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Reclamation of spent solid matrices used in adsorption of malachite green and methyl violet dyes from aqueous solution

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Abstract

Hazardous solid waste, a bye product of toxic analyte adsorption is a serious setback to the application of cheap and efficient adsorption process for the removal of dyes from industrial effluents. This hazardous solid waste comprises of spent solid adsorbents which are deleterious to the environment. In this research work, solid spent adsorbents made from raw (RWL), activated (AWL) and chemically modified (CWL) water lily adsorbents loaded with Malachite green and Methyl violet (MG-Loaded and MV-loaded) dyes were evaluated for their desorption potentials, by employing different regenerating agents including HCl, CH_3CHOOH, H_2SO_4, H_2O, and NaOH. In addition, the prepared dye-loaded adsorbents were subjected to repeated cycles of adsorption/desorption in other to ascertain their regeneration capabilities. The results of the desorbing eluent potentials revealed that acetic acid, sulphuric acid and sodium hydroxide offered best recoveries with different desorption efficiency for the studied spent adsorbents and where found to increase with increase in concentration. The efficiency of the regenerated adsorbent after five successive cycles revealed that adsorption efficiency decreases from the first to the last cycle thus: 97.10% - 37.39%, 96.96% - 37.74%, 95.21% - 29.63% for MG-loaded onto RWL, AWL and CWL and 96.17% - 40.10%, 95.35% - 44.12%, 93.99% - 38.20% for MV-loaded onto RWL, AWL and CWL respectively. All the adsorbents prepared demonstrate good reusability after five successive adsorption/desorption cycles and therefore signifying water lily as a potential adsorbent for toxic dyes removal from wastewater.

1. Introduction

The concept of sustainable development goals (SDGs) adopted worldwide in year 2015 advocate for the people to use a recycled component, renewable resources, biodegradable product, energy reducing utilities, pollution free/lowering materials, feasible and cheap object etc. [1]. However, one of the main pillar of sustainable development goal is recycling the used materials [2]. Adsorption has become a widely used techniques in many industries on a large scale for purification, separation, compliance purposes [3]. The major class of adsorbents used to adsorb a different pollutant with varying concentration in aqueous solution are activated carbons, polymeric adsorbents, organic, inorganic and zeolites etc. This technique is widely used or preferred over other techniques such as

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coagulation, ozonation, oxidation, ion exchange, membrane filter, biological, irradiation process etc... due to effective removal of all pollutants recovery from real as well as synthetic wastewater, feasibility of low cost adsorbents, easily adaptable, simplicity of design and friendly operations [4-7]. Although adsorption techniques in the liquid phase is advancing at different industrial and commercial levels, there is still serious challenges of reducing or minimizing and exploiting adsorbents continuously with minimal loss of efficiency. Therefore, economical application of an adsorbent depends on efficient means of regenerating and recycling after its adsorptive capacity have been reached [8]. This problem of solid waste can be overcome by regeneration of spent adsorbents using different processes [9-10].

The major concern with adsorption approach is the danger of adsorbates being leached into the environment when the spent adsorbents are dumped without proper desorption of the pollutants in them. This make the regeneration of spent adsorbents such an economical and of environmental importance [10]. The major effective regeneration process is desorption process i.e reversing the process of adsorption. This desorption technique provides compensative ideas about the class of adsorption ie physical or chemical adsorption. Its focus is about the performance of adsorbent for subsequent reuse which usually reduce the cost of adsorption process. The exhausted adsorbent is treated with suitable solution, solvent or both to break and overcome the bonds between adsorbent-adsorbate thereby liberating or realizing adsorbates back to the solution [11]. These reused adsorbents are required in order to make the process economically and environmentally viable.

