Adsorptive Removal of Reactive Blue-23 (RB-23) from Aqueous Solutions by Low-Cost Adsorbent and Nano-Particle: Comparative Evaluation.

Shruti S Kubyal[1]
Dr. Manjunath N. T.[2]
1. *Research Scholar - Visvesvarayya Technological University, Belagavi, Karnataka.*
2. *Professor (Retired) University of B. D. T. College of Engineering, Davanagere, 577004, Karnataka.*

Abstract: - The most difficult task is determined to be the treatment and disposal of wastewater from textile mills, particularly colored effluents. Researchers from all around the world have attempted to remediate dye effluents with nanoparticles and inexpensive adsorbents. The investigation conducted to assess the viability of extracting RB-23 from aqueous solution utilizing ZIV (nanoparticles) and rice husk, a low-cost adsorbent, under various experimental circumstances, is presented in this work. Additionally, an effort has been made to fit isotherm models to the experimental data. According to the analysis, the data, within the bounds of statistical significance, fit into both the Langmuir and Freundlich isotherms. Additionally, the data presentation and analysis showed that the pseudo second order kinetic model had a high correlation coefficient and corresponded extremely well with the experimental data. When testing under ideal circumstances, it has been shown that nanoparticles adsorb more color than Rice Husk.

***Keywords**: Textile mill, RB-23, Rice husk, Nano-particles, Isotherms, Kinetics.*

1. Introduction

Many industrial operations, such as those that create rubber, textiles, leather, cosmetics, paper, and food, emit large amounts of dyes into the environment. Out of all of these, the textile industry is the one that uses dyes the most. Globally, a sizable volume of colored wastewater from textile companies and mills is discharged into waterways each. Dyes in water are highly apparent and unsightly even at very low concentrations. The dyes have an effect on aquatic environments because they can prevent photosynthesis in the water. Certain colors can also result in cancer and mutations and are stable against biological deterioration. Therefore, in order to lower the environmental danger, wastewater containing dyestuffs needs to be treated before being released into water bodies.

To remove dyes from colored wastewater, a variety of treatment techniques have been devised and put to use, including chemical, biological, and physical ones. (Sources: Akbari et al., 2002; Amin et al., 2011; Bayramoglu et al., 2009; Khayet et al., 2011; Hsueh et al., 2005; Sarayu et al., 2007; Shaikh et al., 2014). These methods include, among others, ozonation, electrochemical, membrane filtration, coagulation, and advanced oxidation processes. These methods do, however, have advantages and disadvantages. As a result, the adsorption method is now frequently used as an improved replacement. The adsorption method produces non-toxic byproducts and is the most efficient at eliminating color from diluted solutions. It also has a cheap initial cost. Researchers that have studied the ability of cheap adsorbents to remove color using batch and column techniques have shared their findings. Furthermore, Bharathi and Ramesh (2013) included the low-cost adsorbents that have been studied by several researchers, such as peanut hull, sawdust, coir pith, orange peel, rice husk, and leaf powder.

Nanotechnology has received a lot of attention lately, and numerous publications have described the use of different nanoparticles for the treatment of colored effluents. According to the researchers' deductions, nanomaterials have greater dye removal capacities, vast surface areas, and atoms that are available for chemical reactions. (Kulkarni et al., 2016; Daniel and Shobha, 2015; Nidhi et al., 2016; Abiyu et al., 2016; Arafat et al., 2015; Anitha et al., 2015).

This study presents the findings from studies on the assessment of the adsorption potential of nanoparticles (ZIV) and low-cost adsorbents (rice husk) in the decolorization of RB23 from aqueous solution. Adsorption kinetics and isotherms were also investigated.

2.0 Materials and Methodology

2.1 Preparation of Synthetic Coloured Samples

RB23, a dye that is sold commercially, was acquired from Colortex. One gram of dye was dissolved in one thousand milliliters of double-distilled water to create a thousand mg/l stock solution. Double-distilled water is used to dilute the calculated amount of stock solution in order to prepare additional working solutions or concentrations.

2.2 Preparation of Rice Husk Adsorbent

The naturally occurring rice husk, also known as paddy waste, was gathered and processed using the method described by Oidde et al (2009). The actions taken are outlined below. To remove waste materials like dust, stones, dirt, etc., the gathered rice husk was washed. After being cleaned, the rice husk was rinsed with distilled water and allowed to air dry. 300 micron-sized particles are obtained by sieving the dried material. The 300 micron-sized rice husk particles were activated for 24 hours with 10% nitric acid, then washed with distilled water and baked at 1050 degrees Celsius.

2.3 Synthesis of ZIV Nano particle

The nano ZIV in ethanol medium was created by dissolving 5.406 g $FeCl_3.6H_2O$ and vigorously stirring it in a 4/1 (v/v) ethanol/water mixture (240 ml ethanol + 60 ml deionized water) in a 1-liter beaker with sodium borohydride acting as a reducing agent. The atmosphere was used to do this process. But only a 0.1 M sodium borohydride solution (that is, 3.783 g of $NaBH_4$ dissolved in 1000 ml of deionized water) was produced; additional borohydride is needed to produce more iron nanoparticles. The iron chloride solution was aggressively agitated at 670 revolutions per minute while the borohydride solution was gradually added using a burette. When the first drop of sodium borohydride solution was added, black solid particles immediately formed; this prompted the addition of sodium borohydride in its entirety to expedite the reduction reaction. The mixture was agitated for ten more minutes after the full borohydride solution was added. The black iron nanoparticles were extracted from the liquid phase by filtering two sheets of Whattman filter paper using the vacuum filtering technique. The solid particles were washed three times with 25 ml portions of 100% ethanol in order to remove all of the water. Since the washing process halts the rapid oxidation of zerovalent iron nanoparticles, it is perhaps the most significant stage in the synthesis process. Finally, the generated nanoparticles are allowed to dry for a full

3. Batch Studies

The batch investigations were carried out at room temperature in an open environment. A 100 ml aqueous colored sample with a certain color concentration was placed in a 250 ml stoppered conical flask that was dry and clean. The sample's pH was changed by adding acid or alkali. The predetermined amount of adsorbent was added to the flask. Using the glass rod, the flask's contents were first swirled. After that, the ingredients were stirred for a predetermined (variable) amount of time at 140 rpm in a shaker. After that, the dye solutions were centrifuged at 300 rpm for five minutes. Following the pipetting out of the clear solution, the adsorbance at a wavelength optimal for a certain hue was measured using a spectrophotometer to ascertain the rate of decolorization. The percentage of dye decolorization was obtained from the calibration curve of the dye solution. Every color and adsorbent combination was evaluated again, along with the pH, stirring time, and adsorbent dosage. The % of dye/color removal was calculated using the relationship below.

$$\% \text{ dye removal}=(C_i-C_e)100/C_i$$

where C_i and Ce denote, respectively, the dye's beginning and ending concentrations.

