Environmental Science
Water Research & Technology



PERSPECTIVE





Cite this: *Environ. Sci.: Water Res. Technol.*, 2023, **9**, 1558

# The removal efficiency of emerging organic contaminants, heavy metals and dyes: intrinsic limits at low concentrations

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In this work, we exploit Langmuir adsorption isotherms to compare the performance of different materials (adsorbents) in removing organic contaminants (adsorbates) from water. The removal efficiency observed reaches an intrinsic limit at low concentrations. We also demonstrate quantitatively how multi-step adsorption processes achieve better purification efficiency than single-step adsorption performed using much smaller amounts of adsorbent material. We demonstrate how such performance is strongly affected by adsorbent concentration. Only the use of both the parameters obtained from Langmuir adsorption isotherm ($Q_m$ and $K_L$) modelling allows one to compare materials tested under different experimental conditions by different groups, whereas most published reviews focus only on $Q_m$ which is rather limited for comparing the performance of different materials studied under different conditions. Finally, we present some guidelines for data reporting in future work and reviews.

Received 19th August 2022,
Accepted 9th April 2023

DOI: 10.1039/d2ew00644h

rsc.li/es-water

**Water impact**

For materials science applied to water purification, it is strategic to compare the performances of different adsorbents, the use of appropriate parameters is an open question. In the present work we show how a widely used and intuitive parameter as removal efficiency is not suitable for such purpose, while the isotherm's parameters, *i.e.* Langmuir model, are the effective ones.

## Introduction

More than 30 000 chemicals including drugs, pesticides, additives *etc.* are used every day for domestic and industrial purposes, and over 21 000 chemicals have been registered under the European procedures of registration, evaluation, authorisation and restriction of chemicals (REACH).† Thus fast and reliable tests are required for comparing how different materials can remove from water a large and continually increasing number of organic contaminants.[1]

Adsorption is one of the most important water treatment technologies, particularly for the removal of organic contaminants from waste water, drinking water and industrial effluents.[2] In many published works the removal efficiency is reported as a simple percentage (weight of molecules adsorbed/total weight of molecules in the original solution), measured at a specific concentration, which is the most intuitive approach for waste water treatment (WWT) plants and prototypes.[1a] There is, however, no scientific evidence that removal efficiency values measured at different concentrations, or under different experimental conditions (adsorbent, pH, adsorbate, temperature, *etc.*) can be compared directly.

The most common method used for modelling the adsorption of different contaminants on a given material is based on a semi-empirical equation which takes into consideration the octanol–water partition coefficient of a target adsorbate molecule ($K_{ow}$).[3] After finding the partition coefficient, this approach is able to model experimental adsorption data for many organic molecules[2] including pesticides,[4] but shows significant deviation for bisphenols,[5] some active pharmaceutical ingredients[6] and water soluble organics.[2] An alternative approach measures the weight of contaminant adsorbed at equilibrium ($q_e$, in mg $g^{-1}$) for different equilibrium concentrations of the adsorbate molecule in solution ($c_e$, in mg $L^{-1}$). Some reviews compare the performance of different materials by reporting removal efficiency, but considering that the data was acquired under different experimental conditions, the usefulness of these data is questionable.

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† European Chemicals Agency, ECHA, **https://echa.europa.eu/universe-of-registered-substances** retrieved July 27, 2020.

The aim of this communication is to compare results based on isotherm approaches to calculate unambiguously the removal efficiency ($R$). Most work reported so far focusses on the calculation of adsorption capacity assuming a monolayer of adsorbate forms on the material, yielding a quantity $Q_m$. This value can be estimated theoretically using Langmuir[7] or similar adsorption models, as well as by extrapolation of the experimental isotherm curve. The extensive literature on adsorption phenomena has been used to validate our approach and show the consistency of our model of removal efficiency prediction.

## Materials and methods

The vast majority of papers studying adsorption report the data as adsorption isotherms and test different theoretical models to obtain the main physical parameters. In the present work we have considered only the Langmuir isotherms and have collected from the literature parameters obtained experimentally for validation purposes.

Many previous works report data giving the removal efficiency at low concentrations, since for practical purposes the adsorption is carried out at low concentration and $R$ is usually reported as a parameter changing as a function of pH or other external parameters. Here we have considered only the papers where the isotherms are presented graphically, in order to allow verification of overall data quality.

