Removal of Basic Dye From Aqueous Solution By Adsorption On Melon Husk In Binary And Ternary Systems

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Abstract

The adsorption behaviour of a cationic dye (methylene blue) in binary and ternary solutions on the husk of melon (*Citrullus lanatus*) seed was investigated in order to elucidate the effects of competitive adsorption on the kinetics and thermodynamics of the sorption process. The experimental findings showed that adsorption equilibrium was reached within 120 min either in single, binary or ternary mixtures; and the adsorption processes in all the systems studied were described by the pseudo-second order kinetics with the initial rate constant increasing as the concentrations of the competing dyes were increased. Five different equilibrium isotherm models (Freundlich, Temkin, Langmuir, Harkin-Jura and Dubinin-Radushkevich) were applied and Langmuir was the best-fitting one for the adsorption of methylene blue dye in single system ($R^2 > 0.99$), while the binary and ternary systems were best described by Freundlich model ($R^2 > 0.99$). The sorption processes were thermodynamically feasible as ΔG values were negative. Adsorption in both single and binary systems was exothermic while that of ternary system was endothermic.

Keywords: melon husk, binary dye system, ternary dye system, methylene blue, Competitive adsorption, isotherms, thermodynamics, basic dye

1. Introduction

It may be obvious that environmental pollution is inevitable as a result of industrialization, urbanization, increasing human population and sophistication in human activities. Enlightenment about the associated problems has, however, led to a rise in the level of awareness on the significance of reducing, to the tolerable minimum, the harmful substances contained in the wastewater from manufacturing and processing industries before their eventual discharge into the environment (Regine and Volesky, 2000 and Dionysiou *et al*., 2004). The need to attain this feat has constituted a serious challenge to industrial firms, process and environmental scientists and even administrators.

Dyes are very important pollutants in wastewater as colour is the most obvious indicator of water contamination; the presence of even a very small amount in aquatic medium makes it unpleasant (Ju *et al*., 2008). They are being used in various establishments such as textile/dyeing, carpet, pharmaceutical, food and other industries for colouring of products. This has led to a dramatic increase in the production of synthetic dyes as over seven hundred tones of more than 10,000 different dyes are reportedly being produced annually worldwide (Nigam *et al*, 2000; Garg *et al.*, 2004; Alzaydien, 2009); resulting in the generation of coloured wastewater (Aksu, 2001**)**. Effluents from these industries are highly coloured, and their discharge into rivers and lakes makes water from these sources unfit for domestic, agricultural and industrial purposes (Abdullah *et al*, 2005; Tumin *et al*, 2008; Gopalakrishnan *et al*, 2009; Palit, 2009; Praveen *et al*, 2010). Apart from the adverse effect on the aesthetics of the aquatic environment, making the water undesirable for drinking and other recreational purposes because of its abnormal and undesirable appearance (Vasanth *et al.*, 2004), the presence of dyes also has inhibiting effect on the process of photosynthesis, thus affecting aquatic ecosystem due to reduced light penetration; they also have negative effects on several other biological processes (Rennin *et al*., 2007; Ragnathan *et al*., 2007; Karaca *et al*., 2008) It causes eutrophication and general perturbation of aquatic life (Renmin *et al*., 2007, Batzias and Sidiras, 2007).

A number of technologies have been applied over the years for the treatment of dye-containing wastewaters. Adsorption method using activated carbon has been widely used because of its simplicity and high efficiency resulting from its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity (Batzias and Sidiras, 2007**)**.

However, its widespread use is restricted due to relatively high cost (Babel and Kurniawan, 2003), and problems like high temperature combustion, pore blocking and hygroscopicity associated with its production (Abdel Wahab *et al*., 2005**)**. This has led to the search for new, efficient and cheaper adsorbents for treating dye wastewaters.

As such, numerous alternatives especially agricultural by-products are being investigated to determine their capacities for removing dyes from aqueous solution, using Methylene Blue as the model dye. These include guava leaf powder (Ponnusami *et al.*, 2008), dehydrated wheat bran carbon (Özer and Dursun, 2007), wheat shell (Bulut and Aydin, 2006), bamboo charcoal (Zhu *et al.*, 2009), silver fir (*Abies amabilis*), sawdust (Zafar *et al.*, 2008) and activated carbon from sugar beet molasses (Aci *et al.*, 2008).

The present study attempts to use the seed husk of melon (*Citrullus lanatus)*, as a nonconventional, natural low-cost adsorbent for decolourising aqueous solutions of dye in single, binary and ternary dye systems and to investigate the effects of competitive adsorption on the kinetics and thermodynamics of the adsorption.

2. MATERIALS AND METHODS

2.1 Preparation of adsorbent

Melon seed husk used in this work was obtained from local farm produce markets in Ogbomoso metropolis, Southwest Nigeria. Debris and other relatively big foreign materials were hand-picked from the husk, after which it was thoroughly washed with distilled water (to remove soil and dust), drained and dried. It was then ground and sieved. It was washed again several times with large quantities of distilled water until the wash water was clear so as to ensure the removal of any soluble component that may interfere with adsorption processes. It was then oven-dried at 105 ^{o}C and stored in air-tight containers as melon seed husk (MSH) adsorbent.

2.2 Characterization of Adsorbent

2.2.1 Morphological Study

The surface morphology of the adsorbents was examined on Hitachi 2300 Scanning electron microscope. Samples were coated with gold before being subjected to SEM analysis.

2.2.2 Infrared spectroscopy

The IR spectrum of the MSH was recorded with FTIR BX Spectrophotometer by Pelkin Elmer in the range of 4000 cm^{-1} to 450 cm^{-1} using KBr disk as reference.

2.3 Preparation of adsorbate

The main adsorbate used in this study was methylene blue, a cationic dye (Color index (C.I), 52015; $\lambda_{max.}$, 664 nm; molecular weight, 355.90, supplied by M & B Laboratory Chemicals**)**, in a single, binary or ternary system with: congo red (by Timstar Laboratory Suppliers) and methyl orange (by BDH Chemicals) in different mass ratios; their chemical structures are given in Figure 1. The dyes were obtained in commercial purity, and were used without any further purification. Stock solutions of the dyes were prepared by dissolving 500 mg of each of them separately in distilled water to make a 500 mg/L solution. Appropriate working solutions were prepared from the stock solution by accurate dilution with distilled water. Experimental solutions of ternary dye mixture of desired concentrations were prepared by mixing appropriate volumes of the stock solutions and accurately diluting it with distilled water.