Further kinetics of adsorption were determined by using following mass balance equation.

$$q_e=(C_i-C_e)V/m$$

where V is the volume of sample, l
m- weight of the adsorbent, g

3.1 Measurement of decolourization

Using a spectrophotometer, the treated colored samples from batch and continuous column investigations were examined.

The percentage of adsorptions for known color concentrations at specified wavelengths for a given color using a spectrophotometer. The ideal wavelengths for the colors taken into consideration for the current study, RB23, were nm. Calibration curves (color intensity vs. % adsorption) were created using this data. The spectrophotometer was used to store the samples for analysis, and the percentage of adsorption was noted. The color intensity was read from the calibration curve in accordance with the reported percentage of adsorption. By knowing the colors of the influent and effluent concentrations, the removal efficiency was further computed.

4. Results and Discussions

To assess the adsorption of RB23 onto Rice Husk and ZIV under various experimental circumstances, batch tests were carried out. The removal effectiveness of RB23 at constant pH-7 was tested for the effects of initial dye concentration (15, 30, 45, and 60 mg/l), adsorbent dosage (Rice husk: 50, 70, and 90g; ZIV: 50, 70, and 90 mg), and stirring duration (40, 60, 80, and 100 min). Bar charts and linear graphs are used to illustrate the experiment results (fig 1 to 8).

Based on the analysis of experimental data the following inferences are drawn.

4.1 Effect Of Adsorbent Dose

It has been noticed that as adsorbent dosage increases, color removal increases. More surface area and more adsorption sites being available at larger adsorbent dosages are the reasons for this.

4.2 Effect Of Stirring Time

According to the data, 80 minutes was enough to reach equilibrium and that the adsorption of RB23 increased with an increase in contact time. Adsorption does not greatly increase with further time. This is because there were initially more empty sites available. The reason for this is that the adsorbent molecules on the solid and bulk phases are repulsed by one another.

4.3 Effect Of Initial Concentration

According to the reported experimental observations, the proportion of dye removed decreased as the dye concentration increased. In comparison to samples with greater initial dye concentrations, the percentage of adsorption was higher at lower concentrations because nearly all of the adsorbate in the solution could interact with the binding sites. Even lower initial dye concentration provides the push to overcome the obstacle to dye mass transfer between the aqueous and solid phases. Many researchers have seen and recorded such trends in the process of removing dyes from wastewaters (Meena Soni et al : 2012, Shivakumar et al : 2012, Velmurugan et al : 2010, Hamid et al : 2014, Subha& Nanasivayam : 2009).

52.5% is the minimum color removal achieved by rice husk, with the following experimental variables: The maximum removal effectiveness of 82.6% is obtained at the optimal dose of adsorbent (tried) of 90g, stirring time of 100 min, and initial dye concentration of 15 mg/l. Adsorbent dosage of 50g, initial color concentration of 60 mg/l, and stirring time of 20 min.

Under the same testing conditions, but with an adsorbent dosage of 50 mg and 90 mg, respectively, the minimum and maximum removal efficiencies with ZIV nanoparticles are determined to be 63.5% and 89.3%.

Furthermore, the outcomes amply demonstrated the potential of nanoparticles. ZIV is much higher when adsorbing RB23 than when using rice husk, a traditional, less expensive adsorbent. Additionally, ZIV has demonstrated better removal efficiency at low dosages (90 mg) than rice husk at larger dosages (90 g). Because of their small size in comparison to other typical adsorbents, nanoparticles have a relatively large surface area, which is the reason for this. The unique crystal forms and lattice organization of the nanoparticles also contribute to their increased chemical reactivity. Due to the high-energy adsorption sites they contain, nanoparticles offer superior binding energies or interaction potentials for physisorption than conventional adsorbents (Dharmenra et al., 2008, Dave and Sharma, 2015, Gayatri et al., 2012).

4.4 Adsorption Isotherms

The adsorption isotherm models explain the sorption mechanism, surface properties, and affinity of the adsorbent. The Langmuir and Freundlich equilibrium models are the two that are most commonly used. The Langmuir isotherm can be expressed as

$$C_e/q_e=(1/q_{max})R_L+(1/q_{max})C_e$$

where qe is the amount of adsorbate in the adsorbent at equilibrium (mg/g), Ce is the equilibrium concentration (mg/l), and qmax and RL are the Langmuir isotherm constants related to free energy. The previous equation can be linearized to get the maximum capacity, or qmax, by plotting Ce/qe vs. Ce. The characteristics of the equilibrium parameter, RL, a dimensionless constant, or the Langmuir isotherm, are defined as follows: RL=(1/1+bc0), where b is a Langmuir constant (found from the graph) and C0 is the initial dye concentration (mg/l). An RL value between 0 and 1 indicates good adsorption.Additionally, the following equation represents the Freundlich isotherm's linear form:

$$\log q_e= \log K_f+1/n \log C_e$$

where the slope (1/n) and intercept (K_f) of the straight line plot of logqe vs. logCe serve as constants. The favorable adsorption process is represented by 1/n values less than 1.

Figures 9 to 11 display the Langmuir and freundlich plots for the rice husk and ZIV under investigation. Additionally, the correlation coefficients R^2 and the Langmuir and Freund constants are shown in Tables 1 and 2.

The obtained ZIV and rice husk RL values, which are 0.491 and 0.309, respectively, demonstrate the isotherm shape that is ideal for color adsorption onto both materials. It follows that the experimental data were consistent with the Langmuir model. Furthermore, color adsorption is advantageous under the examined conditions, as indicated by 1/n values between 0 and 1 (Freundlich).

These numbers, along with the R2 values that were found (which were almost 1.0), suggest that, within the bounds of statistical significance, the experimental data fit into both isotherms.

4.5 Adsorption Kinetics

By analyzing the kinetic adsorption data, the adsorption process's kinetics were examined. The study of adsorption kinetics provides a description of the solute uptake rate. The several kinetic models that are available to study the controlling mechanism of the adsorption process and understand the behavior of the adsorbents. In the current work, the kinetic data were analyzed using the pseudo first order and second order kinetic models.