The experimental data of the isotherm shown as an example in Fig. 1 is taken from our previous publication.[8]

## Results and discussion

Fig. 1 shows a typical isotherm obtained for rhodamine B adsorption on a polysulfone support coated with graphene oxide.[8] We see that $q_e$ at high concentrations corresponds approximately to the theoretical value estimated from the Langmuir isotherm model $Q_m$ (continuous red line in Fig. 1) assuming the formation of a single monolayer of molecules on the available adsorbent surface.

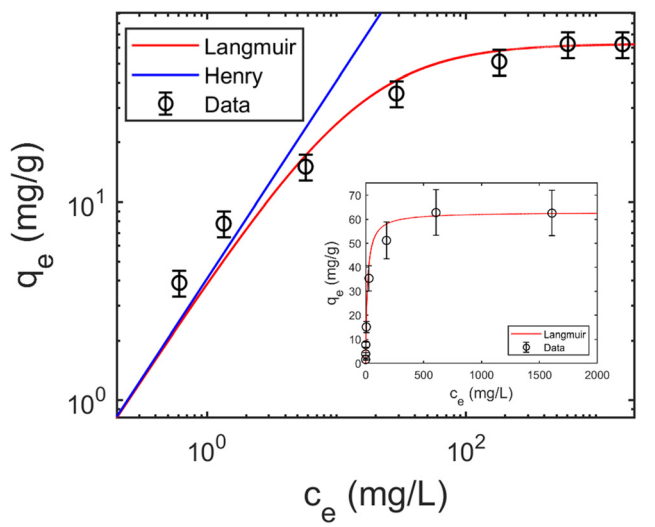


**Fig. 1** Adsorption isotherm with Langmuir fit, plotted in logarithmic scale (log–log plot), $Q_m$ = 63.0 mg g$^{-1}$, $K_L$ = 65.2 mL mg$^{-1}$, $V$ = 25 mL, $M$ = 50 mg. Inset: Isotherm plot in linear scale.

The Langmuir isotherm equation, which should ideally contain all the information about the adsorption mechanism, is:

$$q_e = \frac{Q_m K_L c_e}{1 + K_L c_e} \quad (1a)$$

Here $q_e$ is the ratio between the mass of the contaminant adsorbed and the mass of adsorbent at equilibrium with an adsorbate in solution; $Q_m$ is the theoretical value obtained from the Langmuir isotherm model, assuming only a monolayer of adsorbed molecules; $K_L$ is the equilibrium constant of the adsorption reaction, which is often seen as a coefficient proportional to the affinity of the adsorbate for the adsorbent. From eqn (1a) we can see that $1/K_L$ is also the concentration reached assuming 0.5 of a monolayer (ML) coverage. In the low concentration regime ($c < 1/K_L$), the Langmuir isotherm can be approximated using the simpler Henry isotherm:[9]

$$q_e = Q_m K_L c_e \quad \text{when} \quad c_e < 1/K_L \quad (1b)$$

At each point of the isotherm $q_e(c_e)$, the $q_e$ adsorbed at equilibrium is estimated from the initial concentration of adsorbate $c_0$ and the adsorbent concentration expressed as mass $M$ in volume $V$ (eqn (2)).

$$q_e = (c_0 - c_e)\frac{V}{M} \quad (2)$$

Combining eqn (1a) and (2) we obtain a quadratic equation where the variable is the equilibrium concentration $c_e$.

$$\frac{\alpha c_e}{1 + K_L c_e} = c_0 - c_e \quad (3a)$$

$$c_e = \frac{-\alpha + K_L c_0 - 1 + \sqrt{(\alpha - K_L c_0 + 1)^2 + 4K_L c_0}}{2K_L} \quad (3b)$$

where $\alpha = Q_m K_L M/V$. The physical meaning of $\alpha$ is the ratio of the mass of adsorbate molecules forming a monolayer coverage ($Q_m M$) divided by the mass of molecules in solution when the coverage reaches 0.5 ML ($V \cdot 1/K_L$). The solution of eqn (3a) is valid for all concentrations. The fraction of contaminants removed $R$ can be calculated if $c_e$ and $c_0$ are known:

$$R^L = 1 - \frac{c_e}{c_0} = 1 - \frac{-\alpha + K_L c_0 - 1 + \sqrt{(\alpha - K_L c_0 + 1)^2 + 4K_L c_0}}{2K_L C_0} \quad (4)$$