For the above stated reasons, the study on regeneration and recovery is an important area of research interest which need to be fully explored [12]. The adsorbents could be regenerated via chemical, thermal, solvent, biological, ultrasonic, electrochemical methods [13]. Yunusa *et al*. [14] reported Crystal violet recovery from *Balanites aegyptiaca* seed shell activated carbon adsorbent using NaOH solution and then recycled five times with an adsorption efficiency of 92.08%. The same adsorbent was also used by Yunusa *et al*. [15] for the removal of Cr^{6+} from aqueous solution. NaOH solution was used for this regeneration to obtain six cycles with an adsorption efficiency of 80.10%. Malachite green dye was removed from aqueous solution using desert date seed shell as an adsorbent with a removal efficiency of 52.02%. The regeneration of the desert date seed shell loaded Malachite green was optimized to produced 5 cycles using acetic acid solution [16]. While Ali *et al*. [17] reported the removal efficiency of 85% of Malachite green dye using EDTA phytogenic magnetic nanoparticles. A total of five cycles was obtained when 3-marcapto propanic acid was used as a regenerating reagent.

Therefore, this research work will focus in preparing different adsorbents from water lily leaves (RWL, AWL, CWL), loading them each differently with dye solution of Malachite green or Methyl violet. Desorption studies using different desorbing agents of acids (HCl, H_2SO_4, HNO_3, CH_3COOH), base (NaOH) and distilled water will be carried out with the intention of establishing the extent of reusability of the spent adsorbents.

2. Methodology

2.1 Sample Collection and Adsorbents Preparation

The water lily leaves (WLL) were obtained from Gubi Dam, Bauchi State, Nigeria. The raw adsorbent was prepared according to the method reported by Öznur *et al.* [18]. The leaves were washed thoroughly with distilled water to remove dust impurities and shade dried for 72hours. After drying it was ground and sieved into a working size of 300µm and stored in an airtight container as raw sample (RWL). For chemically activated water lily adsorbent, method reported by Amode *et al.* [19] was adopted. 10g of RWL sample was treated with 100ml solution of 1.0M KOH solution in a beaker. The

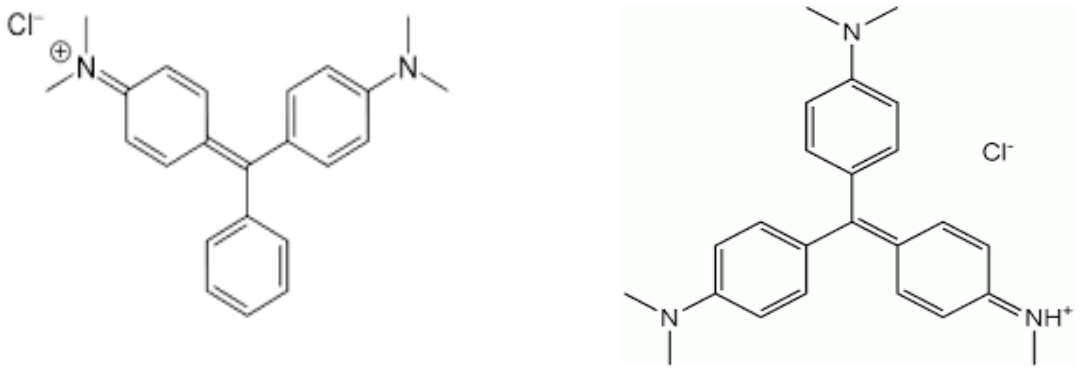
mixture was stirred thoroughly with magnetic stirrer and then allowed to age for 24 hours to achieve good absorption of the chemical into the interior of the adsorbents (precursor). The sample was washed severally with 0.1M HCl to neutralize excess KOH and finally with hot distilled water severally. The resultant sample was air dried, ground and sieved to a working size of 300µm and labelled AWL.

The carbonized adsorbents (CWL) were prepared in a muffle furnace. Leaves were ground and segregated to granular mesh size with an earlier semi-carbonization for 15 min at initial temperature of 200℃. Later, the furnace temperature was raised to a temperature of 500℃ for 45 min for the sample to undergo complete carbonization [20]. The sample was dried, ground and sieved to obtained a working size of 300µm and finally the sample was stored in air-tight container for further experimental studies.