Equation for pseudo first order kinetic model is:

$$\log(q_e-q_t)=\log q_e-k_1t/2.303$$

where qe is the adsorption capacity at equilibrium (mg/g), qt is the amount of adsorbate adsorbed at time t (mg/g), and k1 is the pseudo first order rate constant (min–1). The log (qe-qt) verses t plot's slope and intercept have a linear connection that provides qe and k1, respectively.

Second order kinetics' linear form is written as

$$t/q_t=1/k_2q_e^2+t/q_e$$

Again slope and intercept of the plot of t/q_t verses t gives q_e and k_2 respectively.

The comparison of qe produced via graph with experimental data determines whether the adsorption process obeys first or second order kinetics. The kinetic models are considered to be obeyed if these values are comparable within the statistical bounds.

Figures 12 and 13 display pseudo first and second order kinetics plots. Table 3 presents the constants (k_1 & k_2) that were computed from graphs and R2 in addition to the qe values (from the graph and the experiment).

Table 3's values indicate that the pseudo first order model is not well-fitting. However, with the pseudo second order kinetic model, the uptake capacities matched the experimental data quite well, and the R2 values were also found to be significantly higher than those of the pseudo first order kinetics. The adsorption of the color by both traditional adsorbent and nanoparticle is thus inferred to be properly characterized by the pseudo second order reaction rate mode, which has a strong correlation coefficient and, consequently, the chemical adsorption process discovered to govern the adsorption rate.

5. Conclusions

The following conclusions are reached in light of the findings of the current studies and the conversations that followed. The decrease in removal efficiency indicates that the adsorption capacity of RB23 by both adsorbents decreases as the starting color concentration Co increases. The highest elimination is noted for CO concentrations of 15 mg/l. There is a clear correlation observed between the adsorbent dosage, stirring time, and removal efficiency. It is found that nanoparticle ZIV has a higher capability for color adsorption than rice husk. The freundlich and Langmuir isotherms were consistent with the experimental results. Second order kinetics was likewise followed by the outcomes.

Table 1: Langmuir Constants

Adsorbent	q_{max}	b(l/mg)	R_L	R^2
Rice Husk	8.584	0.069	0.491	0.9852
ZIV	7.716	0.149	0.309	0.9757

Table 2: Freundlich Constants

Adsorbent	K_f(mg/g)	1/n	R^4
Rice Husk	0.7373	0.675	0.9959
ZIV	1.195	0.5838	0.9736

Table 3: Kinetic Constants

Kinetic	Adsorbent	K_1	K_2	q_e(mg/g)		R^2
				From Graph	Experimental	
Pseudo First order	Rice Husk	0.859	-	0.861	1.346	0.8191
	ZIV	0.562	-	0.562	1.461	0.8875
Pseudo second order	Rice Husk	-	0.075	1.370	1.346	0.9952
	ZIV	-	0.067	1.490	1.461	0.9944