For low concentrations[10] ($c < 1/K_L$), we can, however calculate $R$ using the approximation in eqn (1b) (Henry adsorption isotherm):

$$\alpha c_e = c_0 - c_e \quad (5a)$$

$$\frac{c_e}{c_0} = \frac{1}{\alpha - 1} \quad (5b)$$

Thus, the removal efficiency becomes:

$$R^H = 1 - \frac{c_e}{c_0} = \frac{\alpha - 2}{\alpha - 1} \quad (6)$$

Noteworthy, eqn (6) indicates that, in low-concentration regimes, $R$ does not depend on the initial concentration $c_0$; which is evident in Fig. 2A, which plots $R$ *vs.* $c_0$. The approximated Henry model (blue line, eqn (6)) slightly underestimates the exact solution (Langmuir model, red line, eqn (4)) but the difference is within experimental error (*ca.* 3%). Fig. 1 also confirms that eqn (6) is valid only at low concentration ($\alpha > 2$, or $C < 1/K_L$) although this low-concentration regime is, in fact, the most important one when dealing with water purification. As the concentration becomes $c > 1/K_L$, the removal efficiency rapidly decreases, as has been shown experimentally.[11–13] Fig. 2B shows how the removal efficiency can be tuned by changing the concentration of the adsorbent ($M/V$), this plot is sometimes reported for low concentration studies.[14] A primary conclusion of this analysis is that the removal efficiency is not an intrinsic parameter of the adsorption process. Both the plots in Fig. 2 are commonly reported in the literature, but they are univocally derivable from isotherm and adsorbent concentration ($M/V$).[13]

In this work we have chosen to focus the attention to Langmuir isotherms, since it is the most used model for describe the monolayer adsorption on an homogenous surface, but with the consideration developed here above the multilayer adsorption can be considered: the Brunauer–Emmett–Teller (BET) isotherm can be approximated to the Henry isotherm as well, by substituting $K_L = C_{BET}/C_S$, where $C_{BET}$ is the thermodynamic equilibrium BET constant and $C_S$ the solubility of adsorbate, both obtained from BET fit. While the Freundlich model has no analytical approximation at low $C$, since the derivate of the Freundlich isotherm is a singularity at zero concentration, thus cannot be used for a similar comparison at low concentration. In a practical case was reported that for low concentration – when often the isotherms is well described by Henry (linear) model – the fit of Freundich equation ($q_e = K_F \cdot c_e^{1/n}$) can be performed with $n = 1$,[10] but in this specific case no advantages can be found by using Freundlich instead of Henry.

We tested the accuracy of eqn (6) using a wide range of data published in the literature, since the parameter $\alpha$ can be calculated from such data. Different adsorbate groups were chosen: organic molecules, arsenic and other heavy metals. In order to understand how $\alpha$ influences the removal efficiency, Fig. 3 shows the experimental values available in the literature together with those calculated using eqn (6). The points with $R > 90\%$ are nicely aligned along the plateau