2.2 Preparation of Stock Solution

Stock solution of Malachite green (**Figure 1a**) and Methyl violet (**Figure 1b**) dyes were prepared by dissolving 1g of each dye in 1000ml volumetric flask at room temperature and shaken until homogenous solution is obtained [21]. The sample of required concentration were prepared by diluting the stock solution with distilled water to a required concentration using dilution formula.

$$C_1V_1 = C_2V_2 \qquad \text{Eqn. 1}$$



(a) **(b)**

Figure 1. Structure of (a) Malachite Green (b) Methyl Violet

2.3 Adsorption Equilibrium Experiments

For this experiment, the batch adsorption was adopted because of its simplicity. The batch experiments were carried out to determine the optimum conditions for equilibrium adsorption of MG and CV dyes differently onto RWL, CWL and AWL adsorbents. The results obtained after optimization experiments were used to conduct the batch adsorption experiments in a controlled shaker. The enriched adsorbents were prepared by shaking 0.1g of the adsorbents (RWL, CWL and AWL) with 50ml of 50mg/l dye (MG and MV) solution differently at 150rpm for 30 minutes in a shaker at 303K. After reaching equilibrium, the contents were filtered and the enriched adsorbents were labelled for regeneration studies [19].

2.4 Regeneration Studies

In this study, method reported by Yunusa *et al.* [14] was adopted with little modification. Regeneration experiments were performed to investigate the feasibility of recycling the spent adsorbents recovery of the dyes from aqueous solution phase.

2.4.1 Selection of the Desorbing Agents

The regeneration was explored by batch desorption using neutral, basic and acidic desorbing agents: distilled water, 0.1M NaOH, 0.1M H_2SO_4, 0.1M HCl and 0.1M CH_3COOH. These chosen concentrations will be used in the first instance to ascertain the best desorbing agents for each of the adsorbent loaded dye samples [14].

2.4.2 Desorption Equilibrium Experiments

In desorption experiments, upon the enriched dye adsorbent samples (0.15g) were added 50ml 0.1M of the aforementioned desorbing agents differently at 303K. Each sample content was shaken at 150rpm for 120 minutes and the filtered. After reaching equilibrium, the contents were filtered and the concentration of residual un-adsorbed MG and MV dyes were measured at their respective working wavelength (λ_{max} = 615.50 nm and 582.37 nm) using Perkin-Elemer UV-visible spectrophotometer (Hitachi 2800 model) [14].

2.4.3 Effect of Desorbing Eluent Concentration

The desorbing solution concentration effect was investigated using the eluent solution offering highest recovery for each of the desorbed dye loaded samples. Similar procedure was repeated for each best eluent as conducted in desorption equilibrium experiments by varying the concentration of the best desorbing agent for each sample from 0.2M to 1.0M respectively [16].

2.4.4 Reusability Studies

The reusability of the adsorbents was evaluated using five successive cycles of adsorption-regeneration and the amount adsorbed/desorbed at various cycled was recorded. The desorption efficiency was computed using the equation;

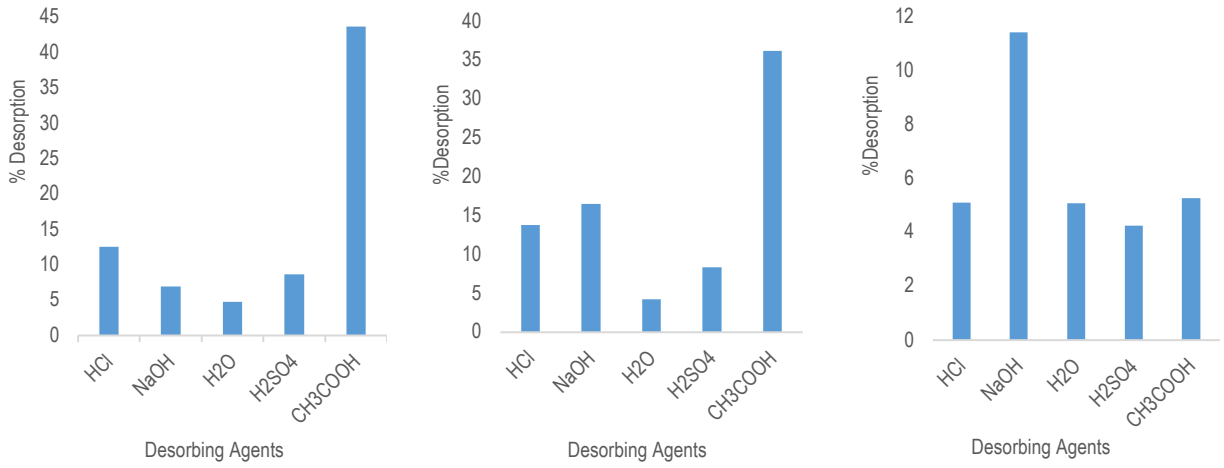
$$Desorption\ efficiency\ (\%) = \frac{C_{des}}{C_{ads}} x100 \qquad \text{Eqn 2}$$

