MANSOURA JOURNAL OF CHEMISTRY
Official Journal of Faculty of Science, Mansoura University, Egypt
E-mail: scimag@mans.edu.eg ISSN: 2974-4938

Removal of Hg(II) and acid yellow dye using chitosanmontmorillonite nanocomposite

F.T. Abdelwahed[a]*, Rania M. Eltabey*[a]*, M.M. El-Defrawy*[a]

[a] *Chemistry Department, Faculty of Science, Mansoura University, Egypt.*

Received:24/5/2021
Accepted:10/6/2021

Abstract: Chitosan-glutaraldehyde / nano-montmorillonite composite has been successfully prepared. The structure of the prepared bio sorbent has been confirmedby Fourier transforms infrared spectroscopy (FTIR),transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The adsorption kinetics and isotherm behaviors of Hg(II) and acid yellow dye (A17) molecules onto the prepared chitosan nanocomposite had been studied and describedby pseudo-first, pseudo-second order and Langmuir, Freundlich isothermmodels, respectively. Experimental data exhibit high adsorption capacities equal 125 and 302 mg /g for Hg(II) and A17, respectively.

keywords: Chitosan, Nano-montmorillonite, Adsorption, Hg(II), Textile acid yellow dye.

1.Introduction

There is no doubt that water crisis is the main world issue which attract public attention due to its harmful effect on respiratory system (i.e., dyspnea), cardiovascular, nervous system of human beings' skin (dermatitis), and eyes (irritation to eyes). Unfortunately, this issue continues to get worst with the use of different synthetic chemicals for various applications including heavy metals and dyes [1-3].

Among heavy metals, Hg(II) has been found to be one of the most toxic metals as it threatens not only human but alsoaquaticsystem even though directexposure[4,5].Textile dyes such as acid yellow dye 17(A17) is another severethreatbecause discharging wastewaterdownrightsoil,leaves water unsuitable due to water colorization [6-8].

Several methods such as flocculation, adsorption, biodegradation, chemical oxidation, in addition tophotocatalysis have beenused for treatment of polluted water. Amongst them, adsorption is interesting techniqueowing to its simplest,effectiveness, economical and greatlyefficient[9-11].

Chitosan (CS), as an adsorbent, has been used on large scale due to possessing large number of functional groups, abundance, hydrophilicity, biodegradability, and non-toxicity[12,13]. In order to improve its capacity and selectivity, several materials can incorporate or grafted with it such as montmorillonite (MMT) clay.It is the mainly utilized adsorbent due toits high active surface area and greatcation exchange capacity[14,15].Therefore,the modification of CS with MMT can enhance adsorption process towards polluted water[16,17].

Hence, in this study, the potential of chitosan polymer functionalized with nano-montmorillonite as a strong sorbent towards straightforward and rapid removal of Hg(II) ions and A17 was examined

2.Experimental

2.1. Materials

All chemical substances including chitosan (CS)of 92% deacetylation percentage, montmorillonite (MMT), glutaraldehyde 50%, mercuric chloride ($HgCl_2$) were provided by Sigma-Aldrich Trading Co., Ltd. In addition, acid yellow dye (A17) was purchased from the Dye Star Company, Brazil.

2.2.Characterization

The chemical structure of the dye has been shown in Fig. (1). FTIR (Perkin Elmer Spectrum BX) absorption spectra of the prepared composite was calculated over range varies between 400–4000 cm^{-1}. A Metrohm 692 pH meter was used for pH measurements. A17 concentration was investigated utilizing Jasco UV - Visible spectrophotometer (model

V-530, Japan) at 425 nmwavelength.The uptake quantity of Hg (II) was studied with the aid of Agilent's 5100 ICP-OES (Agilent technologies, Australia).

2.3. Preparation of chitosan composite

1g of CS was dispersedwithin 1% aqueousacetic solution and stirring. Then was furtherdisplacedinto flask for re-precipitationusing 0.1M sodium hydroxide solution.Clay (1 % w/w of CS) diffusedfor 24h in water was mixedwith the CS solution, agitated with stirrer. Then, NaOH solution was added dropwise under high stirring condition for precipitation. Later, (5% w/w) of glutaraldehyde crosslinking were added dropwise and allowed for cross linking at 45°C. The obtained precipitate was allowed for washingwith deionized water then for drying [18]. The expected chemical structure of chitosan nano-montmorillonite composite is shown in Fig.(2).