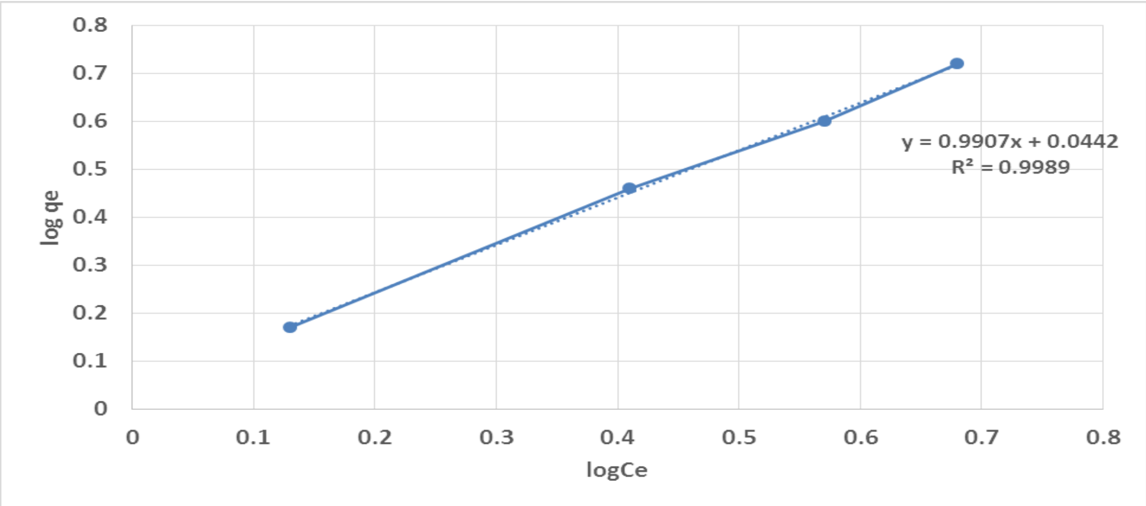

Fig 9: Freundlich Isotherms Plots for RB23, RH

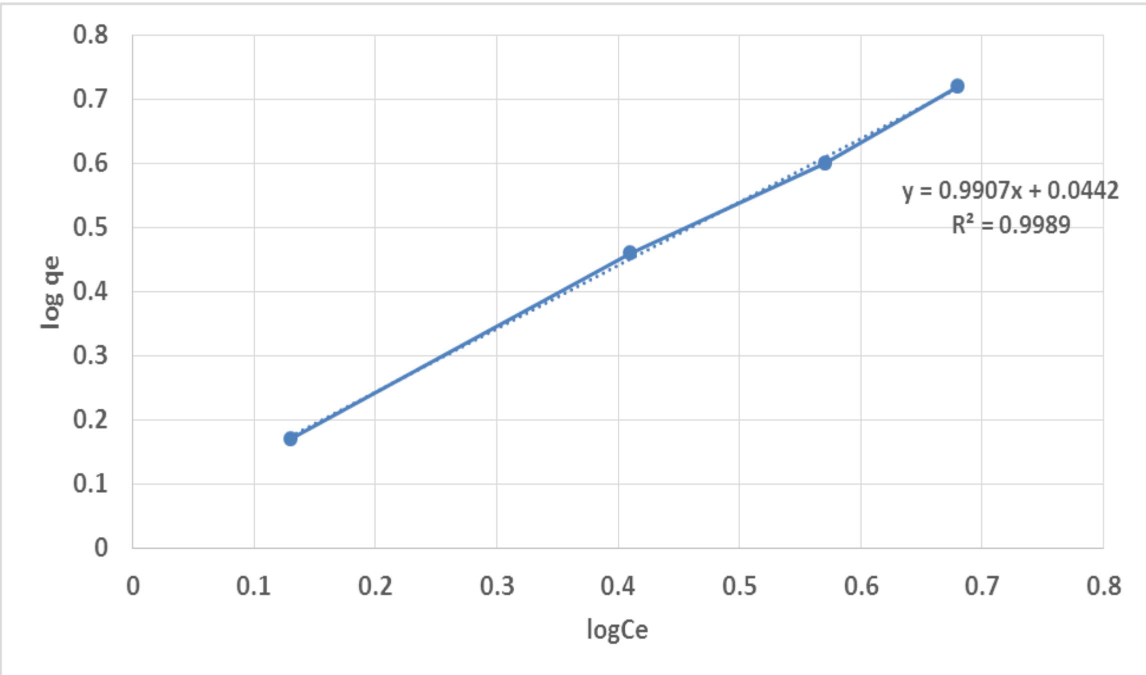

Fig 10: Freundlich Isotherms Plots for RB23, ZIV

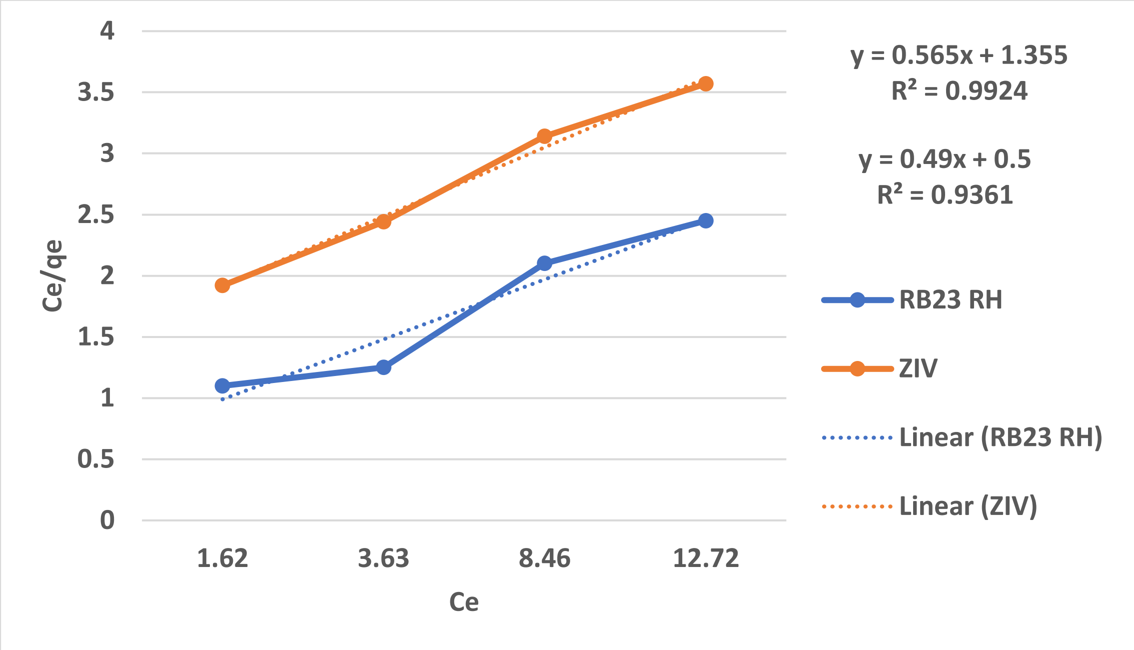

Fig 11: Langmuir Isotherms Plots for RB23