Where C_{des} and C_{ads} represents the concentration of MG and MV each desorbed and adsorbed in mg/l respectively [15].

3. Results and Discussion

3.1 Selection of Desorbing Agents

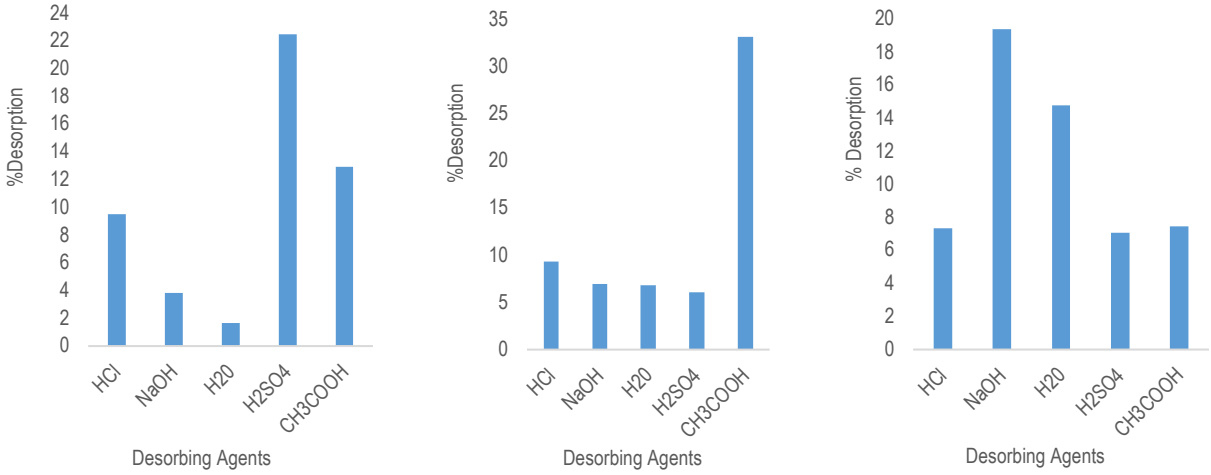
To probe the possibility of regeneration of MG-loaded and MV-loaded adsorbents, desorption studies was carried out using different desorbing agents and the results are as presented in **Figures 2 and 3**. **Figures 2a – b** shows that acetic acid offered best desorption for MG-loaded for AWL and RWL adsorbents. This could be probably due to the fact that acetic acid lowers the solution pH and $H^+_{(aq)}$ compete favorably with the cationic dye such as MG for the adsorption sites of the adsorbents [22], while NaOH was slightly higher than any other desorbing solution with desorption of MG-loaded onto CWL adsorbent. Similar trends were observed by Yunusa and Ibrahim [16] and Neupane *et al.* [23]. The lowest recovery was recorded by H_2O of 4.73% and 4.25% for MG-loaded onto AWL and RWL respectively, while H_2SO_4 recorded lowest recovery of 4.26% on MG-loaded onto CWL. It's imperative to report that addition of other desorbing agents (HCl, H_2SO_4, H_2O) did not yield relatively higher recovery as compared to acetic acid and sodium hydroxide respectively. H_2SO_4 and HCl being strong acidic might probably be repelled by the positive ion of the cationic dyes [16].



(a) **(b)** **(c)**

Figure 2. Screening of desorbing agents for MG-Loaded onto (a) AWL recovery (b) RWL recovery (c) CWL recovery.