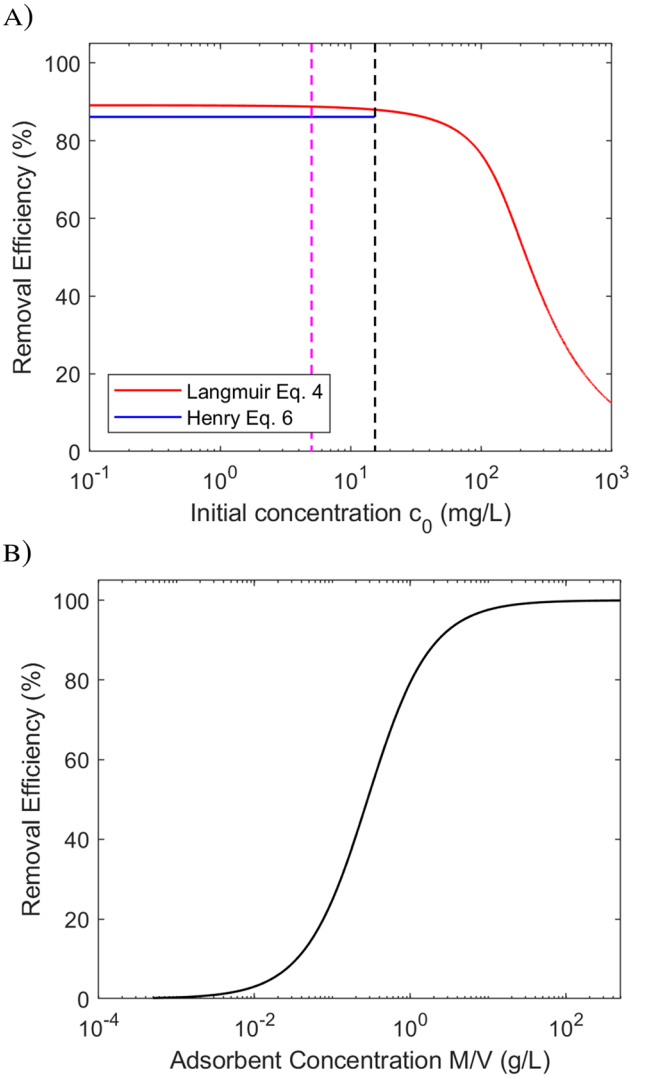


**Fig. 2** (A) Removal efficiency (%) as a function of initial concentration of adsorbed molecules, showing also a common numerical value of low concentration (5 ppm, magenta dotted line) and the low concentration limit, $1/K_L$ = 15 ppm (black dotted line). (B) Removal efficiency (%) as a function of adsorbent concentration.

of the curve, and the best accuracy is obtained for $\alpha > 10$. Fig. 3 can be considered as a different way of visualizing the isotherm in Fig. 1, providing an intuitive validation of the Langmuir fit at low concentrations. It should be stressed that, for a good fit, a consistent set of measurements is required over a wide range of concentrations: in the example reported in Fig. 1, 7 different concentration values are reported, correctly spaced along a logarithmic scale. In other works, however, a good fit was obtained by acquiring more points at only at low concentrations.[15]

The previously published data show that the relative experimental error in $K_L$ is the most influential factor in the overall uncertainty in the removal efficiency, $R$: typically, this error reaches 20%, and in some cases even 50%.[8] Fig. 3 shows how a 20% error could lead to considerable uncertainty in the determination of $R$ at low $\alpha$.

