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Prediction of Binding Free Energies for Dyes Removal Using Computational Chemistry

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***Abstract*—**Dye removal is an environmental concern because the textile industries have been increasing by world population and industrialization. Adsorption is the technique to find adsorbents to remove dyes from wastewater. This method is low-cost and effective for dye removal. This work tries to develop effective adsorbents using the computational approach because it will be able to predict the possibility of the adsorbents for specific dyes in terms of binding free energies. The computational approach is faster and cheaper than the experimental approach in case of finding the best adsorbents. All starting structures of dyes and adsorbents are optimized by quantum calculation. The complexes between dyes and adsorbents are generated by the docking method. The obtained binding free energies from docking are compared to binding free energies from the experimental data. The calculated energies can be ranked as same as the experimental results. In addition, this work also shows the possible orientation of the complexes. This work used two experimental groups of the complexes of the dyes and adsorbents. In the first group, there are chitosan (adsorbent) and two dyes (reactive red (RR) and direct sun yellow (DY)). In the second group, there are poly(1,2-epoxy-3-phenoxy) propane (PEPP), which is the adsorbent, and 2 dyes of bromocresol green (BCG) and alizarin yellow (AY).

***Keywords*—**Dye removal, binding free energies, quantum calculation, docking.

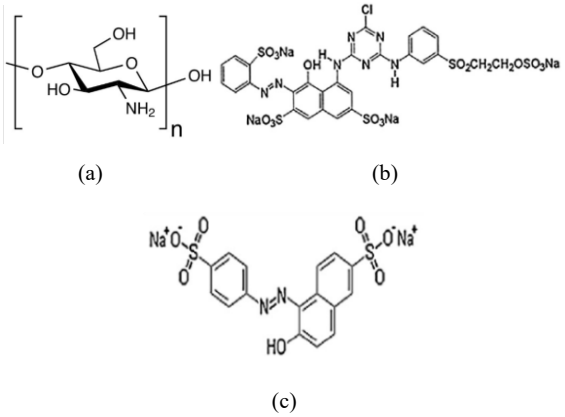
I. Introduction

CURRENTLY, environmental problems have been dramatically increasing because of expansion of population and industrialization. Two thirds of dyes produced in the world are used by textile industries and discharged to stream resulting in wastewater [1]. Therefore, it is very challenging to solve the wastewater problems due to dye effluents because of theirs toxicity and harm for human health.

Experimental researchers have been proposing many techniques [2], [3] to remove dyes from the effluents. One of the efficient and well-known methods is adsorption because this method is not complicated and low-cost [4]. The principle of adsorption is to find the efficient adsorbents for dyes removal. Therefore, computational approach [5] can be an alternative way to help the experimental researcher to predict the possibility of the adsorbents that prefer to bind specific dyes [6].

This work has been trying to predict whether the binding free energies (ΔG) obtained from computations [7] can be ranked as same as experiments results. This work have selected the experimental results of dyes-adsorbent complexes from [6] and [8] to be references and compare to our computational approach. To test our computed results in this work, two testing sets of experimental data have been compared. First set is the chitosan (CS) used for removing of RR and DY [6]. Second set is the modified PEPP used for removing BG and AY [8].

According to the experimental data [6], [8], CS and PEPP are polymers which are derived from deacetylation of chitin and modification of PEPP with diethanol amine, respectively. The obtained ΔG of the first sets are -2.56 and -1.96 kcal/mol for CS-RR and CS-DY, respectively. The obtained ΔG of the second sets are -12.29 and -8.52 kcal/mol for PEPP-AY and PEPP-BCG, respectively. The 2D structures for the first set [6] and the second set [8] are shown in Figs. 1 and 2, respectively.



(a) (b)

(c)

Fig. 1 (a) CS; (b) Reactive red 198 (RR); (c) Direct sun yellow (DY)

II. Computational Approaches

A. Generate Starting Structures

The 3D starting structures of four dyes and two adsorbents are built from Avogadro program [9]. Since, these structures were obtained from Avogrado which were not been optimized. Therefore, there were following two steps for optimization of these structures. First, the optimization has been performed by quantum calculations based on basis set of HF/6-31G(d,p). Second, the first optimized structures have been continuously performed by quantum calculations based on basis set of B3LYP/6-31+G(d,p) to get the better precision. All obtained