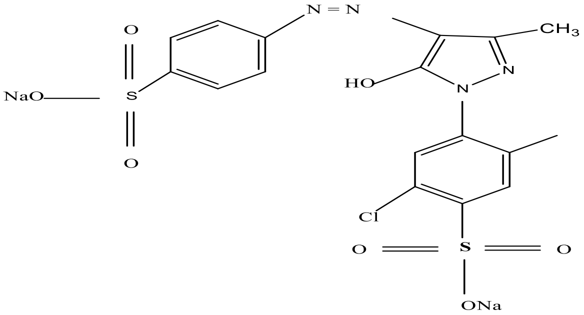

Fig.(1): Chemical structure of acid yellow dye 17 (A17)

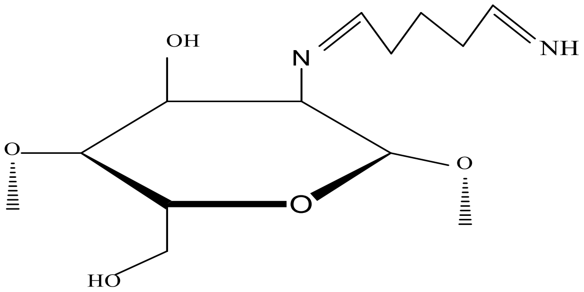

Fig. (2): Proposed chemical structure of CS-nano MMT sorbent

Adsorption studies using batch method.

Adsorption experiments were conducted at 25°C by vibrating 0.02 g of prepared compositealongside25 mL of initial conc (100 and 20mg/ L) of A17 as well as Hg(II)rangingpH values (2-6) with different time intervals (5-240) min.Uptake value (q_e) was performed using(Eq. 1)

$$q_e = (C_i - C_f)\ V/W.(1)$$

where $C_i$and C_f are the initial and equilibriumconcentration, respectively. Where V is the solution volume; W is the sorbentmass.

3. Results and Discussion

3.1.Assignment of polymeric sample

3.1.1. FTIR

FTIR investigation of prepared composites, as seen in Fig. (3), the basic absorption peaks of CS (NH stretching, OH stretching, and the intermolecular hydrogen bonds) appeared at 3455 cm^{-1}, bands at 2923 and 2860 cm^{-1} are corresponding to (CH stretching). Peaks at 1652 as well as 1558 cm^{-1} are related to amide (IandII),consequently[18].Furthermore,MMT shows characteristic peaks at 640 and 464 cm^{-1} suggesting the existence of (Al, Mg)–OH and Si-Al-O bonds,while bandnear 1048 $cm^{-1}$is corresponded toSi-O vibrations[19-21].Afterwards adsorption, the strong band intensityassigned to -OH groups decreased and shifted from 3455 to 3492 cm^{-1} and3469 cm^{-1} for Hg(II) besides A17, respectively, which obviously confirm that hydroxyl groups have great impact on removing efficiency. Furthermore, the intensity of (—NH) group peak is decreased. As forthe prepared composite after adsorption of Hg(II),spikes at 1652 and 1558 are moved to 1641 in addition to 1569 cm^{-1} after adsorption of A17 [22]

cm^{-1} are changed near 1645 and 1554 cm^{-1}respectively, while those peaks Theseresults indicate the chelation of Hg(II) with CS nitrogenatomsas well as electrostatic attractionbetween anionic dye and NH_3^+ of CS.

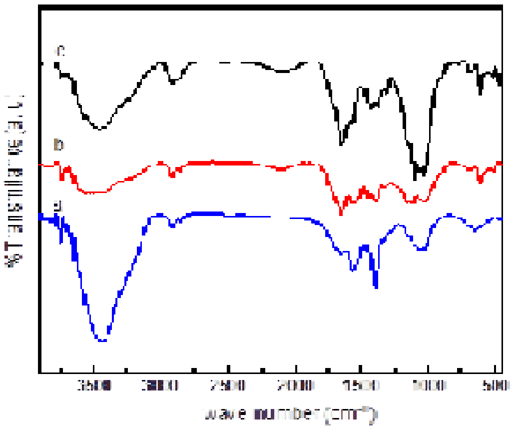

Fig. (3): FTIR spectra for (a) chitosan nano-montmorillonite composite, (b) composite after adsorption of Hg(II), and (c) after A17adsorption .