2.4 Batch Adsorption Studies

2.4.1 Equilibrium studies

Dye mixture solutions of different initial concentrations, C_o, of methylene blue in a single system and with fixed concentrations of congo red, and together with methyl orange in binary and ternary systems respectively, were prepared through serial dilution of the stock solutions of the dyes. 20 cm^3 of each of the solutions was mechanically agitated with 0.05 g of the various adsorbents for 120 min in a horizontal shaker at 30 ^{o}C. The adsorbent-adsorbate mixtures were then filtered, and the filtrates analysed at wavelength 664 nm as stated above to determine the residual concentration of the dye.

2.4.2 Effect of contact time

The effect of contact time on the adsorption process of the dye-melon husk systems was studied by shaking dye solutions of different concentrations with a fixed mass of MSH adsorbent, in several tightly covered reaction flasks. For each adsorption experiment, samples were withdrawn at predetermined time intervals, and the dye-adsorbent system was separated by filtration. Then concentrations of residual solutions were measured by reading the absorbance changes at the wavelength of maximum absorbance (λ_{max}= 664 nm).

2.5 Analytical methods

The absorbance of the filtrate was determined with UV–Visible Spectrophotometer (Genesys 10 UV-VIS Scanning Spectrophotometer) adjusted at λ_{max} (664 nm) of methylene blue. By referring to the calibration curve of the dye, the corresponding concentration of the dye in the equilibrium solution was obtained. The percentage removal or sorption of the dye and equilibrium adsorption capacity, q_e (mg/g) was evaluated as follows

$$\% \ Sorption = \frac{100(C_o - C_t)}{C_o} \qquad (1)$$

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (2)$$

$$q_t = \frac{(C_o - C_t)V}{m} \qquad (3)$$

where q_e and q_t are the amounts of MB dye adsorbed (mg/g) at equilibrium and at any time, t; C_o and C_t are the initial concentration (at $t = 0$) and its concentration at time $t = t$ (mg/L); m is the mass of the adsorbents (g); V is the volume of dye solution (L).

3. RESULTS AND DISCUSSION

3.1 Characterization of MSH adsorbent

The FTIR spectrum of MSH (Fig. 2a) displays a number of absorption peaks, indicating the complex nature of MSH adsorbent. The spectrum revealed diagnostic bands at 3448 cm^{-1} representing bonded – OH in the oxygen-containing functional groups. The positions of the C–H (2920 cm^{-1}), aliphatic C – C (1273 cm^{-1}) and aromatic C = C (1604 cm^{-1}) and carboxyl/carbonyl (1733 cm^{-1}) vibrations, contributed by those in the structure of cellulose, hemicellulose and lignin, which are common components of plant materials, are indicated by the spectrum of MSH (Olajire, 2012). Thus, the FTIR spectrophotometric analysis indicates that the adsorbent has potential adsorption sites as represented by functional groups such as COOH, C = O, and C=C.

The FTIR spectrum of the adsorbent after dye uptake in the ternary dye system is shown in Figure 2b. When compared with the FTIR spectrum of the adsorbent before any adsorption (Fig. 2a), there were remarkable differences in the position or occurrence of some diagnostic bands. There was a slight shift in the position of –OH or –NH band at 3448 cm^{-1} in MSH before adsorption to 3381 cm^{-1} after adsorption. A major shift was also observed in C=C stretch from 1604 to 1656 cm^{-1}. The C=O stretch at 1733 cm^{-1} did not even feature at all after the adsorption (Fig. 2b). These may be as a result of the attachment of the dye molecules, both cationic (methylene blue) and anionic (congo red and methyl orange) at these positions.

The Scanning Electron Microscope (SEM) was used to study the surface morphology of the adsorbent. The surface textural structure of MSH is presented as scanning electron micrographs (× 1000) (Fig. 3). The SEM images of MSH showed the irregular texture and porous nature of the surface of the adsorbent. Its apparent rough surface is a pointer to high surface area (Demirbas *et al.*, 2004), which enhances adsorption. The X-ray diffraction plots of MSH is also shown in figure 4.

3.2 Effect of initial concentrations of dyes

The effect of the initial concentration of methylene blue on its adsorption onto MSH is shown in Figure 5 for single, binary and ternary systems. Adsorption capacity (q_e) increases with increasing initial concentration of methylene blue in all the systems. An increase in the initial concentration of the dye from 10 mg/L to 50 mg/L in the single dye system (SDS) for instance, resulted in an increase in adsorption capacity (q_e) from 1.98 to 9.63 mg/g. The increase in the initial concentration of the dye enhances the interaction between the dye molecules and the surface of the adsorbent. There was, however, a corresponding decrease in percent sorption with increasing initial concentration of methylene blue. Similar observation was also reported by other researchers (Azhar *et al.*, 2005; Daniela and Doina, 2005) where there was a decrease in percentage removal of adsorbate with increase in its initial concentration but resulting in increased adsorption capacity of the adsorbent for the adsorbate.

At low initial concentrations of methylene blue dye relatively high percentage sorptions were observed as a result of the high ratio of adsorbent surface binding sites to the dye concentration, meaning that a fewer number of dye molecules were competing for the available binding sites on the adsorbent (Gupta and Mohapatra, 2003). With increasing MB dye initial concentration however, the sorptive surface to dye concentration decreases leading to reduced percent sorption (Bansal *et al.*, 2009). Slight reductions in adsorption density were observed in the binary and ternary systems when compared with the single dye system (Figure 5). The decrease became more pronounced (that is, adsorption capacity for methylene decreased) with increasing concentration of congo red in the binary system.

3.3 Equilibrium isotherm studies

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. The equilibrium adsorption isotherm is very important to design the adsorption systems. For solid-liquid systems, several isotherms are available.The results obtained from adsorption equilibrium experiments in this study were fitted to five adsorption isotherms: Langmuir, Freundlich, Temkin, Dubinin- Radushkevich and Harkin-Jura models, so as to elucidate the mechanism of the adsorption process.