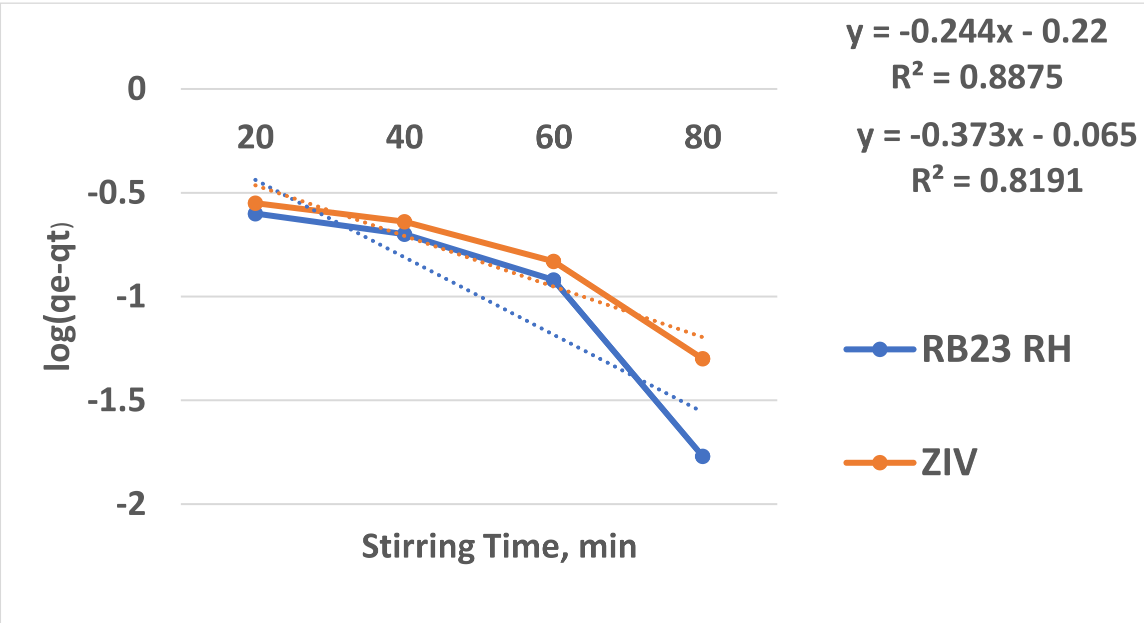

Fig 12: Pseudo First order plots for RB23

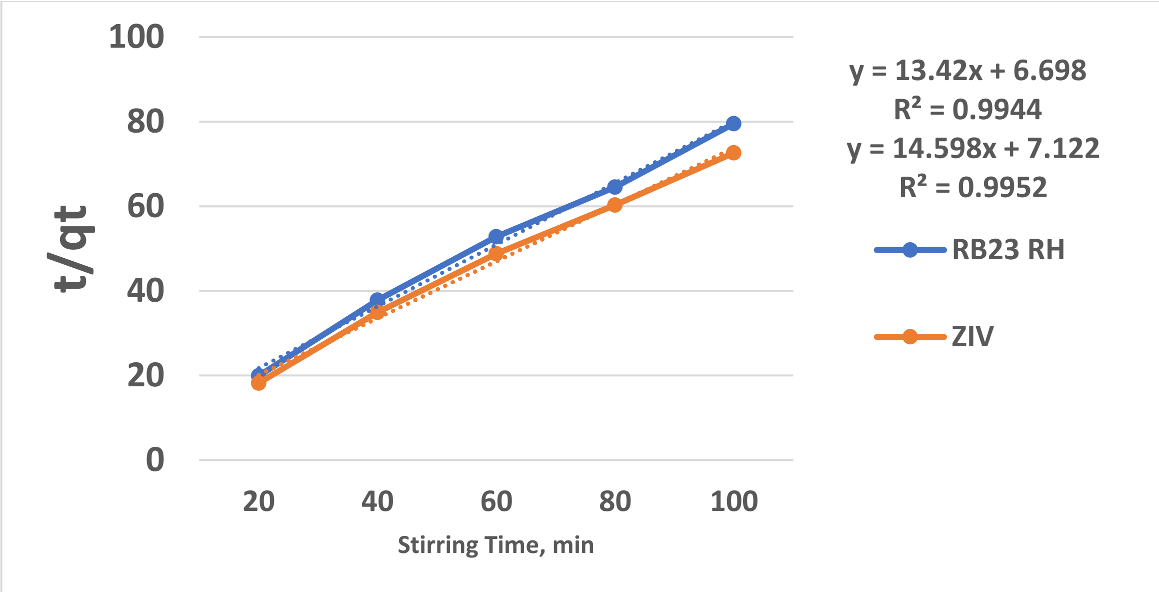

Fig13: Pseudo Second order plots for RB23.

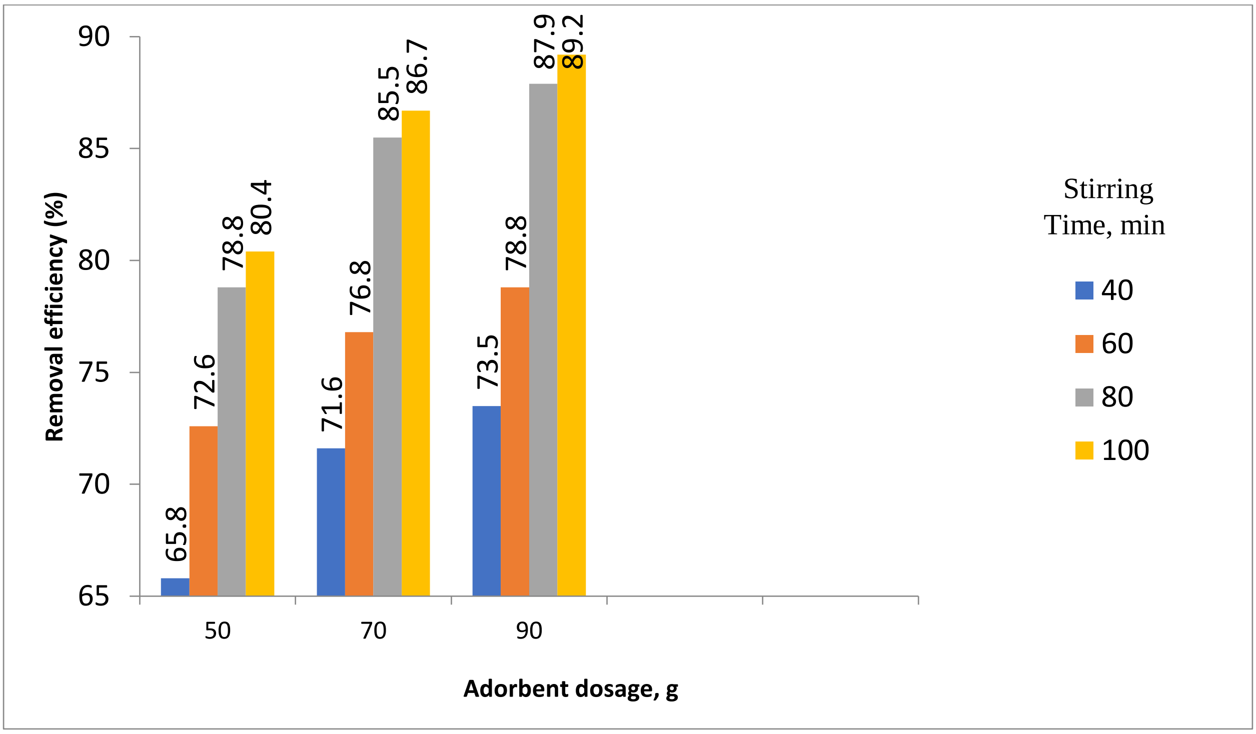

Fig 1: Effect Of adsorbent dosage on removal of RB23 by ZIV.
(C_0=15mg/l)