3.1.2 TEM

Fig. 4 implies TEM image of CS-MMT nanocomposite in which dark lines refer to nano-MMT while bright ones denote intercalated CS matrix. It is observed that size of particles is lower than 100nm so it suggests well preparation of nanocomposite.

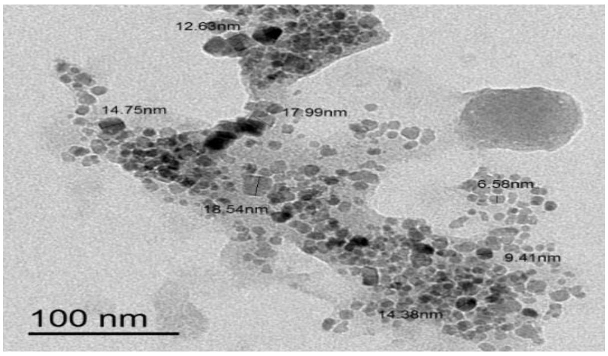

Fig. (4) TEMimage of CS-MMT nanocomposite

The surface morphology of prepared nanocomposite after adsorption of A17 and Hg(II),respectively presented in (Fig. 5a and b) display smoother and river-like morphologies.

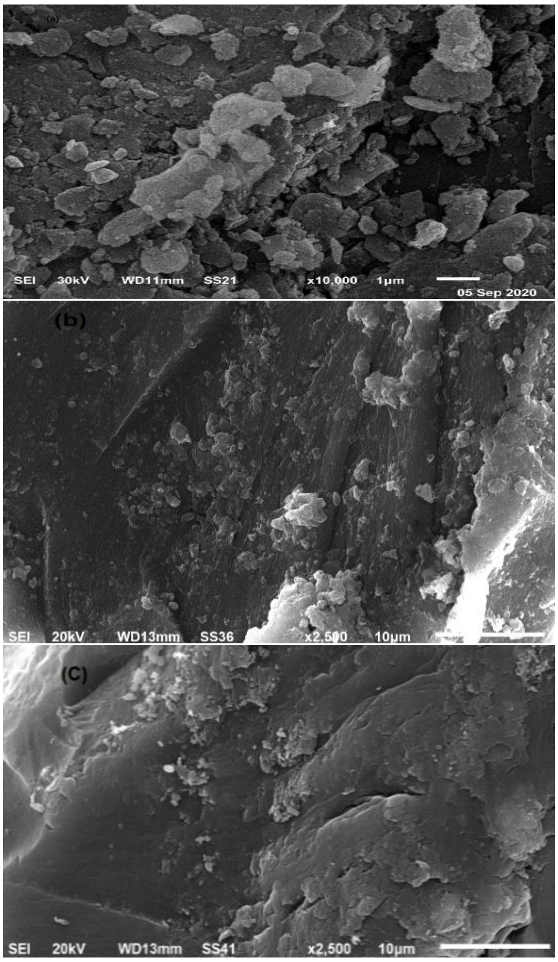

Fig.(5) (a) SEM of CS-MMT, (b) SEM of CS-MMT-A17 and (c)SEM of CS-MMT-Hg(II)

2. Optimization of adsorption of Hg(II) and A17 by CS-MMT nanocomposite

3.2.1. Effect of initial pH

The impact of pH on Hg(II) and A17 adsorption has been studied by stirring of 25 mL mixture of Hg(20 mg/L), (100 mg/ L) of A17and 20 mg of adsorbent at pH values (2-6). The equilibrium adsorption (q_e) was plotted against the pH. From Fig. (6), it can be concluded that $q_e$reaches its maximum near pH value equal 4 for both A17 and Hg(II) [23].