The Langmuir isotherm equation takes the form (Langmuir, 1918; Ho *et al.*, 2002):

$$qe = \frac{q_m k_a c_e}{1 + k_a c_e} \qquad (4)$$

where q_e is the amount of dye adsorbed per unit mass at equilibrium (mg/g); q_m is the maximum possible amount of dye that can be adsorbed per unit mass of adsorbent (mg/g); C_e is concentration of sorbate in the solution at equilibrium (mg/L); k_a is the sorption equilibrium constant. The linearised form of equation (4) is :

$$\frac{c_e}{q_e} = \frac{1}{k_a q_m} + \frac{c_e}{q_m} \qquad (5)$$

A plot of $\frac{C_e}{q_e}$ versus C_e gives a straight line with a slope of $\frac{1}{q_m}$ and intercept $\frac{1}{k_a q_m}$.

The Freundlich isotherm (Freundlich, 1906) is an empirical equation given as:

$$q_e = K_f C_e^{1/n} \qquad (6)$$

The linear form of the equation is:

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \qquad (7)$$

where C_e is the equilibrium concentration in mg/L, q_e is the amount of dye adsorbed per unit mass of a MSH (mg/g); K_f and n are Freundlich constants which are measures of adsorption capacity and intensity of adsorption respectively (Malik, 2004).

The Temkin isotherm can be simplified to the following equation (Temkin and Pyzhev, 1940):

$$q_e = \beta \ln K_T + \beta \ln Ce \qquad (8)$$

where $\beta = (RT)/b_T$, is the Temkin constant, T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 J mol $^{-1}$ K^{-1}. The constant b_T is related to the heat of adsorption (kJ/mol.), K_T is the equilibrium binding constant (L/mol.) corresponding to the maximum binding energy.

The Dubinin- Radushkevich equation is given as (Mittal *et al.*, 2007):

$$\ln q_e = \ln X_m - \beta_{\mathrm{E}}{}^{2} \qquad (9)$$

where X_m is the maximum sorption capacity (mg/g)

β is the activity coefficient related to the mean sorption energy (mol^2/ J^2)

ε is Polanyi potential given by

$$\varepsilon = RT \ln(1 + q_e{}^{-1}) \qquad (10)$$

Where R is gas constant and T is temperature in Kelvin. The slope and intercept of a linear plot of ln q_e versus ε^2 are β and X_m respectively.

The Harkin-Jura isotherm model takes into consideration the multilayer adsorption, which can be explained by the existence of heterogeneous pore distribution. The equation is (Basar, 2006; Oladoja *et al.*, 2008).

$$\frac{1}{q_e{}^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right)\log c_e \tag{11}$$

Table 1 summarises the essential equilibrium characteristics of the adsorption of methylene blue by MSH in single, binary and ternary systems. Whereas Langmuir isotherm model gave the best description of methylene blue adsorption in a single system, Freundlich equation was the most suitable model for describing the MB adsorption in binary combination with congo red, and ternary mixture with congo red and methyl orange. This is evident from the high regression factor obtained for the sorption processes (Table 1). The Langmuir isotherm makes an assumption that the adsorption occurs at specific homogeneous sites within the adsorbent (Langmuir, 1918; Ho *et al.*, 2002). It also assumes that the adsorption sites on MSH have the same affinity for the adsorption of a single molecular layer of methylene blue, with no interaction between the adsorbed molecules of the dye. The Langmuir monolayer adsorption capacity, q_m, of MSH for the adsorption systems decreased (from 47.39 through 11.39 to 10.31 mg/g) with increasing concentration of congo red from 5 mg/L through 10 mg/L to 20 mg/L in the binary systems when compared with the single system (Table 2). This may be due to increasing competition for the limited adsorption sites on MSH. However, q_m for the ternary system (22.42 mg/g) was higher than for the binary dye mixture but lower than for the single dye system (Table 1). This shows that the presence together of two anionic dyes (methyl orange and congo red) in the mixture has synergetic effect on the adsorption of methylene blue. This may be as a result of the likely repulsive interaction between the molecules of the two anionic dyes which enhanced the adsorption of the cationic dye (methylene blue). This, therefore, explains the conformity of the adsorption process in binary and ternary systems with the Freundlich isotherm, which takes into account repulsive interaction between adsorbed solute particles. From the Freundlich isotherm, since the values of $1/n < 1$ in all the sorption processes studied, then the adsorption was favourable and the adsorption capacity increased with the occurrence of new adsorption sites. (Lain-chuen et al., 2007). These values also satisfy the condition for heterogeneity, i.e $1< n <10$ (Khalid *et al.*, 2000).

The maximum monolayer coverage, $q_{m,}$ values (a measure of the efficiency and capacity of an adsorbent for an adsorbate in a given sorption system), obtained in this work were compared with those of other adsorbent for methylene blue (Table 2).

A further analysis of the Langmuir equation is made on the basis of a dimensionless equilibrium parameter (Abdel-Ghani *et al.*, 2008; Hameed *et al.*, 2007), which is a constant separation factor K_R, and has been suggested, to express the essential characteristics of the Langmuir isotherm (Sumanjit *et al.*, 2008; Malik., 2004; Hema and Arivoli., 2007; Abdelwahab *et al.*, 2005; McKay *et al.*, 1989). It is a measure of the favourability of the adsorption process (Mittal *et al.*, 2007, Hema and Arivoli, 2007). K_R is calculated thus:

$$K_R = \frac{1}{1 + k_a c_o} \tag{12}$$

where C_o (mg/L) is the initial concentration of MB and K_R (L/mg) is Langmuir constant. The value of K_R indicates the shape of the isotherm to be either linear ($K_R = 1$), unfavourable ($K_R > 1$), favourable ($0 < K_R < 1$), or irreversible ($K_R = 0$). Thus the K_R values between 0 and 1 indicate favourable adsorption (Chiu and Wang, 2009; Ho, 2003). Plots of K_R versus C_o of methylene blue for single, binary and ternary systems at 30 ℃ are shown in Fig. 6. The K_R values were in the range 0.011 to 0.400, which is less than unity, indicating that the adsorption was favourable, more favourable for the higher initial methylene blue concentrations. Also, increasing amount of the other dyes present with methylene blue in the binary or ternary systems increases K_R thus, making the adsorption process to be less favourable than in the single system. The correlation coefficients obtained from the plots of Temkin isotherm were also high (> 0.94. This suggests that there was a sort of interaction between the molecules of the dyes as the isotherm takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process.