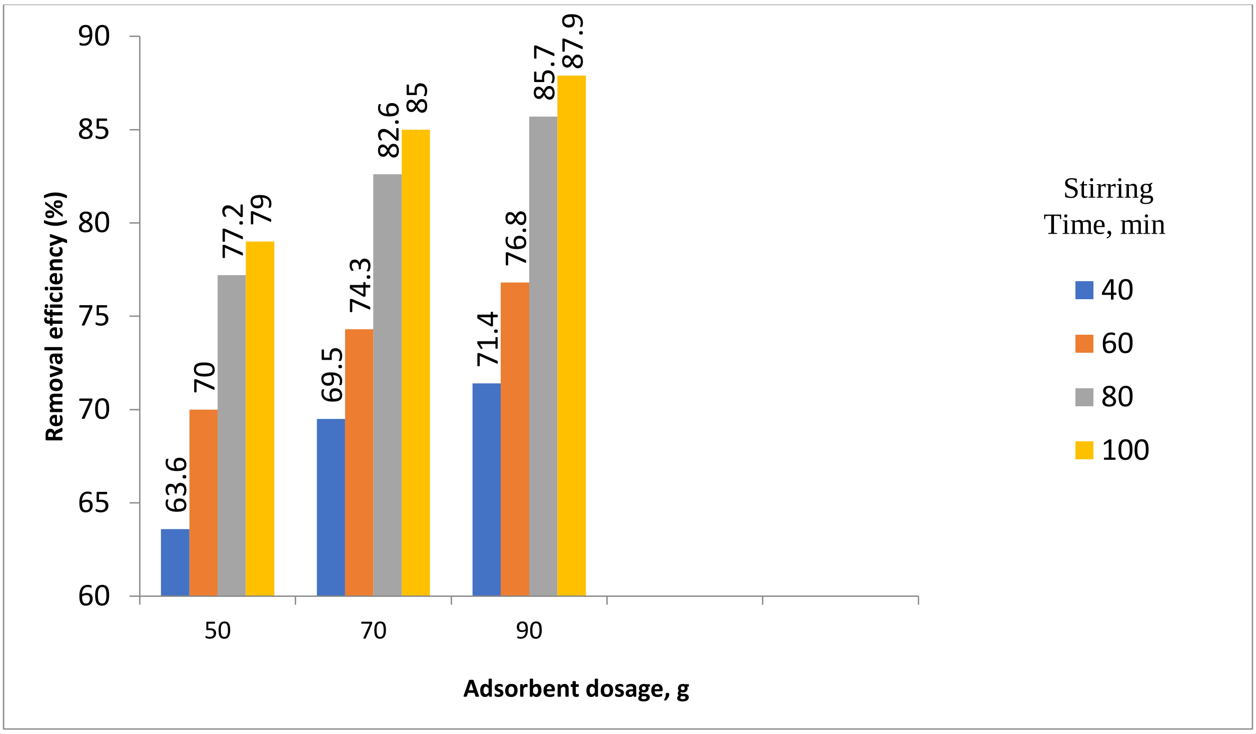

Fig 2: Effect Of adsorbent dosage on removal of RB23 by ZIV.
(C_0=30mg/l)

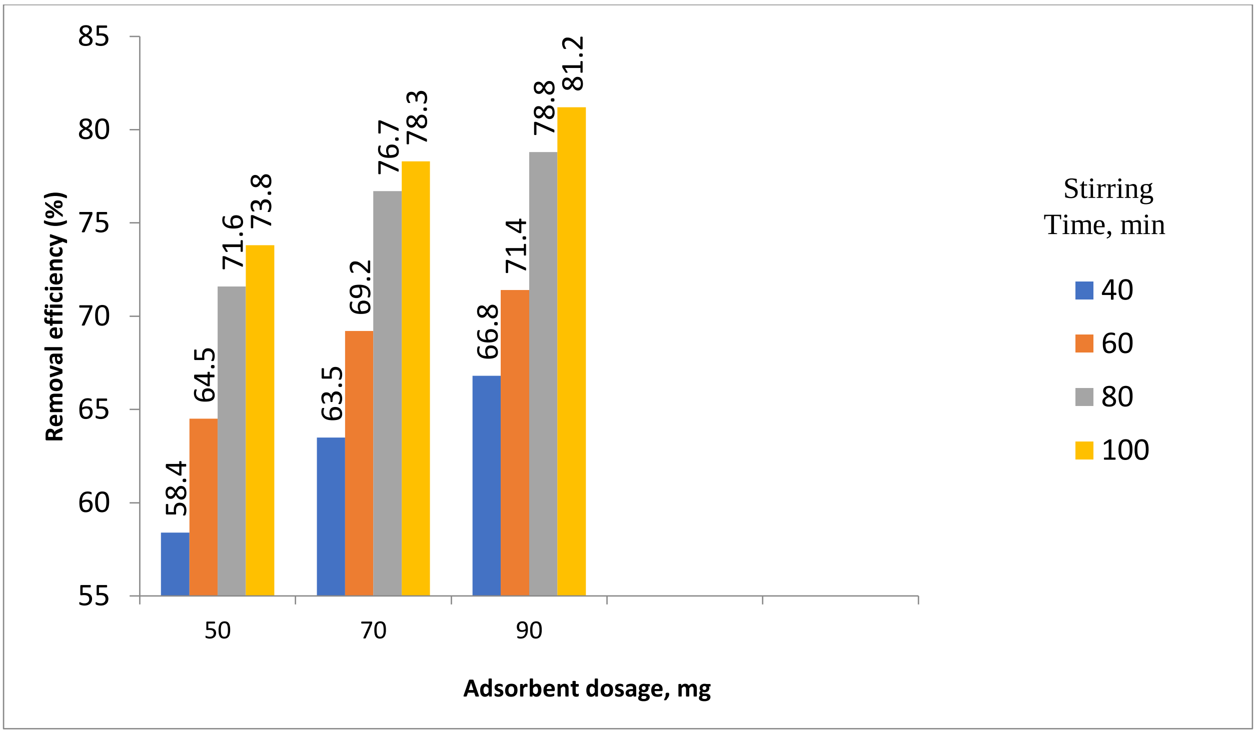

Fig 3: Effect Of adsorbent dosage on removal of RB23 by ZIV.
(C_0=45mg/l)