3.2.2. Effect of contact time

In order to study the influence of the optimal time on the removal capacity of Hg(II) and A17, experiments were carried on 20 mg of adsorbent, 25℃, initial concentrations of 20and 100 mg/ Lof Hg(II) and A17, respectively, with each optimal pH value in 25 ml solution at time intervals varying between (5-240) min. Fig.(7) shows that, at the beginning, the adsorption rate increases then remains constant at 60 and 240 min for Hg(II) and A17, respectively. Therefore, 60 and 240 min were chosen as the equilibrium time for the saturation of both metal ion anddye on the prepared adsorbent.

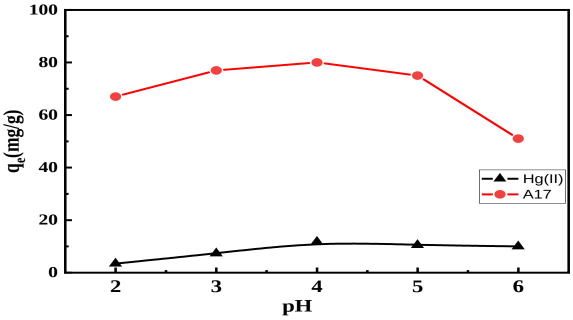

Fig. (6): Influence of pH on of Hg(II) and A17adsorption onto the prepared composite.20mg of adsorbent;time= 240 min; temperature=25 °C; C_i(20 and 100 mg/L)for Hg(II)andA17,consequently.

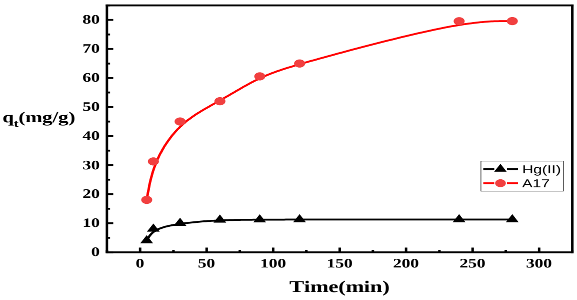

Fig. (7): Influenceof equilibriumtime on adsorption of Hg(II) and A17 on the prepared composite.20mg of adsorbent; pH=4;

temperature =25 °C; C_i (20 and 100 mg/L) for Hg(II)and A17,consequently

3.2.3. Kinetics Analysis

In the kinetics studies for the removal process, the initial pH was adjusted to be 4 for the studied metal and dye carrying out concentrations of 20as well as 100 mg/Lfor Hg(II) and A17 near to 25°C.at various time intervals. The fitting of pseudo-first order expressed by(Eq. 2) as well as pseudo-second order (Eq. 3) models were applied to explain the adsorption kinetics [24,25].

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (2)$$

$$t/q_t = 1/ (k_2 q_{e2}) + (1/q_e) t \quad (3)$$

Here, q_t (mg g^{-1}) representsquantity of A17 and Hg(II) adsorbed at (t) time, k_1 (min^{-1}) and k_2(g $mg^{-1}min^{-1}$) are pseudo-first and second orderkineticsrate constants,consequently,qeis the Hg(II) and A17 amount adsorbed at equilibrium.

Fig. (8 a and b)show the experimental curves of pseudo-first and pseudo-second order adsorption kinetic models, respectively, k_1 and k_2 constantvalues are given in Table(1). Based on data, it has been clarified that model of pseudo-second order is the most probable model for estimating sorption kinetics of both Hg(II) and A17, thanks tothe highestvalues of R^2 (R^2> 0.99)besidesthewell matching of q_e calculated value obtained frompseudo-second-model and $q_{e,exp}$ than that provided by pseudo-first-order model.

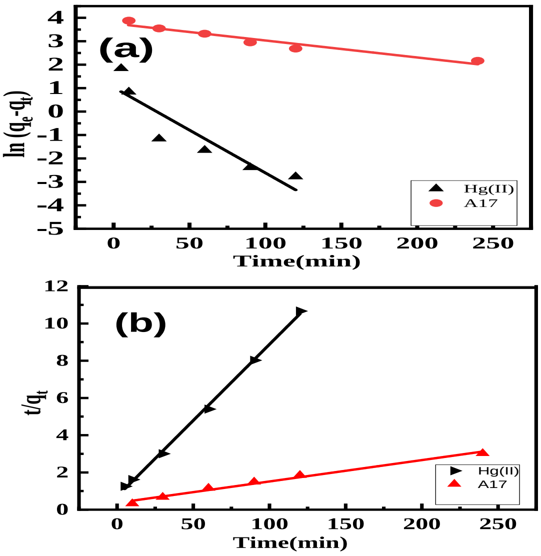

Fig. (8): (a) Pseudo-1st-order, (b) Pseduo-2nd-order kineticsfor Hg(II) in addition to A17 adsorption

Table (1): Constant parameters of pseudo-first-order and pseudo-second-order for adsorption of Hg(II) and A17.