3.4 Contact Time Effect and Kinetics

3.4.1 Effects of contact time

The rate of adsorption of a molecule onto a surface is an important factor in the design of a sorption system (Wankasi *et al.*, 2006). The effect of contact time on the amount of methylene blue adsorbed on various adsorbents MSH was studied using the same initial concentrations of the dye in single, binary and ternary systems. As contact time increases, the residual concentration of methylene blue in the system decreased rapidly at the beginning and the rate later slowed down until the concentration remained virtually constant at about 60 minutes; 2 h was then taken as the equilibrium time to ensure completion of the sorption process (Fig. 7).

The quantity of dye adsorbed per unit mass at a given time, q_t, of MSH increased as contact time was increased, with a rapid rate at the beginning, until equilibrium was reached. The rate of MB sorption was rapid at the beginning; more than 80 - 90% uptake was accomplished in the first 20-30 minutes of the sorption process for all the adsorbate systems, until the adsorbent was saturated, and an equilibrium was attained. The initial rapid phase, was an indication of a spontaneous sorption process, which may be due to a large number of vacant active adsorption sites available at the initial period of the sorption (Wong *et al.*, 2009); making the concentration gradient to be high thus, enhancing the sorption process (El-Nemr *et al.*, 2005).

3.4.2 Adsorption kinetics

In order to study the adsorption of methylene blue onto sodium hydroxide-treated melon seed husk, MSH, and to interpret the results, experimental data obtained from the study of contact time effect were fitted to different kinetic models such as the pseudo-first-order (Annadurai *et al*., 2002), the pseudo-second order (Ho and McKay, 1999; Hameed *et al*., 2007), Elovich (Zeldowitsch, 1934) and an intraparticle diffusion (Annadurai *et al*., 2002; Weber and Morris1963).

The pseudo- first order equation given by Lagergren (1898), is expressed as;

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{13}$$

where q_e and q_t are the amounts of the dye adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant adsorption (min^{-1}).

The pseudo-second order model (Ho, 1995) is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{14}$$

$$h = k_2 q_e^{\ 2} \tag{15}$$

where q_e is the amount of the solute adsorbed at equilibrium per unit mass of adsorbent (mg g^{-1}) , q_t is the amount of solute adsorbed (mg g^{-1}) at any given time t (min) and k_2 is the rate constant for pseudo-second-order adsorption (g mg^{-1} mm^{-1}) and h, known as the initial sorption rate. The values of q_e and k_2 can be obtained from the slope and intercept of the plot of t/q_t versus t respectively. If the sorption follows pseudo-second order, h, is described as the initial rate constant as t approaches zero.

The Elovich model is expressed as (Sparks, 1986; Okiemen and Onyega, 1989);

$$q_t = {}^1/_\beta \ln(\alpha\beta) + \left({}^1/_\beta\right) \ln t \tag{16}$$

where α is the initial adsorption rate (mg/g. min), β is the desorption constant (g/mg) and q_t is the amount of solute adsorbed (mg/g) at any given time t (min.).

A plot of q_t versus *In t* gives a straight line with intercept $\frac{1}{\beta} In(\alpha\beta)$ and slope, $\left(\frac{1}{\beta}\right)$.

The contribution of intraparticle diffusion to the sorption process can also be investigated using Morris-Weber equation (Weber and Morris, 1963) in the following form:

$$q_t = K_{id} \sqrt{t} \tag{17}$$

where q_t is the sorbed concentration at time "t", and "K_{id}" is the rate constant of intraparticle transport. According to Morris and Weber (Weber and Morris, 1963), a plot of sorption capacity at a given time, q_t, versus √t should be a straight line if intraparticle diffusion is involved; and if it is the only rate-determining factor, the line passes through the origin. However, if the plot has an intercept (i.e. does not pass through the origin), it shows that intra-particle diffusion may not be the only factor limiting the rate of the sorption process (Ho and Mckay, 2003). A modified form of Morris-Weber equation that takes care of boundary layer resistance was therefore proposed as (Igwe and Abia, 2007; Mckay and Poots, 1980; Abia *et al.*, 2006):

$$q_t = K_{id}\sqrt{t} + X_i \tag{18}$$

where X_i depicts the boundary layer thickness (Abia *et al.*, 2006).

Figure 8 shows the linear plots of the various kinetics equations for the adsorption of MB dye onto MSH while Table 4 gives the parameters such as rate constants, experimentally observed and calculated adsorption capacities, and R^2 values obtained from the models. For the Pseudo-first model, values of k_1 (min^{-1}) and q_e (mg/g) calculated from slope and the intercept of the plot of log ($q_e - q_t$) versus t (Fig. 9a) of the different systems (single and ternary) are given in Table 3. The results show that the values of R^2 were low and the experimental q_e values do not agree well with the calculated values (q_e, cal.). This shows that the adsorption of methylene blue onto MSH does not follow first-order kinetics.

The initial adsorption rate, α; desorption constant, β, and the correlation coefficients, calculated from the plots of Elovich model for the different sorption systems studied are given in Table 3 as obtained from the linear plots (Fig. 9b). The initial sorption rate, α , of methylene blue by MSH increased astronomically with increasing concentration of congo red in the system. The value of α for the adsorption of methylene blue in single system jumped from 4.39 x 10^4 to 1.5 x 10^{14} and 5.85 x 10^{40} in the presence of 10 mg/L and 20 mg/L of congo red, respectively, while methyl orange inital concentration was kept constant at 10 mg/L. There was, however, a drastic reduction in α (1.5 x 10^{14} to 3.68 x 10^3) when the initial concentration of methyl orange was doubled (10 mg/L to 20 mg/L).

The kinetics for the single and ternary dye systems could best be described by the pseudo-second order rate model. The results in Figure 9c show linear plots for all the four adsorbate systems studied with very high values of R^2 (Table 3) in addition to the good agreement between experimental and calculated values of q_e. Therefore, it can be said that the pseudo second-order kinetics provided a good correlation for the adsorption of Methylene blue onto MSH in contrast to the pseudo first-order model. The pseudo-second order initial rate constant, h, and the overall rate constant, k_2, (g/mg min) increased with increasing concentration of congo red in the system. In fact, h increased by over 100 % when the initial concentration of congo red in the mixture was doubled (from 10 mg/L (B) to 20 mg/L (C)) (Table 4).