Figure 3a shows that H_2SO_4 offered best desorption for MV-loaded (22.50%) onto AWL adsorbent with lowest recovery of 3.83% by water. As similar result was reported by Bhuvaneshwari *et al*. [24]. The acetic acid recovered 12.90% and 33.17% for AWL and RWL adsorbents for desorption of MV-loaded with lowest recovery of 3.83% and 9.35% recorded by NaOH and HCl respectively. NaOH was found to have a higher % recovery of 19 when compared to other desorbing solutions on MV-loaded onto CWL adsorbent as presented in **Figure 3c**. Similar results were earlier discussed for the same CWL adsorbent loaded with MG dye with a percentage recovery of 11.5.



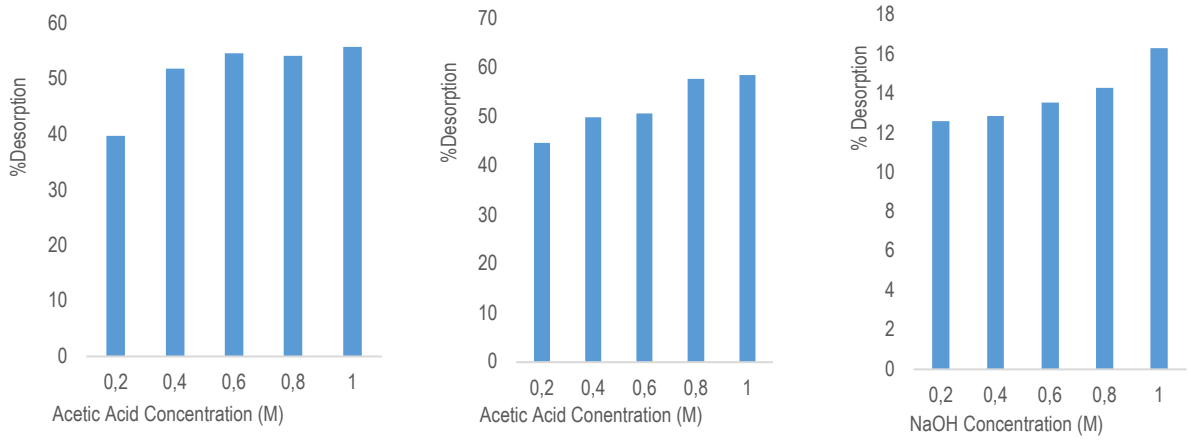
(a) **(b)** **(c)**

Figure 3. Screening of desorbing agents for MV-Loaded onto (a) AWL recovery (b) RWL recovery (c) CWL recovery

3.2. Effects of Concentration on Desorption Efficiency

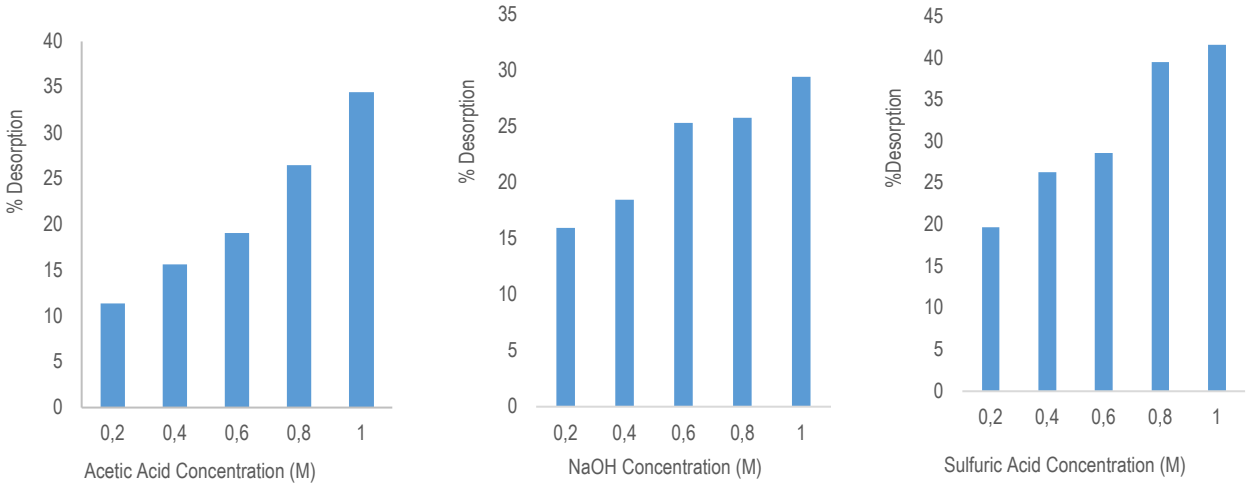
After the determination of the best desorbing agents i.e. CH_3COOH, H_2SO_4 and NaOH as the case may be, the effects of varying their concentrations on both MG-loaded and MV-loaded adsorbents were studied. The variation in desorption efficiency as a function of concentration are shown in **Figures 4 and 5** for MG-loaded and MV-loaded adsorbents. It can be observed from the figures that desorption of MG and MV loaded adsorbents increased with increase in concentration of Acetic acid, H_2SO_4, NaOH respectively. The maximum desorption of 55.75%, 58.52% of MG-loaded onto AWL and RWL