	Pseudo-first-order				**Pseudo-second-order**		
	$q_{e, exp}$	$q_{e, cal}$	k_1	R^2	$q_{e, cal}$	k_2	R^2
HgI)	10.312	2.809	0.0365	0.833	11.031	0.0123	0.999
A17	79.54	42.83	0.0072	0.93625	83.23	0.00036	0.994

Table (2):constants of isotherm modelsof Langmuir and Freundlich.

	Langmuir isotherm			**Freundlich isotherm**		
	q_m	k_l	R^2	n	k_f	R^2
Hg(I)	400	0.002	0.539	0.9404	0.8269	0.998
A17	386.1	0.005	0.886	1.806	2.68	0.995

Adsorption isotherm models

In this study, there are two adsorption isotherm models, Langmuir and Freundlich which were performed to evaluate mechanism of adsorption forHg(II) and A17 dye onto the prepared adsorbent.Langmuir isotherm model,

expressed by Fig.(9a) hypotheses formation of monolayer adsorption on the sorbent surface with fixed active sites and given as illustrated in (Eq.4).

$$C_e/q_e = C_e/q_m + 1/ q_m \quad (4)$$

Hence, q_e is the pollutant amount adsorbed at equilibrium as (mg/ g), q_m (mg /g) is the maximum adsorption capacity of composite, and K_L (L/ mg) is the Langmuir constant. Freundlich isotherm model[26], expressed by Fig.(9b)proposes that adsorption is done on a heterogeneous surfaceand is explained by the consecutive equation (Eq.5) .

$$\text{Log } q_e = \log K_F + 1/n \text{ Log } C_e \quad (5)$$

K_F and n representFreundlich model coefficients(mg/g). The calculatedconstant values of the two measuredmodels (Table 2) confirm that Freundlich model predictswell adsorption mechanism for A17 andHg(II) on the obtainednanocomposite

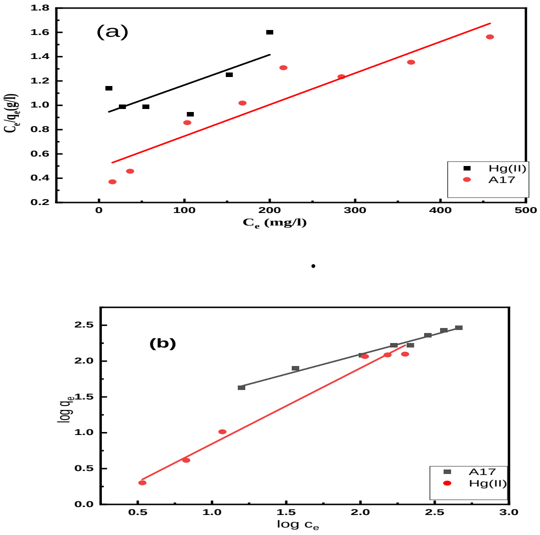

Fig. (9): (a)Langmuir isotherm model , (b)Freundlichisotherm model for adsorption of Hg(II) and A17.

4. Conclusion

The modification of chitosan by montmorillonite as well as crosslinking with glutaraldehyde/ NaOH for using as adsorbent of Hg(II) and A17was investigated. The prepared composite has been characterized by FT-IR,SEM andTEM, which confirmed a successfulgrafting reaction.Kinetic studies were depicted better withpseudo-2nd-order kinetic. Freundlich isotherm model described system equilibrium

5.References

1 N. Rajarathinam, T. Arunachalam, S. Raja, and R. Selvasembian, (2020) “Fenalan Yellow G adsorption using surface-functionalized green nanoceria: An insight into mechanism and statistical modelling,” Environ. Res., vol. **181**, p. 108920, , doi: 10.1016/j.envres.2019.108920.