The plots of q_t against √t for the Weber-Moris intraparticle diffusion model gave straight lines which do not pass through the origin (i. e the intercepts > 0) (Figure). The deviation of these lines from the origin indicates that intra-particle diffusion may be a factor in the sorption process, but it is not the only controlling step (Ong *et al.*, 2007). The rate constants, k_i, and boundary layer thickness, X_i, obtained from the model for the various adsorption systems studied are given in Table 3. The intraparticle rate constants computed fom the slopes of the graphs decreased with increasing concentration of congo red in the single/binary systems. For the single methylene blue system, k_i was 0.455 mg g^{-1} min$^{-1/2}$ while it increased to 0.072 and 0.041 mg g^{-1} min$^{-1/2}$ for binary systems consisting of 5 and 10 mg/L of congo red respectively. The intercepts of the plots are an indication of the level of contribution of boundary layer resistance as it affects the rate limiting step of the sorption process. The larger the intercept, the greater is the contribution of the surface sorption (boundary layer resistance) in the rate–limiting step (Arvoli and Thenkuzhali, 2008). The boundary layer thickness, X_i, of the single system (18.80 mg/g) was lower than those of the ternary systems (Table 3). This implies that there was a stronger resistance in multi-dye systems; an indication of greater contribution to the rate limiting stem. This may be as a result of the overall higher dye concentration in the ternary systems. Similar observation of direct relationship between dye initial concentration and boundary layer thickness was reported by Olajire *et al.*, (2013). The first phase of the bilinear plots is attributable to boundary layer diffusion. Similar trend was reported in the literature (Oladoja *et al*., 2008; Arivoli and Thenkuzhali, 2008; Vadivelan and Vasanthkumur, 2005; Wu *et al*., 2000; Bhattacharya and Sharma, 2004; Lazaridis and Asouhidou, 2003). The second linear portion (phase II) indicates the micropore diffusion (Allen et al., 1989).

3.5 Adsorption thermodynamics

The concept of thermodynamics is originally based on the assumption that energy can neither be created nor lost in an isolated system and therefore, entropy change is the only driving force (Ho., 2003). This is studied by determining the effect of temperature on the adsorption. Thermodynamic parameters like Gibb's free energy change, ΔG^o (KJ/mol), the enthalpy change, ΔH^o (kJ/mol) and entropy change, ΔS^O(J/mol/K) are then calculated (Ncibi *et al.*, 2007; Gong *et al.*, 2009). They are required to understand and predict the nature of adsorption (Pandey *et al*., 2010), by providing in-depth information regarding the inherent energy and structural changes after adsorption (Ramesh *et al.*,2005).

The Gibbs free energy, ΔG^o, is the fundamental criterion of spontaneity. A negative value of ΔG^o establishes the feasibility of an adsorption process (Mittal *et al*., 2007). That is reaction occur spontaneously at a given temperature if ΔG^O is negative; higher negative value reflects more energetically favourable sorption (Ncibi *et al.*, 2007). When ΔH is positive, it implies the process is endothermic, while negative ΔH establishes that the process is exothermic. In a sorption process, a positive ΔS shows good affinity between the adsorbate and the adsorbent

(Mittal *et al*., 2007).

In this work, these parameters were obtained from the following equations:

$$\Delta G = -RT \ln K \qquad (19)$$

$$\Delta G = \Delta H - T\Delta S \qquad (20)$$

Where: ΔS is the standard entropy change (J/mol/K); ΔH is the standard entropy change (J/mol);T is the absolute temperature (K) and K is the equilibrium constant.

ΔH and ΔS were obtained from the intercept and slope of the plot of ΔG against T respectively.

Parameters for adsorption thermodynamics in the adsorption of methylene blue onto MSH in single, binary and ternary dye systems are given in Table 4. It shows the values of ΔG, ΔH and ΔS obtained at different temperatures, 303-323 K, for the sorption processes. For all the adsorbate systems ΔG values were negative, indicating that the adsorption processes studied were all feasible.

The single MB system was exothermic with negative ΔH (-14.82 kJ/mol). ΔH for the binary system is also negative (-11.6 kJ/mol) but less exothermic than the single system. The ternary system was endothermic (ΔH = +23.6 kJ/mol); the sorption process become more feasible with increase in temperature (Table 5). The degree on disorderliness at the MSH/ dye interphase in the ternary dye system increased as shown by positive ΔS value (ΔS = +98.7 J/mol.K). This positive ΔS is an indication of a significant change in the internal structure of MSH as a result of the adsorption of the dye (Juang *et al*., 2007). ΔS values were, however, negative in the single and binary systems, indicating a decrease in randomness (Table 4).

5. Conclusion

The adsorption processes being investigated were described by the pseudo-second order kinetics. The pseudo-second order initial rate constant, h, methylene blue adsorption increased by over 100% (q_m 37.31 to 86.96 mg/g) when the initial concentration of congo red was doubled. In general, h increased with the addition of an acid dye, congo red or methyl orange. The single MB system was exothermic with negative ΔH (-14.82 kJ/mol). ΔH for the binary system is also negative (-11.6 kJ/mol) but less exothermic than the single system. The ternary system was endothermic (ΔH = +23.6 kJ/mol); the sorption process become more feasible with increase in temperature. The degree on disorderliness at the RMH/ dye interphase in the ternary dye system increased (ΔS = +98.7 J/mol.K). ΔS values were, however, negative in the single and binary systems, indicating a decrease in randomness.