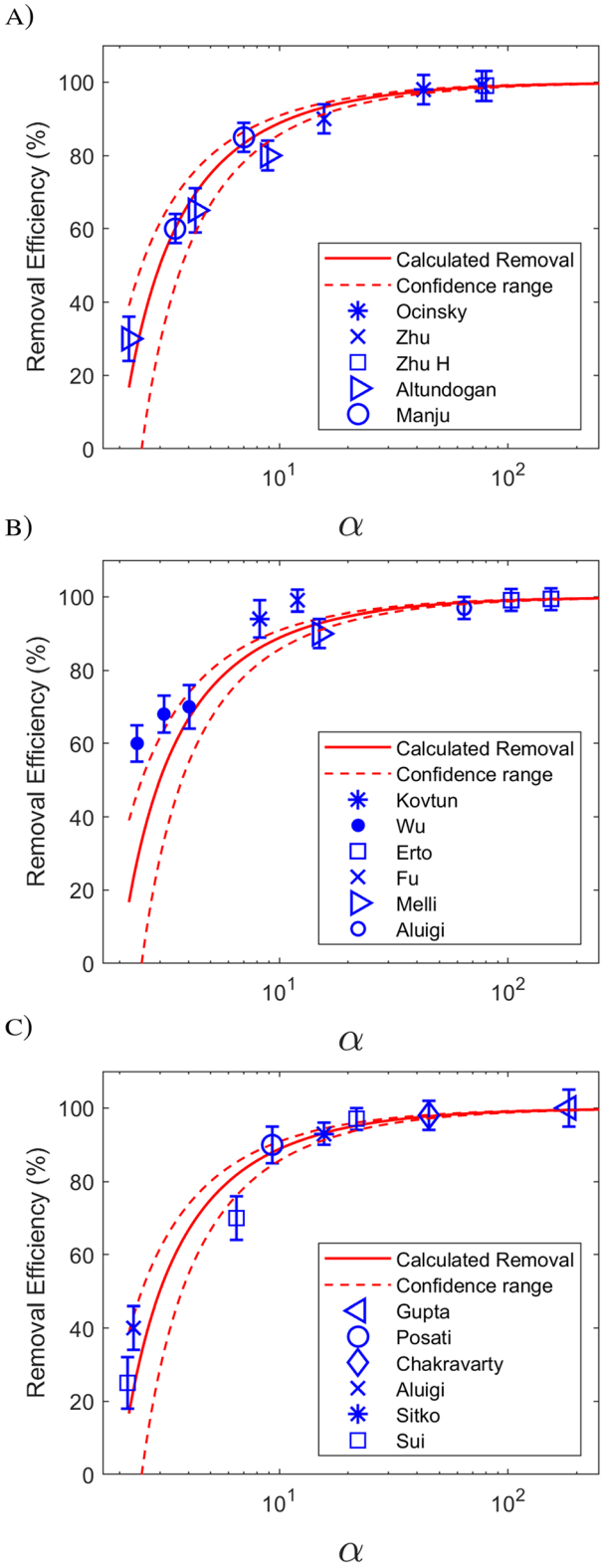


**Fig. 3** Removal efficiency (%) as a function of parameter $\alpha = Q_m K_L M/V$: the experimental points from the literature are compared to the expected behaviour of eqn (6) (red line). Upper and lower confidence ranges, calculated by assuming a 20% relative error in the determination of $\alpha$, are shown as red dotted lines. The experimental points are from papers reported in Table 1. Different adsorbates were considered: (A) arsenic. (B) Organic molecules and (C) other heavy metals.

Once the single parameter approach for calculating $R$ is validated these results can be used to solve a more practical problem, the optimization of adsorbent mass. The amount of adsorbent necessary to achieve a target removal efficiency $R$ can be calculated from eqn (6):

$$M = \frac{V}{Q_m K_L}\frac{2-R}{1-R} \quad (7)$$

Taking as an example, the need to decrease the concentration of a pollutant from 500 ppb (μg $L^{-1}$) to 5 ppb (*i.e.* removal efficiency 99%), for a given material ($Q_m$ and $K_L$) and solution volume $V$, we can calculate the necessary mass of adsorbent required,[16,17] $M^{single}$ using eqn (7). However, a value of $R$ = 99% can also be achieved by two sequential purification steps, each having $R$ = 90%: the first step decreases the concentration from 500 to 50 ppb and the second from 50 to 5 ppb. As can be seen from eqn (7), the same removal efficiency using a single step would require ≈4.5 times the material ($M^{single} = 4.5M^{double}$) used for the two-step approach. The better efficiency of multi-step processes is due to the weak dependence of $R$ on $\alpha$ (proportional to the amount of adsorbent used), as clearly shown in Fig. 2B. Taking another example, in order to increase $R$ from 90% to 99% it would be necessary to increase $\alpha$ (*i.e.* the mass of adsorbent) by a whole order of magnitude.

In a more demanding example, we can reduce the concentration of a test contaminant from 50 ppm to 5 ppb (corresponding to a removal efficiency 99.99%) with either four purification steps (each step having $R$ = 90%) or one single purification step, using a large excess of adsorbent. The single step will, in fact, require ≈227 times more adsorbent (in mass) than the four-step process. Practical considerations such as the cost per purification step may influence decisions on optimisation of the contaminant removal in question.

Concluding, we would like to point out some aspects of the extensive literature on adsorption for pollutant removal purposes and especially, contrary to common assumptions made there, the value of $R$, removal efficiency, cannot be used for a direct comparison between different adsorbents under different conditions. In fact, some papers and reviews (other examples are given in Table 2) report only the removal for one specific case, rendering such data clearly pointless for any realistic comparison of performance with other systems. While most of the reviews focus on the value of $Q_m$, this is not enough for comparing different materials, often giving only a partial view of adsorption performance for a given adsorbate. One example, for arsenic removal (of those given in Table 1) reports that As(III) removal has a larger $Q_m$ with respect to As(V) removal, but As(V) removal shows a larger $K_L$, and thus the product $Q_m K_L$ is similar for both As species and their removal under the same conditions are usually similar too. Here, our model provides a simple explanation of the phenomena observed and described in the literature.