adsorbents and 17.52% desorption for MG-loaded onto CWL adsorbents as demonstrated in **Figures 4a-c** respectively. Irfan *et al.* [25] found that as the concentration of desorbing agents increase initially, there is an increase in efficiency up to certain concentration. Above which the increase in concentration may deteriorate the surface of the adsorbents. On the other hand, the maximum desorption of 34.43%, 29.45% and 41.56% of MV-loaded onto AWL, RWL and CWL adsorbents respectively as demonstrated in fig 5a, b and c. It could be observed that desorption might be function of concentration of desorbing solution. Similar trend was reported by many researchers [14-16, 26].



(a) **(b)** **(c)**

Figure 4. Effect of desorbing agent concentration for MG desorption from (a) AWL (b) RWL (c) CWL.



(a) **(b)** **(c)**

Figure 5. Effect of desorbing agent concentration for MV desorption from (a) AWL (b) RWL (c) CWL

3.3 Reusability Studies

The reusability of the adsorbent was considered as an important parameter in order to quantify whether the adsorption/desorption processes are operationally and economically viable [17]. The efficiency of the regenerated adsorbents after five different adsorption/desorption cycles are presented in **Figures 6a-f**. It can be observed that the adsorption efficiency dropped from 97.10% - 37.39% (**Figure 6a**), 96.96% - 37.74% (**Figure 6b**), 95.21% - 29.63% (**Figure 6c**) and 96.17% - 40.10% (**Figure 6d**), 95.35% - 44.12% (**Figure 6e**), 93.99% - 38.20% (**Figure 6f**) from the first to the fifth cycles for MG-loaded and MV-loaded onto RWL, AWL and CWL respectively. This is an indication that the adsorbents can be reused for the removal of MG and MV from aqueous solution for five

successive cycles. The reason for the reduction in adsorption efficiency is partly due the active sites for adsorption becoming fewer after every successive adsorption-desorption cycles [27]. Similar behaviour was reported for the reusability of regenerated cocoa nut shell activated carbon [28] and reusability of EDTA/corncob or EDTA-GO/Corncob [29].