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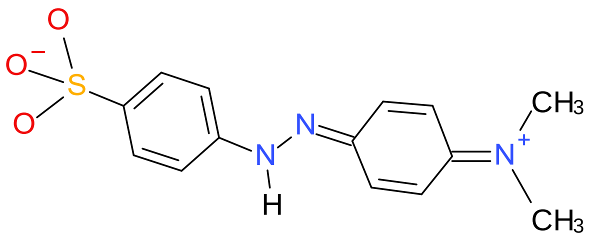
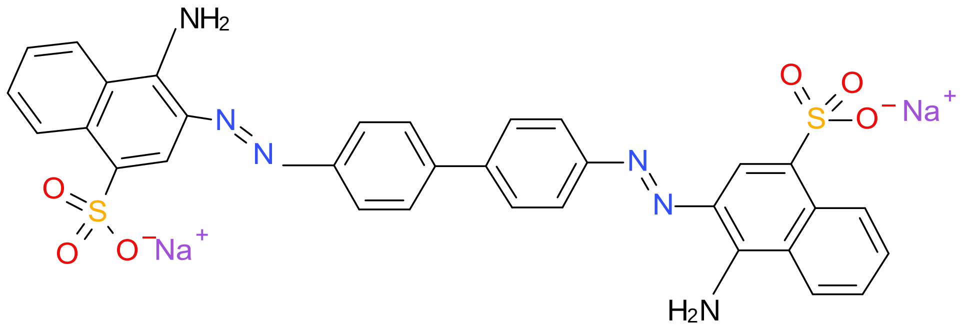
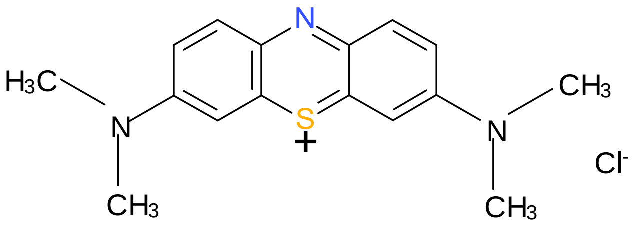


Structure of Methyl orange



Structure of Congo red



Structure of Methylene blue

Figure1: Chemical structures of methyl orange, congo red and methylene blue.

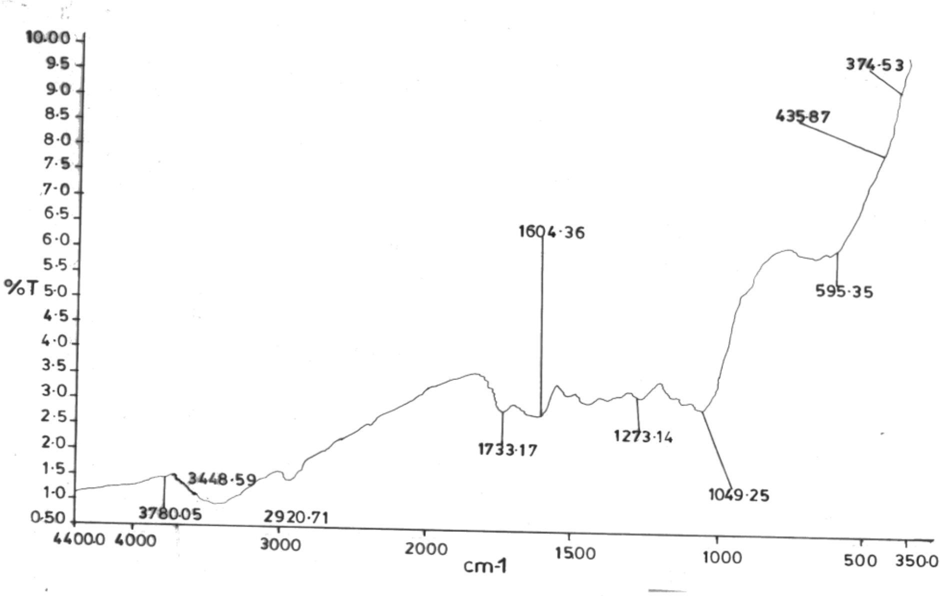


Figure 2a

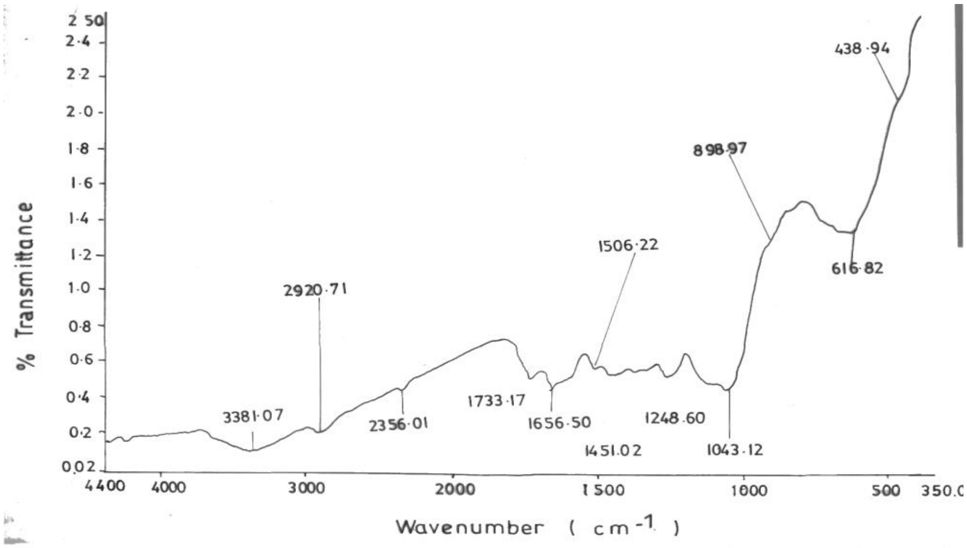


Figure 2b

Fig. 2: FTIR spectrum of raw melon husk (MSH) (a) before and (d) after dye adsorption.

