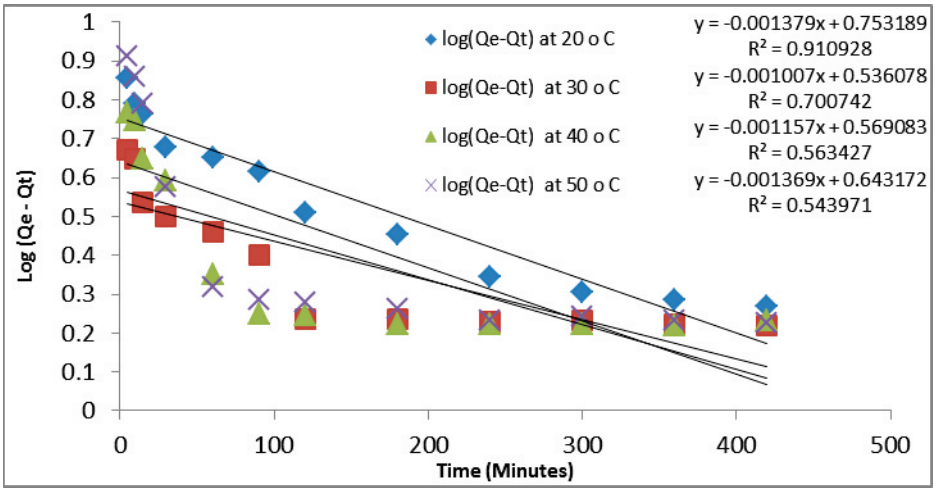
$$\text{Log}\ (qe - qt) = \text{Log}\ qe - k1\ t/2.303\ldots\ldots\ldots\ (2)$$

The first-order rate constant k1 (min -1) for MG and MeG can be obtained from the slope of the plot of Ln (qe – qt) against time t, as shown in Figure 3 (a) and (b) respectively for Bone Ash.

The adsorption first-order rate constants for MG and MeG were found to be in the range of (0.000848– 0.001568) min-1 (0.002319 – 0.003176) min-1 respectively in the temperature range of 20oC to 50oC for adsorption of MG and MeG by Bone Ash. If the adsorption process can be described by pseudo-first order equation, there should be good linear relationship between Log (qe – qt) and t. In the present study, the plot of Log (qe – qt) versus time t was not linear over the entire time range Figure 3 (a) and (b), indicating that more than one mechanism involved in adsorption. This confirms that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics for MG and MeG.



(a)



(b)

Figure3 .Pseudo-first-order kinetics for (a) MG & (b) MeG adsorption by Bone

3.3. Pseudo-second-order model

Adsorption kinetics by the pseudo-second-order model was explained as follows:

$$dq/dt = k2\ (qe-q)2\ldots\ldots\ldots \quad .. (3)$$

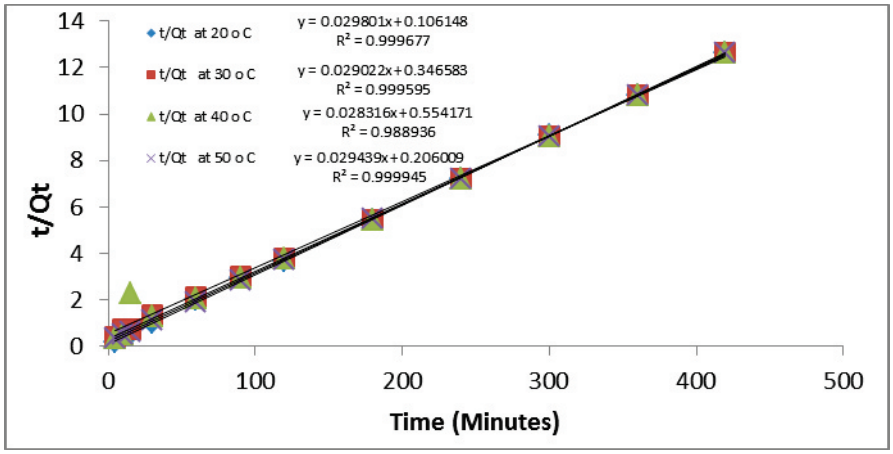
Integrating equation (3) for the boundary conditions:

$q = 0$ to $q = qt$ at $t = 0$ to $t = t$ is simplified as:

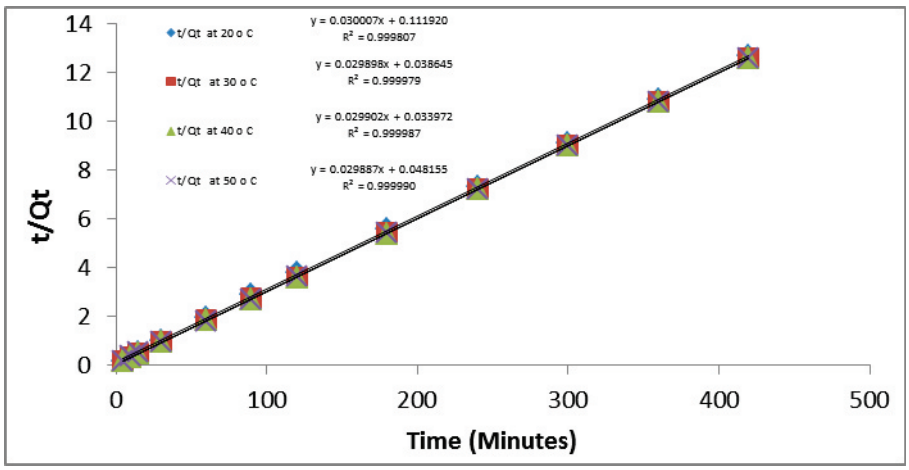
$$t/qt = 1/k2qe2 + t/qe\ldots\ldots\ldots .. (4)$$