**Table 1** Summary of papers used for validate eqn (6) and create the plot in Fig. 3. Various adsorbates were selected: heavy metals (HM), arsenic (As), dyes and emerging organics contaminants (EOCs). Methylene blue (MB), trichloroethylene (TCE), bisphenol A (BPA), bisphenol B (BPB), bisphenol AF (BPAF), rhodamine B (RhB)

| Ref. | Adsorbate | Adsorbent | $Q_m$ (mg g$^{-1}$) | $K_L$ (mL mg$^{-1}$) | $M$ (g) | $V$ (mL) | $\alpha$ | $R^H$ (%) | $R^m$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| Gupta (ref. 12) | Cr(IV) | Sawdust | 42 | 438 | 1 | 100 | 184 | 99 | 100 |
| Posati (ref. 18) | Cu(II) | Polydopamine + polysulfone | 4.5 | 1100 | 0.015 | 8 | 9.3 | 88 | 90 |
| Aluigi (ref. 19) | Cu(II) | Wool keratin nanofiber | 18 | 130 | 1 | 1000 | 2.3 | 25 | 40 |
| Chakravarty (ref. 20) | Cd(II) | Heartwood powder | 10.6 | 857 | 0.5 | 100 | 45.4 | 98 | 97 |
| Sitko (ref. 21) | Pb(II) | Graphene oxide | 1119 | 140 | 0.1 | 1000 | 15.7 | 93 | 95 |
| Sui (ref. 22) | Cu(II) | Graphene | 157 | 69 | 2 | 1000 | 21.7 | 95 | 97 |
| | | oxide + polyethylenimine | 157 | 69 | 0.6 | 1000 | 6.5 | 82 | 70 |
| | | | 157 | 69 | 0.2 | 1000 | 2.2 | 14 | 25 |
| Ociński (ref. 23) | As(V) | Chitosan + MnFe oxides | 27 | 395 | 4 | 1000 | 43 | 98 | 99 |
| Zhou (ref. 24) | As(III) | Reduced graphene | 22.4 | 3500 | 0.2 | 1000 | 15.7 | 93 | 90 |
| | As(V) | oxide + MnFe oxides | 22.2 | 17 300 | 0.2 | 1000 | 76.8 | 99 | 99 |
| Zhu H. (ref. 25) | As(III) | Activated carbon | 18 | 8900 | 0.5 | 1000 | 80.1 | 99 | 99 |
| Altundoğan (ref. 13) | As(III) | Red mud | 0.664 | 334 | 10 | 1000 | 2.2 | 18 | 30 |
| | As(III) | | 0.664 | 334 | 20 | 1000 | 4.4 | 71 | 65 |
| | As(III) | | 0.664 | 334 | 40 | 1000 | 8.9 | 87 | 80 |
| | As(V) | | 0.513 | 1642 | 100 | 1000 | 84.4 | 99 | 99 |
| Manju (ref. 11) | As(III) | Husk carbon | 146 | 24 | 2 | 1000 | 7.0 | 83 | 85 |
| | As(III) | | 146 | 24 | 0.05 | 50 | 3.5 | 60 | 60 |
| Wu (ref. 5) | BPA | Polyvinyl chloride | 0.923 | 1721 | 1.5 | 1000 | 2.4 | 28 | 60 |
| | BPB | | 0.993 | 2101 | 1.5 | 1000 | 3.1 | 53 | 68 |
| | BPAF | | 1.05 | 2574 | 1.5 | 1000 | 4.1 | 67 | 70 |
| Kovtun (ref. 8) | RhB | Graphene oxide + polysulfone | 63.2 | 65.2 | 0.05 | 25 | 8.2 | 86 | 94 |
| Erto (ref. 9) | | | 203 | 127 | 0.6 | 100 | 155 | 99.3 | 99.4 |
| | TCE | Activated carbon | 203 | 127 | 0.4 | 100 | 103 | 99.0 | 99.1 |
| | | | 203 | 127 | 0.45 | 200 | 58.1 | 98.2 | 97.6 |
| Melli (ref. 26) | MB | Agroindustrial wastes | 17.4 | 171 | 0.5 | 100 | 14.9 | 93 | 90 |
| Aluigi (ref. 27) | MB | Keratin nanofibrous membrane | 167 | 385 | 1.0 | 1000 | 64.3 | 98 | 97 |
| Fu (ref. 28) | MB | Polydopamine | 89 | 272 | 0.01 | 20 | 12.1 | 91 | 99 |