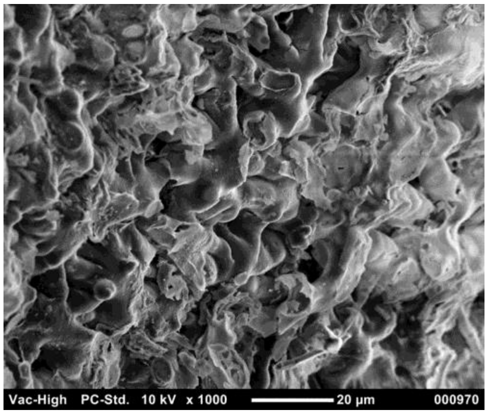


Fig. 3: XRD plot for MSH

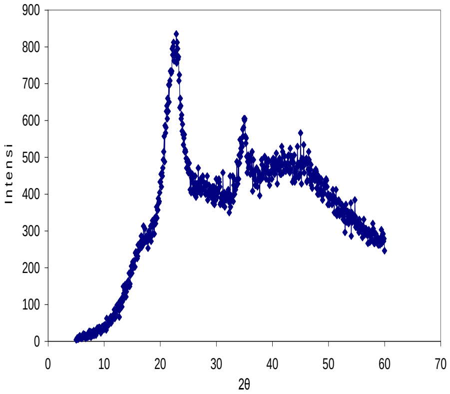


Fig. 4: SEM image of RMH

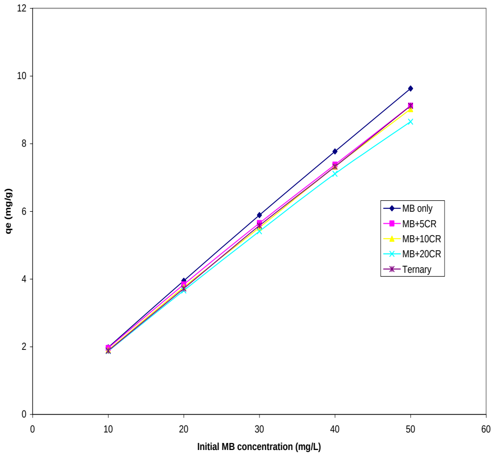


Fig. 5: Effect of initial MB concentrations in single, binary and ternary systems

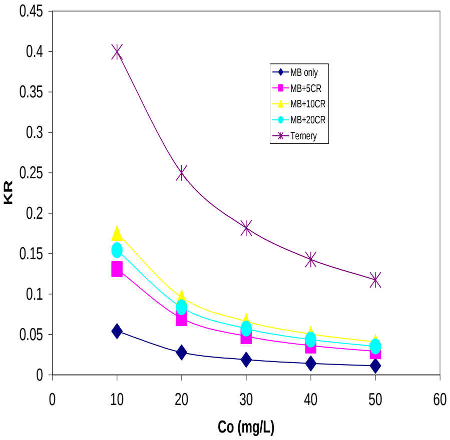


Fig. 6: Plots of K_R against initial MB concentrations in single, binary and ternary systems

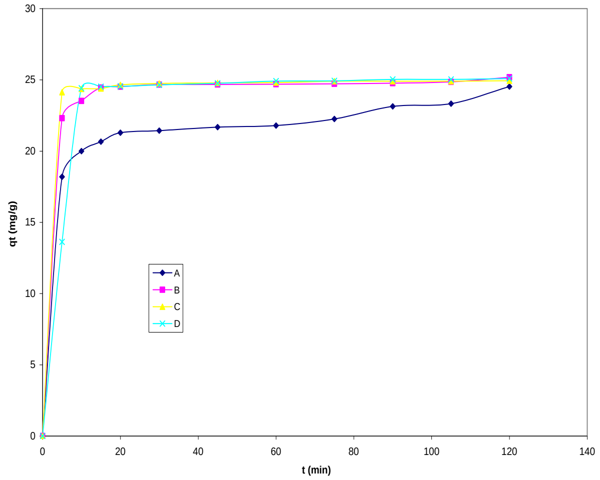
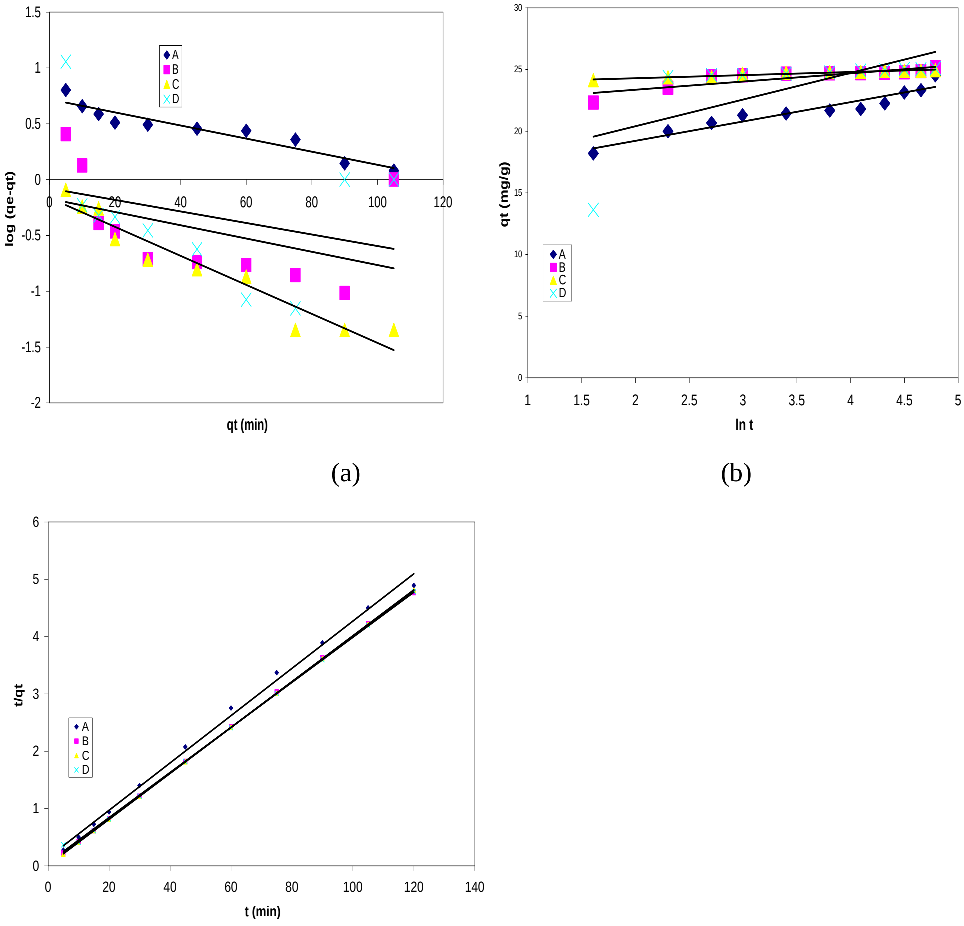