2 A. A. Oladipo and M. Gazi, (2014), “Enhanced removal of crystal violet by low cost alginate/acid activated bentonite composite beads: Optimization and modelling using non-linear regression technique,” *J. Water Process Eng.*, vol. **2**, pp. 43–52, doi: 10.1016/j.jwpe.2014.04.007.

3 G. Sriram *et al.*, (2019), “Xerogel activated diatoms as an effective hybrid adsorbent for the efficient removal of malachite green,” *New J. Chem.*, vol. **43,** no. 9, pp. 3810–3820, doi: 10.1039/c9nj00015a.

4 N. Caner, A. Sarl, and M. Tüzen, (2015) “Adsorption Characteristics of Mercury(II) Ions from Aqueous Solution onto Chitosan-Coated Diatomite,” Ind. Eng. Chem. Res., vol. **54**, no. 30, pp. 7524–7533, , doi: 10.1021/acs.iecr.5b01293.

5 X. Lu, J. Jiang, K. Sun, J. Wang, and Y. Zhang, (2014) “Influence of the pore structure and surface chemical properties of activated carbon on the adsorption of mercury from aqueous solutions,” Mar. Pollut. Bull., vol. **78**, no. 1–2, pp. 69–76, doi: 10.1016/j.marpolbul.2013.11.007.

6 M. D. Teli and G. T. Nadathur, (2018), “Adsorptive removal of acid yellow 17 (an anionic dye) from water by novel ionene chloride modified electrospun silica nanofibres,” *J. Environ. Chem. Eng.*, vol. **6,** no. 6, pp. 7257–7272, doi: 10.1016/j.jece.2018.10.005.

7 M. M. R. Khan, B. Sahoo, A. K. Mukherjee, and A. Naskar, (2019), “Biosorption of acid yellow-99 using mango (Mangifera indica) leaf powder, an economic agricultural waste,” SN Appl. Sci., vol. **1**, no. 11, doi: 10.1007/s42452-019-1537-6.

8 J. Iqbal et al., (2011), “Adsorption of acid yellow dye on flakes of chitosan prepared from fishery wastes,” *Arab. J. Chem.*, vol. **4**, no. 4, pp. 389–395, doi: 10.1016/j.arabjc.2010.07.007.

9 L. Liu, Z. Y. Gao, X. P. Su, X. Chen, L. Jiang, and J. M. Yao, (2015), “Adsorption removal of dyes from single and binary solutions using a cellulose-based bioadsorbent,” ACS Sustain. Chem. Eng., vol. **3**, no. 3, pp. 432–442, doi: 10.1021/sc500848m.

10 R. Kumar, M. O. Ansari, and M. A. Barakat, (2014) “Adsorption of brilliant green by surfactant doped polyaniline/MWCNTs composite: Evaluation of the kinetic, thermodynamic, and isotherm,” Ind. Eng. Chem. Res., vol. **53**, no. 17, pp. 7167–7175, doi: 10.1021/ie500100d.

11 M. Abbas, (2020), “Removal of brilliant

green (BG) by activated carbon derived from medlar nucleus (ACMN) – Kinetic, isotherms and thermodynamic aspects of adsorption," Adsorpt. Sci. Technol., vol. **38**, no. 9–10, pp. 464–482, doi: 10.1177/0263617420957829.

12 W. S. Wan Ngah, L. C. Teong, and M. A. K. M. Hanafiah, (2011) "Adsorption of dyes and heavy metal ions by chitosan composites: A review," Carbohydr. Polym., vol. **83**, no. 4, pp. 1446–1456, doi: 10.1016/j.carbpol.2010.11.004.

13 G. Z. Kyzas, N. K. Lazaridis, and M. Kostoglou, (2014), "Adsorption/desorption of a dye by a chitosan derivative: Experiments and phenomenological modeling," *Chem. Eng. J.*, vol. **248**, pp. 327–336, doi: 10.1016/j.cej.2014.03.063.