Where k2 (g mg-1 min-1) is the second-order rate constant for MG and MeG determined from the plot of t/qt against t, as shown in Figure 4 (a) and (b). The correlation coefficients of the pseudo-second-order kinetic model were higher than 0.9997 for both of them. The pseudo-second-order adsorption mechanism was predominant for adsorption of metal ions by Bone Ash., the plot of t/qt against t present multi linearity for MG and MeG adsorption by Bone Ash. The adsorption second-order rate constants were found to be in the range of (0.001446486– 0.008364575) (g/mg.min) and (0.00804306 –0.026323665) (g/mg.min) in the temperature range of 20oC to 50oC for adsorption of MG and MeG by Bone Ash respectively.

The pseudo second order reaction rate model was found to describe best the kinetic data. The applicability of this model showed that sorption process is complex and involves more than one mechanism. The rate constant k2, the correlation coefficient R2 and removal capacity at equilibrium state (qe) for MG and MeG were calculated and presented in table 1 (a) and (b) respectively.



(a)



(b)

Figure4 .Pseudo-second-order kinetics for (a) MG & (b) MeG adsorption by Bone Ash

Table 1. Pseudo-first-order and Pseudo-second-order model comparison adsorption rate constants for (a) MG & (b) MeG by Bone Ash

(a)

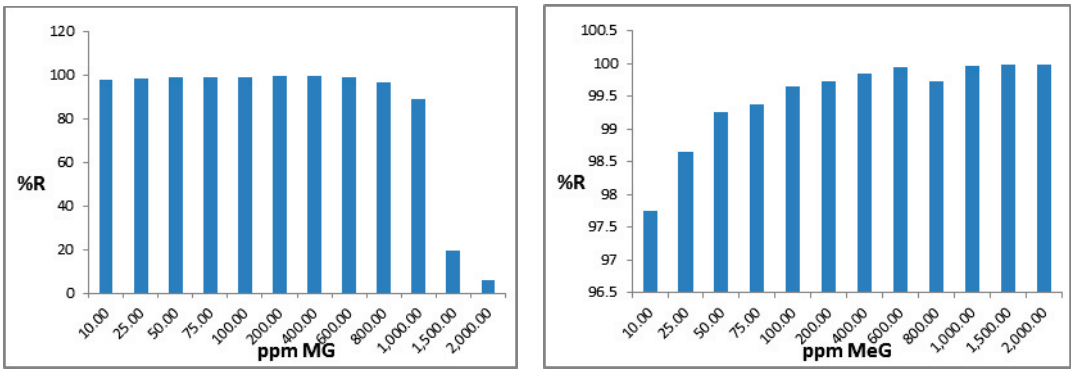
			Peseudo First Order kinetics				Pseudo Second Order Kinetcis			
Temp	Initial Conc. ppm(Co)	Qe exp.	Qe calc. (mg/g)	k1 (min-1)	R2	% Deviation in Qe	Qe calc. (mg/g)	k2 (g/mg.min)	R2	% Deviation in Qe
20	200	35	3.65	0.000848	0.350138	89.57	33.56	0.008364575	0.999677	4.11
30	200	35	6.63	0.001555	0.328701	81.057	34.46	0.002429753	0.999595	1.54
40	200	35	6.72	0.001568	0.31623	80.80	35.32	0.001446486	0.988936	-0.91
50	200	35	5.4	0.001333	0.295714	84.57	33.97	0.004206518	0.999945	2.94

(b)

			Peseudo First Order kinetics				Pseudo Second Order Kinetcis			
Temp	Initial Conc. ppm(Co)	Qe exp.	Qe calc. (mg/g)	k1 (min-1)	R2	% Deviation in Qe	Qe calc. (mg/g)	k2 (g/mg.min)	R2	% Deviation in Qe
20	200	35	5.66	0.003176	0.910928	83.8286	33.33	0.008043	0.999677	4.771429
30	200	35	3.44	0.002319	0.700742	90.1714	33.45	0.0231267	0.999595	4.428571
40	200	35	3.71	0.002665	0.563427	89.4	33.44	0.0263237	0.988936	4.457143
50	200	35	4.4	0.003153	0.543971	87.4286	33.46	0.0185484	0.999945	4.4

3.4. Effect of Adsorption on %Adsorption

The effect of adsorption and removing of MG and MeG were found that it can be seen by increasing the dye concentration (from 10 to 800 ppm and 10 to 2000 ppm respectively) added to fixed amount (0.3gm) of the bone. The removal efficiency started with the range (96 – 99) % for both of them until the sample solution reach more than 800 ppm and 2000 ppm concentration of MG and MeG as shown in Figure 5 (a) and (b) respectively. The efficiency of removal of MG beyond 800 ppm decreased to less than (30) %.



(a) (b)

Figure5 .Effect of adsorption dose on % removal of (a) MG & (b) MeG by Bone

4. Conclusion:

The current work was achieved to evaluate the performance of the bone prepared from Cow to be used in the removal of MG and MeG. It was found that the proposed methodology using bone powder can be efficiently utilized as an adsorbent for removal of MG from aqueous solution. Economically, the protocol was simple, cheep and useful with obtaining reliable results. A capacity of the test was found to be efficient for such removal of dyes in the performed conditions. The adsorption kinetics can be well described by the pseudo-second-order model equation for both types of the dyes.

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