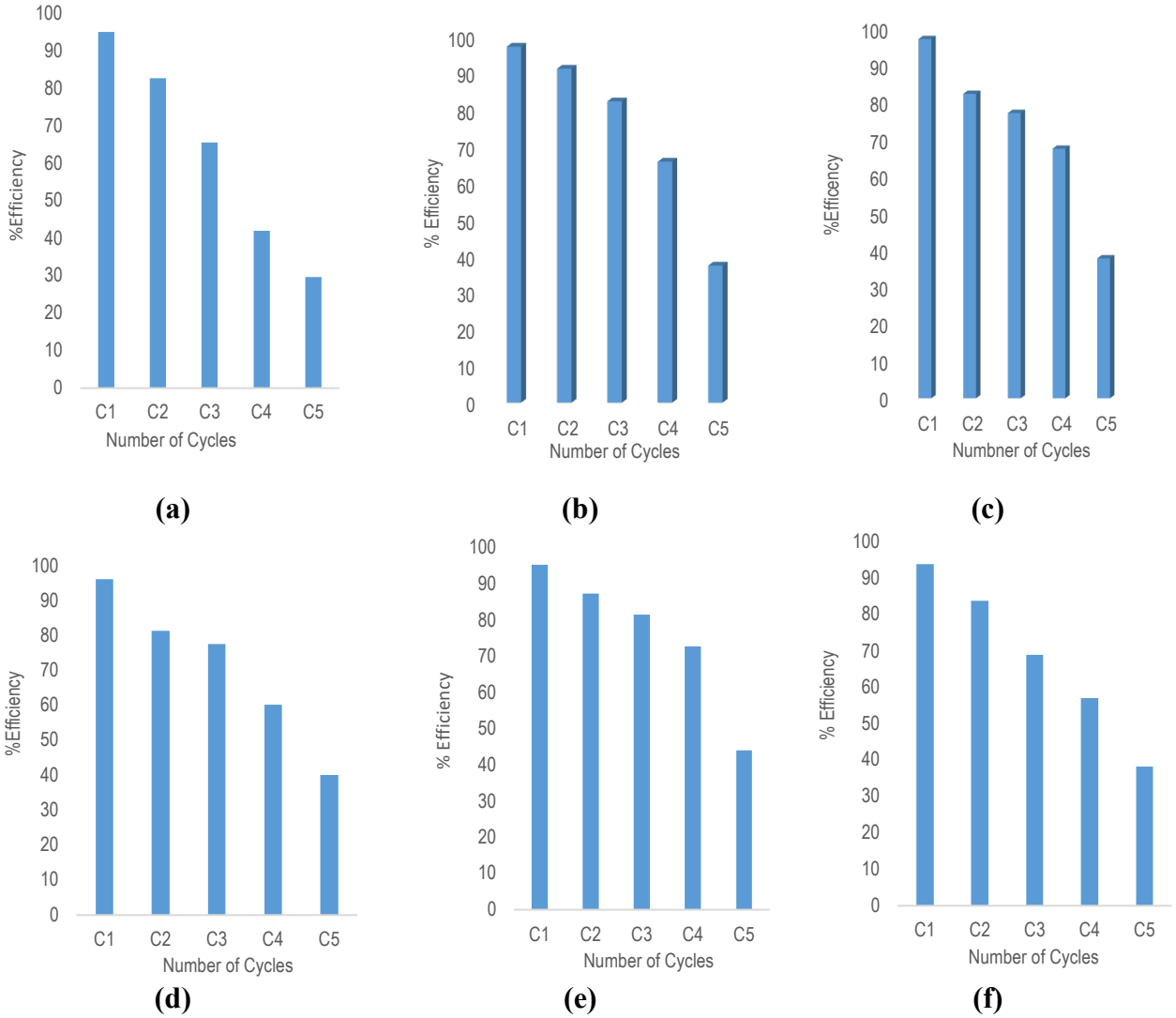


Figure 6. Efficiency of regenerated adsorbents after five successive cycles (a) MG-Loaded onto RWL. (b) MG-Loaded onto AWL. (c) MG-loaded onto CWL. (d) MV-Loaded onto RWL. (e) MV-Loaded onto AWL. (f) MV-Loaded onto CWL.

Conclusion

The adsorption/desorption of MG and MV using adsorbent derived from waterlily was investigated in this study. Three different adsorbents (RWL, AWL & CWL) were prepared and loaded with MG and MV dyes differently to obtain six types of dye loaded samples. Six different desorbing agents (HCl, H_2SO_4, CH_3COOH, H_2O, NaOH) as eluents guided by standard methods. Acetic acid, Sulphuric acid and Sodium Hydroxide offered the best recovery for both MG-loaded and MV-loaded adsorbents respectively. Variation of concentration of the selected desorbing agents demonstrated that recovery increases with increasing desorbing agents before reaching equilibrium and recovery decline dramatically. All the adsorbents prepared (RWL, AWL & CWL) demonstrate good reusability after five successive adsorption/desorption cycles.

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Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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