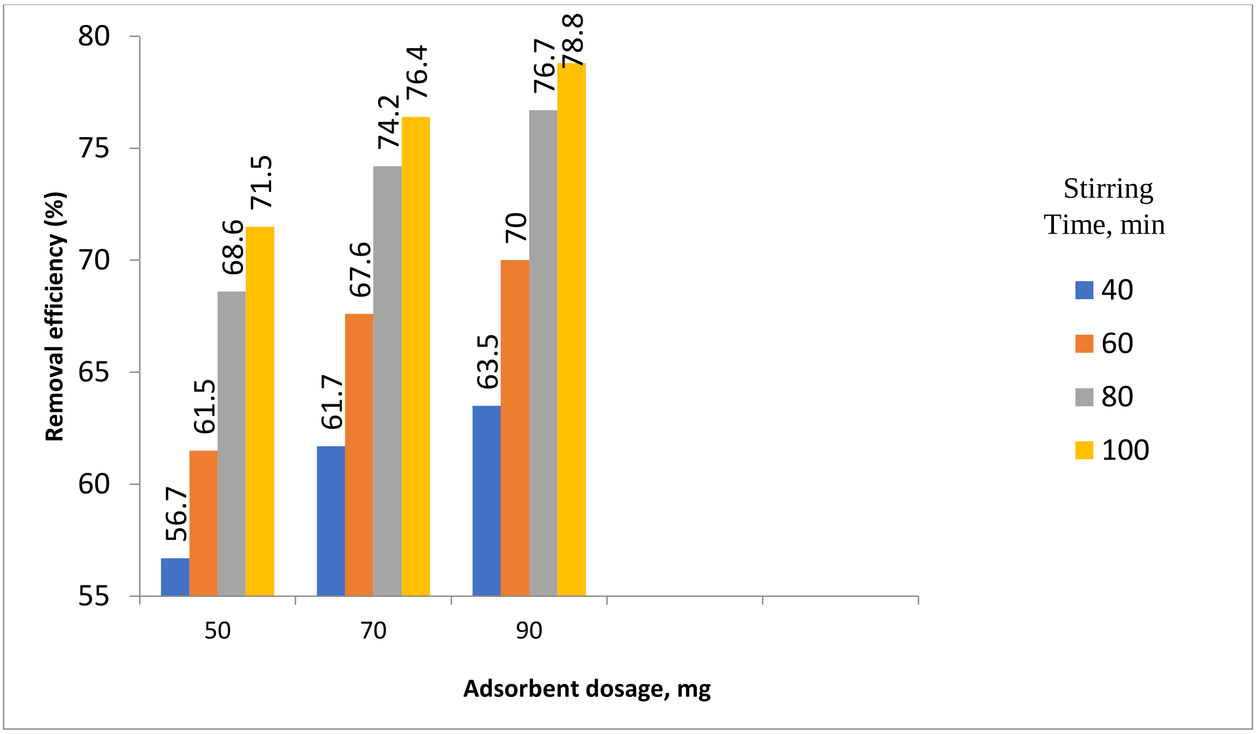

Fig 4: Effect Of adsorbent dosage on removal of RB23 by ZIV. (C_0=60mg/l)

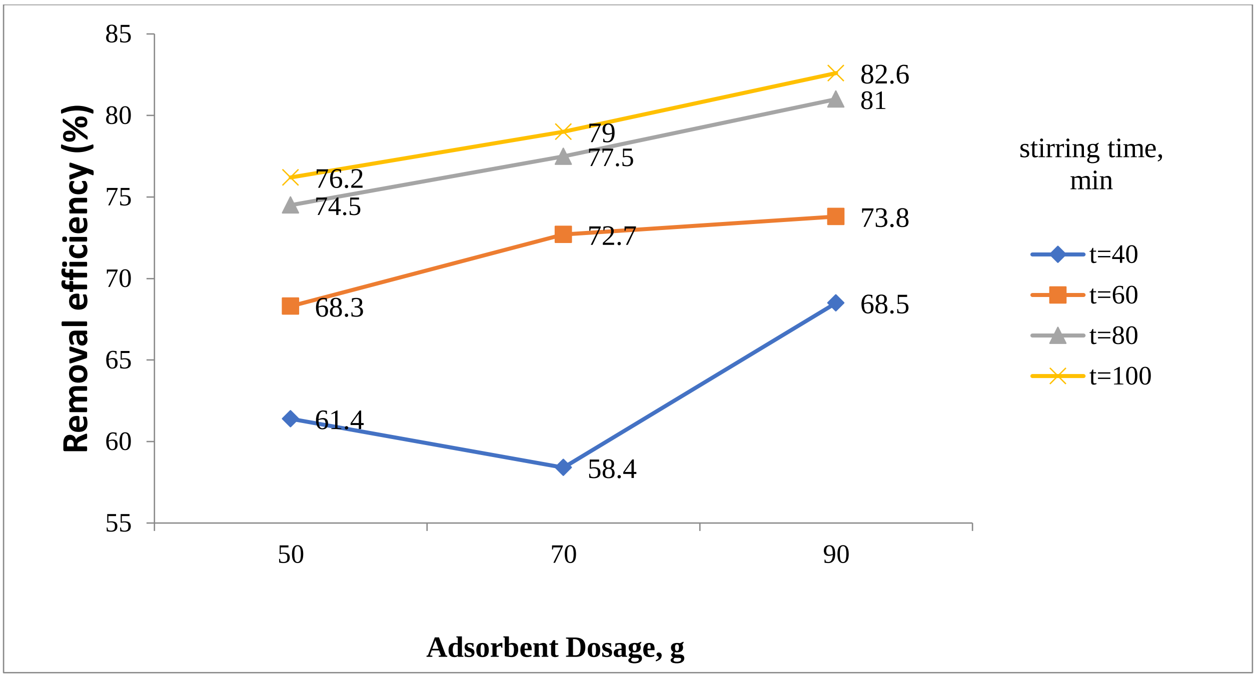

Fig 5: Effect Of adsorbent dosage on removal of RB23 by RH. (Co=15mg/l)

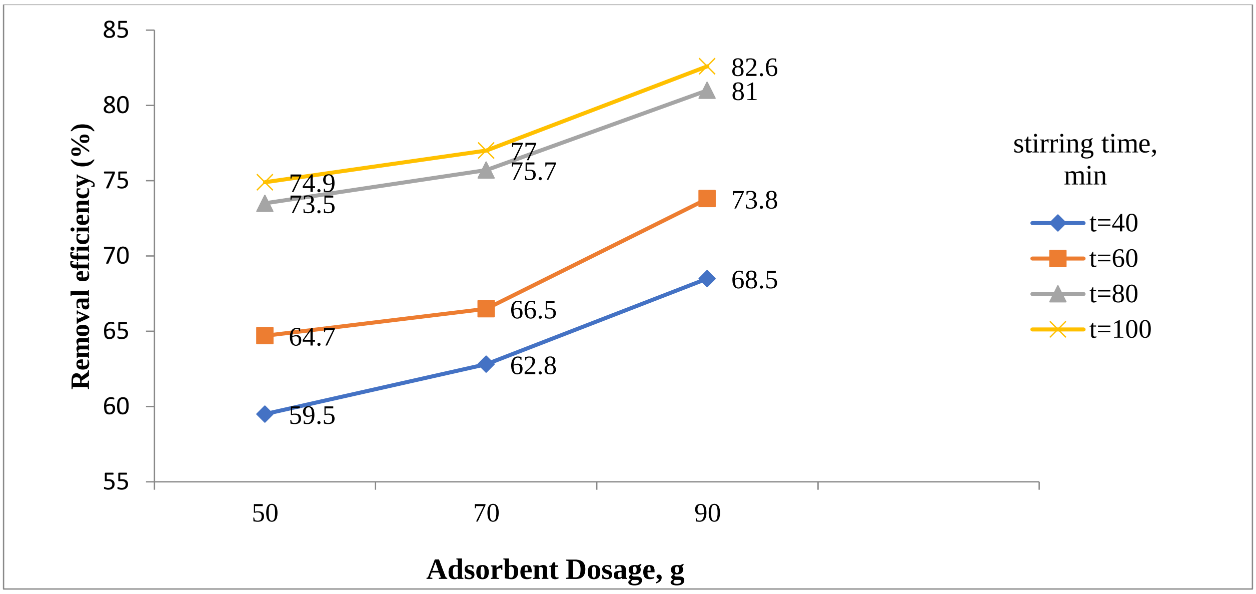

Fig 6: Effect Of adsorbent dosage on removal of RB23 by RH. (Co=30mg/l)