14 E. Aladağ, B. A. Fil, R. Boncukcuoğlu, O. Sözüdoğru, and A. E. Yilmaz, 2014), "Adsorption of Methyl Violet Dye a Textile Industry Effluent onto Montmorillonite-Batch Study," *J. Dispers. Sci. Technol.*, vol. **35,** no. 12, pp. 1737–1744, (doi: 10.1080/01932691.2013.873865

15 E. De António, C. Liu, C. I. Ezugwu, and S. Mao, (2019). "Applied Clay Science Molybdenum disulfide / montmorillonite composite as a highly efficient adsorbent for mercury removal from wastewater," no. November,

16 J. Luo, G. Han, M. Xie, Z. Cai, and X. Wang, (2015), "Quaternized chitosan/montmorillonite nanocomposite resin and its adsorption behavior," *Iran. Polym. J. (English Ed.*, vol. **24**, no. 7, pp. 531–539, doi: 10.1007/s13726-015-0343-2.

17 C. Umpuch and S. Sakaew, (2013). "Removal of methyl orange from aqueous solutions by adsorption using chitosan intercalated montmorillonite," *Songklanakarin J. Sci. Technol.*, vol. **35**, no. 4, pp. 451–459,

18 P. Gogoi, A. J. Thakur, R. R. Devi, B. Das, and T. K. Maji, (2016). "A comparative study on sorption of arsenate ions from water by crosslinked chitosan and crosslinked chitosan/MMT nanocomposite," *J. Environ. Chem. Eng.*, vol. **4**, no. 4, pp. 4248–4257, 2016, doi: 10.1016/j.jece. 09.027.

19 H. Zeng, L. Wang, D. Zhang, F. Wang, V. K. Sharma, and C. Wang, (2019), "Amido-functionalized carboxymethyl chitosan/montmorillonite composite for highly efficient and cost-effective mercury removal from aqueous solution," *J. Colloid Interface Sci.*, vol. **554**, pp. 479–487, doi: 10.1016/j.jcis.2019.07.029.

20 N. Nematidil, M. Sadeghi, S. Nezami, and H. Sadeghi, (2019). "Synthesis and characterization of Schiff-base based chitosan-g- glutaraldehyde / NaMMTNPs-APTES for removal Pb 2 + and Hg 2 + ions," vol. **222**, no. June,

21 I. M. M. Kenawy, M. M. Eldefrawy, R. M. Eltabey, and E. G. Zaki, (2019), "Melamine grafted chitosan-montmorillonite nanocomposite for ferric ions adsorption: Central composite design optimization study" *J. Clean. Prod.*, vol. **241**, p. 118189, doi: 10.1016/j.jclepro.2019.118189.

22 Y. Sheth, S. Dharaskar, M. Khalid, and S. Sonawane, (2021), "An environment friendly approach for heavy metal removal from industrial wastewater using chitosan based biosorbent: A review," Sustain. Energy Technol. Assessments, vol. **43**, no. August 2020, p. 100951, doi: 10.1016/j.seta.2020.100951.

23 M. a A. Khalek, G. a Mahmoud, and N. a El-kelesh, (2012). "Synthesis and Characterization of Poly-Methacrylic Acid Grafted Chitosan-Bentonite Composite and Its Application for Heavy Metals Recovery," Chem. Mater. Res., vol. **2**, no. 7, pp. 1–8,

24 M. Tanyol, N. Kavak, and G. Torlut, (2019), "Synthesis of poly(An-co-vp)/zeolite composite and its application for the removal of brilliant green by adsorption process: Kinetics, isotherms, and experimental design," Adv. Polym. Technol., vol. **2019**, doi: 10.1155/2019/8482975.

25 G. Z. Kyzas, P. I. Siafaka, E. G. Pavlidou, K. J. Chrissafis, and D. N. Bikiaris, (2015), "Synthesis and adsorption application of succinyl-grafted chitosan for the simultaneous removal of zinc and

cationic dye from binary hazardous mixtures," *Chem. Eng. J.*, vol. **259**, pp. 438–448, doi: 10.1016/j.cej.2014.08.019.

26 M. Saif Ur Rehman, I. Kim, N. Rashid, M. Adeel Umer, M. Sajid, and J. I. Han, ,(2016) "Adsorption of Brilliant Green Dye on Biochar Prepared From Lignocellulosic Bioethanol Plant Waste," Clean - Soil, Air, Water, vol. **44**, no. 1, pp. 55–62, doi: 10.1002/clen.20130095