Fig .7: Effect of contact time on MB adsorption onto RMH in SDS and TDS

(A) SDS: ([MB]= 50 mg/L); (B) TDS: ([MB]=50 mg/L; [CR]=10 mg/L and [MO]=10 mg/L); (C) TDS: ([MB]=50 mg/L; [CR]=20 mg/L and [MO]=10 mg/L); (D) TDS: ([MB]=50 mg/L; [CR]=10 mg/L and [MO]=20 mg/L)



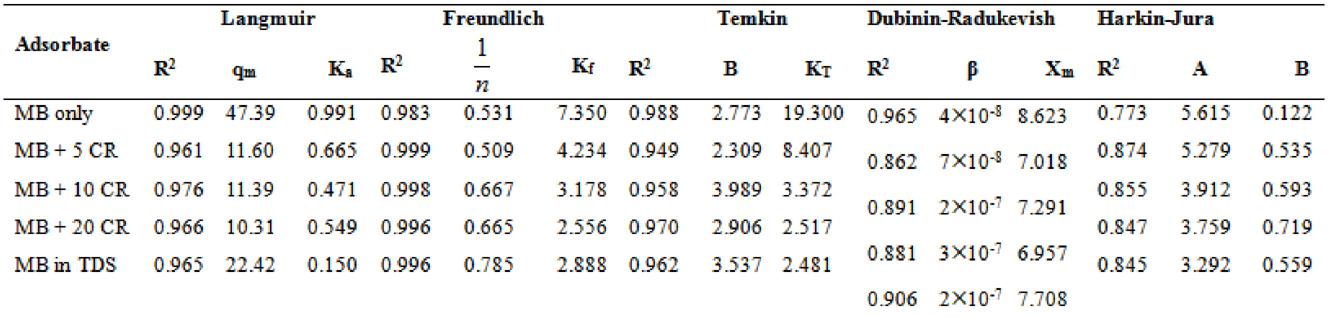
(a)

(b)

(c)

Fig.8: Plots of Pseudo-first order (a), Elovich (b) and Pseudo-second order (c) for the sorption of MB onto MSH

Table 1: Isotherm Parameters for MB Adsorption onto MSH in Single, Binary and Ternary Systems



Adsorbate	Langmuir			Freundlich			Temkin		Dubinin-Radukevish			Harkin-Jura		
	R^2	q_m	K_a	R^2	$\frac{1}{n}$	K_f	R^2	B	K_T	R^2	β	X_m	R^2	A	B
MB only	0.999	47.39	0.991	0.983	0.531	7.350	0.988	2.773	19.300	0.965	4×10^{-8}	8.623	0.773	5.615	0.122
MB + 5 CR	0.961	11.60	0.665	0.999	0.509	4.234	0.949	2.309	8.407	0.862	7×10^{-8}	7.018	0.874	5.279	0.535
MB + 10 CR	0.976	11.39	0.471	0.998	0.667	3.178	0.958	3.989	3.372	0.891	2×10^{-7}	7.291	0.855	3.912	0.593
MB + 20 CR	0.966	10.31	0.549	0.996	0.665	2.556	0.970	2.906	2.517	0.881	3×10^{-7}	6.957	0.847	3.759	0.719
MB in TDS	0.965	22.42	0.150	0.996	0.785	2.888	0.962	3.537	2.481	0.906	2×10^{-7}	7.708	0.845	3.292	0.559

Table 2: Comparison of maximum monolayer adsorption of some adsorbents for methylene blue dye

Adsorbent	q_m (mg/g)	References
MSH	47.39	This work
MSH (in binary system)	11.60	This work
MSH (in ternary system)	22.42	This work
P. Oceanica Fibres	5.56	Ncibi *et al.*, (2007).
Sawdust	19.41	Ansari and Mosayebzadeh (2010)
Langsat peel	45.45	Mohd Salleh *et al.*,(2012)
Rice bran	54.99	Wang *et al.*, (2008)
Polypyrole/Sawdust	34.36	Ansari and Mosayebzadeh (2010)
Palm Kernel Fibre	671.78	Vasanth Kumar *et al.*, (2008)
Walnut sawdust	59.17	Ferrero, (2007)
Oak sawdust	29.94	Ferrero, (2007)
Gulmohar leaf powder	186.22	Ponnusami *et al.*, (2009)
Acid modified calotropis procera leaf powder	192.31	Oyelude and Owusu, (2011)
Hen feathers	134.76	Chowdhury and Saha (2012)
	143.20	Kannan and Sundaran (2001)
Miswak leaves		
Neem Leaf Powder	200	Elmorsi (2011)
	19.61	Bhattacharya and Sharman (2005)

Table 3: Rate and Diffusion Parameters for the Adsorption of MB onto MSH in single, binary and ternary systems

Adsorbate system	**PSEUDO-FIRST ORDER**				**PSEUDO-SECOND ORDER**				**ELOVICH**			**WEBER-MORRIS**		
	$q_{e_{expt}}$	**$q_{e_{mod}}$**	**K_1**	**R^2**	**R^2**	**$q_{e_{mod}}$**	**h**	**K_2**	**R^2**	**α**	**β**	**R^2**	**k_i**	**X_i**
A	24.531	1.511	-0.014	0.908	0.9966	24.213	6.906	0.012	0.914	43879.18	0.637	0.849	0.455	18.803
B	25.182	0.675	-0.014	0.199	0.9999	25.13	37.313	0.059	0.754	1.5×10^{14}	1.502	0.715	0.072	24.186
C	24.944	0.686	-0.029	0.925	1	25	86.957	0.139	0.942	5.85×10^{40}	4.003	0.934	0.041	24.5
D	25.098	0.834	-0.012	0.868	0.9993	25.445	17.794	0.027	0.449	3683.814	0.463	0.970	0.086	24.187

Table 4: Thermodynamics parameters for the adsorption of methylene blue in Single, Binary and Ternary Systems on MSH .

Temperature	Single System			Binary System			Ternary System		
	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS
(K)	($kJmol^{-1}$)	($kJmol^{-1}$)	(J/mol. K)	($kJmol^{-1}$)	($kJmol^{-1}$)	(J/mol. K)	($kJmol^{-1}$)	($kJmol^{-1}$)	(J/mol. K)
303	-7.42	-14.82	-24.50	-7.01	-11.6	-14.8	-6.42	+23.6	+98.7
313	-7.10			-6.84			-7.05		
323	-6.93			-6.71			-8.39		