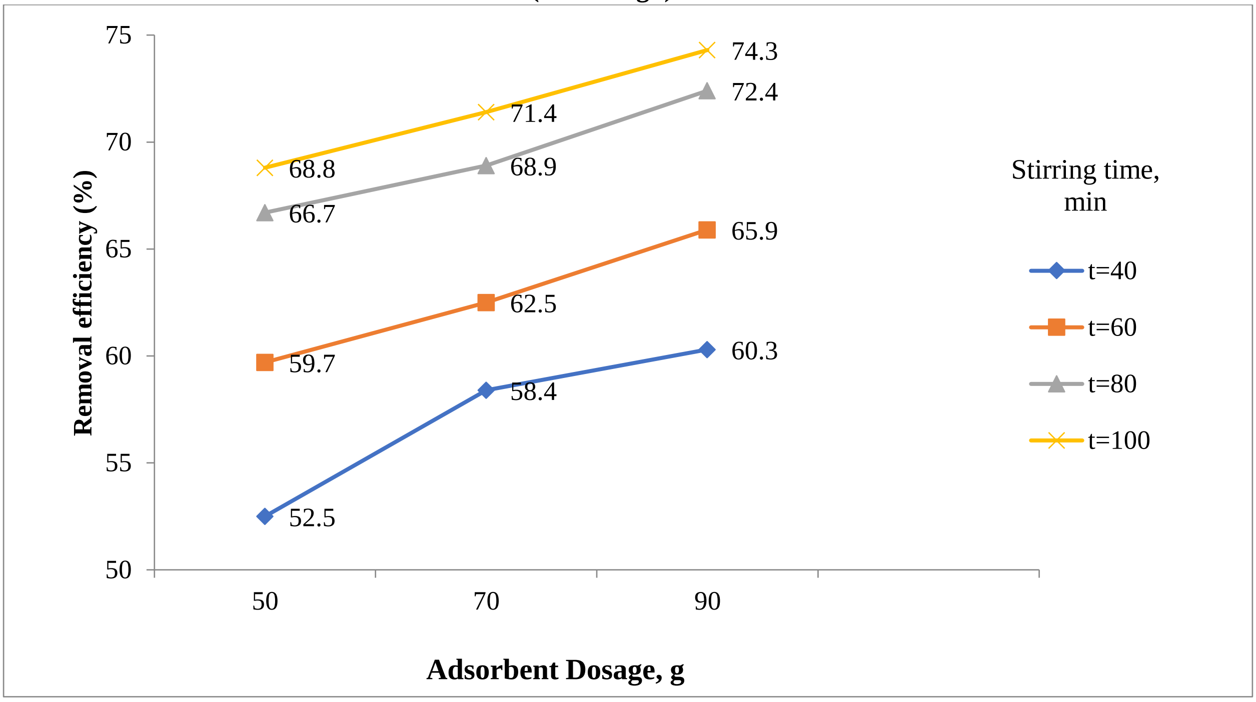

Fig 7: Effect Of adsorbent dosage on removal of RB23 by RH. (Co=45mg/l)

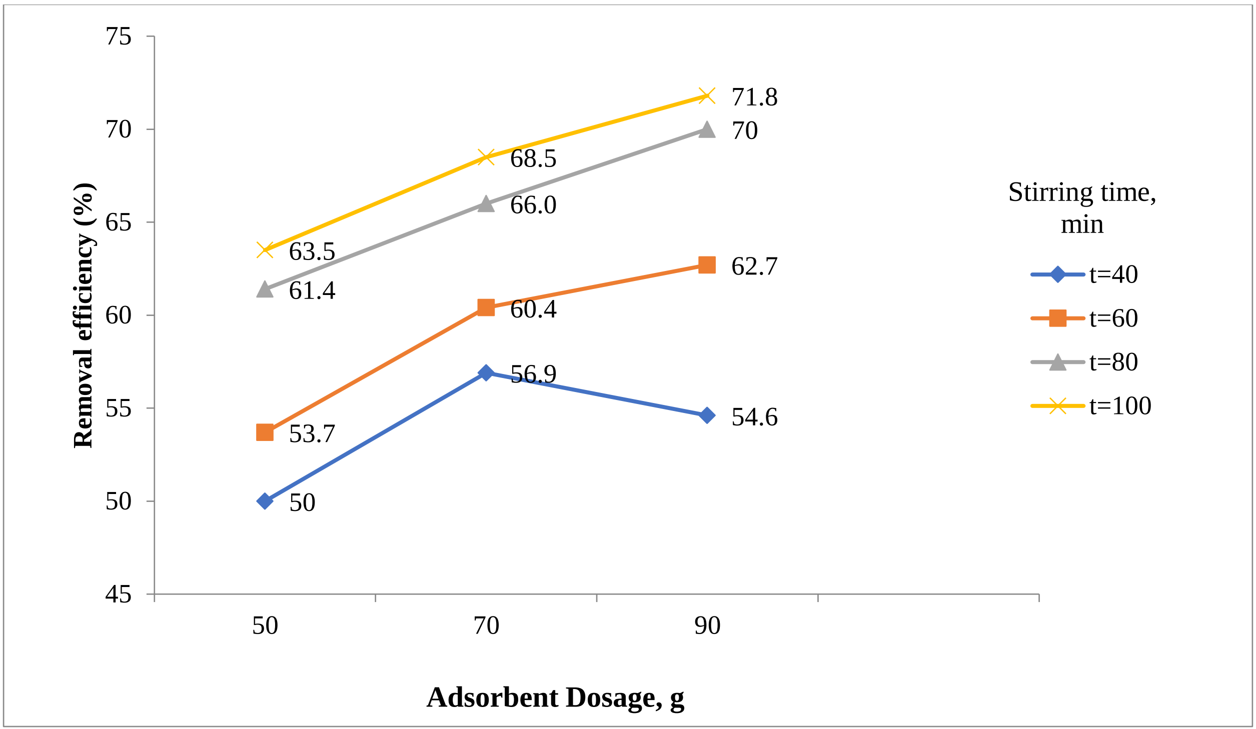

Fig 8: Effect Of adsorbent dosage on removal of RB23 by RH. (Co=60mg/l)

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