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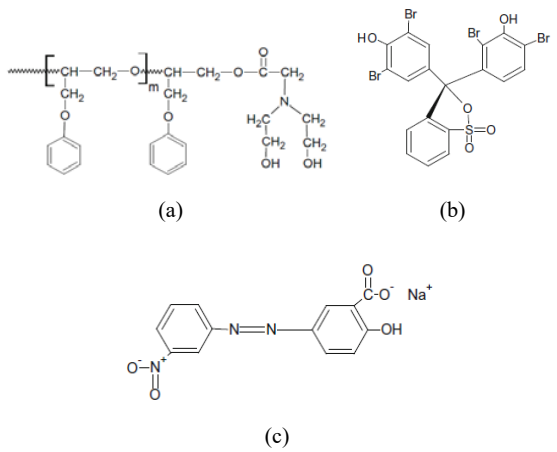
optimized structures have been shown in Fig. 1.



(a) (b)

(c)

Fig. 2 (a) Modification of PEPP (b) Bromocresol green (BG) (c) Alizarin yellow (AY)

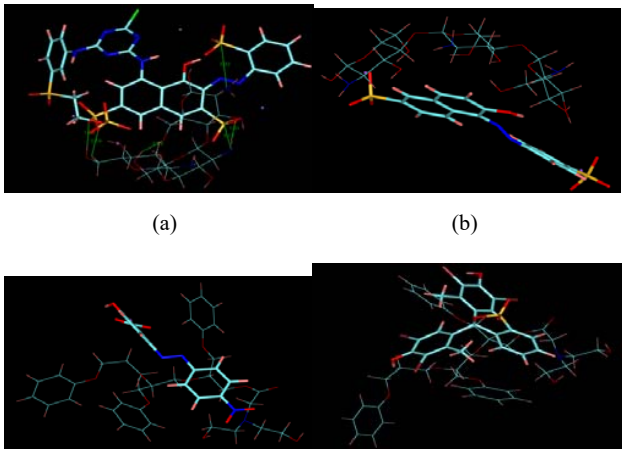
B. Generate Dyes Complexed with Adsorbents and Binding Free Energies by Docking

The optimized structures from Section II *A* were converted from Gaussian output files to the PDB file format using Avogadro program. Then, all PDB files were opened and saved in the PDBQT file format in AutoDockTools (ADT) which is the molecular graphical visualization tool. In our work, the adsorbents and dyeswere set as the receptor and ligand, respectively, in ADT. The condition to generate grid map was set to 60 X 60 X 60 points with spacing of 0.375 Å based on AutoGrid program. AutoDock program [10] was used to search conformation and calculate binding free energies based on Lamarckian genetic (LGA) algorithms. The population and energy function evaluation were set to 50 individuals and 2.5 x 105 with 27,000 for maximum number of generations. We followed the methods of Chen et al. [11].

III. Results and Discussion

A. Orientations of the Dyes and Adsorbents Complexes obtained from Docking

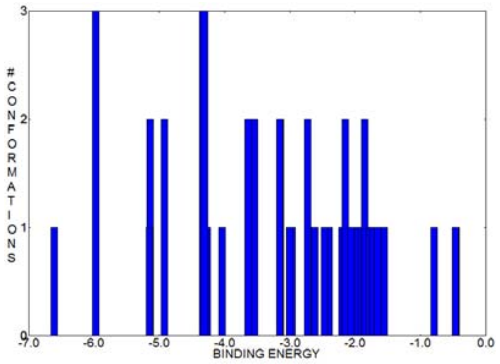
The docking program provides the orientations of the complexes (lowest ΔG values from docking) between dyes and adsorbents which are shown in Fig. 3. The stick and line represent the dye and the adsorbents, respectively. The blue, cyan, red, yellow, green, purple, and pink atoms are nitrogen, carbon, sulphur, chorine, sodium, and hydrogen, respectively. Figs. 3 (a) and (b) represent the CS-RR and CS-DY, respectively. It appears that the CS-RR has H-bonding and π–π interactions [12] while the CS-DY has only π–π interactions. The H-bond interactions of CS-RR are located in the green lines. Figs. 3 (c) and (d) show the PEPP-AY and PEPP-BG interactions, respectively, which are found only π–π interaction.



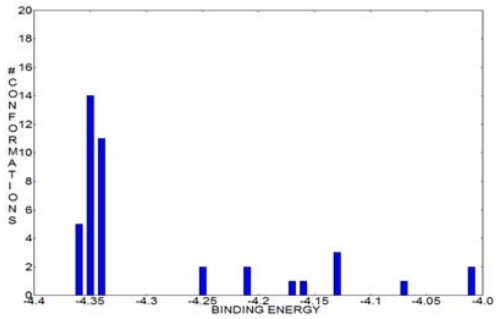
(a) (b)

(c) (d)

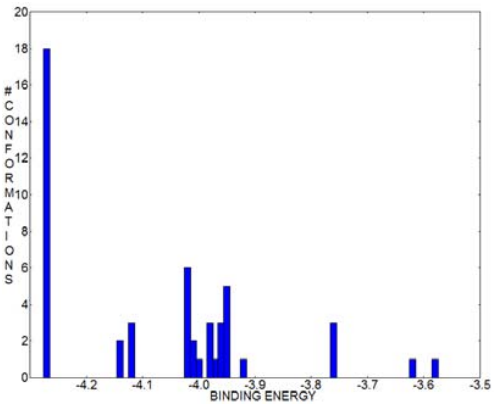
Fig. 3 The obtained structures from docking (a) CS (line) and RR (stick) (b) CS (line) and DY (Stick) (c) PEPP (line) and AY (Stick) (d) PEPP (line) and BG (Stick)



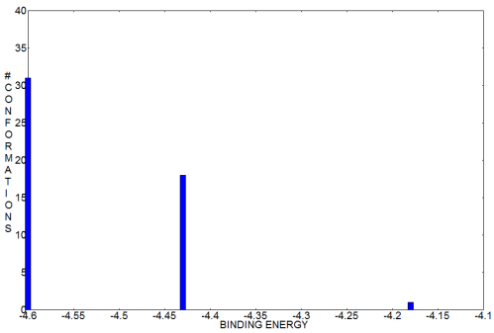
(a) CS-RR



(b) CS-DY



(c) PEPP-BG



(d) PEPP-AY

Fig. 4 Number of conformations (*Y* axis) and □G (*X* axis) for CS-RR, CS-DY, PEPP-BG, and PEPP-AY

C. Binding Free Energies of the Dyes and Adsorbents Complexes obtained from Docking

There are 50 values of ΔG from docking results for each complex as show in the following histogram (Y axis: number of conformation, X axis: ΔG) in Figs. 4 (a)-(d) for the CS-RR, CS-DY, PEPP-BG, and PEPP-AY, respectively. In the case of CS as the adsorbents, it appears that the numbers of possible conformations for CS-RR complex are greater than the CS-DY complex. Therefore, ΔG values of the CS-RR are wide range between -0.5 to -7.0 Kcal/mol, while ΔG values of the CS-DY are short range between -4.0 to -4.4 kcal/mol. To compare the ΔG values of CS-RR and CS-DY, the lowest ΔG value from docking was chosen and compare. It appears that ΔG values of CS-RR and CS-DY are -6.61 and -4.36 kcal/mol which implies that the CS-RR complex is more favorable than the CS-DY complex. This result agrees very well with the experimental data as shown in Table I.

In the case of PEPP-BG and PEPP-AY complex, it shows that the numbers of possible conformations for PEPP-BG complex are greater than the PEPP-AY complex. All ΔG values of PEPP-AY are definitely higher than all ΔG values of PEPP-BG. The lowest ΔG values of PEPP-AY and PEPP-BG are -4.60 and -4.27 kcal/mol, respectively, which implies that the PEPP-AY complex is more favorable than the PEPP-BG. This result also agrees with the experimental data as shown in Table I.

TABLE I
COMPARISON OF THE *ΔG* OBTAINED FROM THE DOCKING (ΔG_{DOCK}) AND EXPERIMENTAL (ΔG_{EXP}) DATA [6], [8].

Complexes	□G_{dock} (kcal/mol)	□G_{exp} (kcal/mol) at 30 °C
PEPP-AY	-4.60	-12.29
PEPP-BCG	-4.27	-8.52
CS-DY	-4.36	-1.96
CS-RR	-6.61	-2.56

IV. CONCLUSION

This work presents the approach to calculate the ΔG using Docking program. The results show that the calculated ΔG can be ranked as same as the experimental data very well for two experimental groups. This work suggests to optimize the structures obtained from Avogadro by quantum calculation with basis set of HF/6-31G(d,p) and B3LYP/6-31+G(d,p) for step 1 and step 2, respectively. In addition, the Docking program also can provide both of the binding free energies and the interaction details of the complexes for dyes and adsorbents. This can give us some details to design the new effective adsorbents in the future. In addition, our further work will perform the Classical Molecular Dynamics (MD) simulations for more details of their molecular interactions.

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