Thus, as supported by the above equations and considerations, the performance of materials (removal efficiency) depends on the product of $Q_m$ and $K_L$. Only these two main parameters allow a direct comparison between different adsorbents at the same concentration. $Q_m$ and $K_L$ should always be reported correctly when comparing different adsorbents, only one review was found in such form.

It should become a basic requirement when publishing scientific work, whether reviews or individual studies, on the comparison of removal performance of different materials that $Q_m$ and $K_L$ values be reported instead of using the value

**Table 2** Summary of reviews that report adsorption on different adsorbents of heavy metals (HM), arsenic (As), dyes and emerging organics contaminants (EOCs). $Q_m$ and $K_L$ columns report whether the review reports the data

| Ref. | Adsorbate | Adsorbent | $Q_m$ | $K_L$ | Comment |
|---|---|---|---|---|---|
| Wu (ref. 29), 2010 | HM | Chitosan | Y | Y | All data reported correctly |
| Bhatnagar (ref. 30), 2011 | Fluoride | Various materials | Y | N | Removal is used in text for comparison |
| Gupta (ref. 31), 2013 | Dyes | Nanotubes | Y | N | — |
| Hua (ref. 32), 2012 | HM | Various materials | Y | N | Removal used in text for comparison |
| Gupta (ref. 33), 2008 | Dyes | Various materials | Y | N | Removal used in tables for comparison |
| Ngah (ref. 34), 2011 | Dyes & HM | Chitosan composites | Y | N | Removal used in text for comparison |
| Ngah (ref. 35), 2008 | HM | Plants wastes | Y | N | Removal used in text for comparison |
| Bailey (ref. 36), 1999 | HM | Low cost adsorbent | Y | N | Does not use removal |
| Crini (ref. 37), 2006 | Dyes | Low cost adsorbent | Y | N | Does not use removal |
| Mohan (ref. 38), 2007 | As | Various materials | Y | N | Removal used in text for comparison |
| Sağ (ref. 39), 2001 | HM | Fungal biomass | Y | N | Does not use removal |
| Anastopoulos (ref. 40), 2014 | Dyes | Agricultural peels | Y | N | Removal used in text for comparison |
| Kyzas (ref. 41), 2015 | EOCs | Various materials | N | N | Uses only removal values for comparison |
| Sousa (ref. 42), 2022 | EOCs | Microalgal | N | N | Uses only removal values for comparison |
| Ahmad (ref. 43), 2021 | EOCs | Biochar-Iron | N | N | Uses only removal values for comparison |
| Zheng (ref. 44), 2022 | EOCs | Metal organic frameworks and graphene oxide | Y | N | Removal used in text for comparison |
| Gogoi (ref. 45), 2018 | EOCs | Various materials | N | N | Uses only removal values for comparison |

 

of removal efficiency, since the latter can not provide valid comparisons for choosing, in practice, the most effective and inexpensive approach. Removal efficiency should be considered as a target value, which can be potentially reached by any adsorbent by tuning suitable concentrations of $M/V$, and which should be the effective cost parameter.

## Conclusions

The removal efficiency $R$ of contaminants through adsorption depends critically upon isotherm parameters ($Q_m$ and $K_L$) and adsorbent concentration ($M/V$), and can be modelled at low concentration as a function of the combined parameter $\alpha = Q_m K_L M/V$. The removal efficiency $R$ reaches its largest value at low contaminant concentration ($c < 1/K_L$); at these levels, removal efficiency can be considered constant. An increase in single-step removal efficiency from 90% to 99% requires an increase in the quantity of adsorbent materials of one order of magnitude. Compared to single-step adsorption processes, multi-step processes allow greater removal of contaminants with lower quantities of adsorbent material, and such increased efficiency should thus be preferred and encouraged whenever possible. Future reviews comparing the adsorption performances of different materials must be encouraged, if not obliged, to report both the parameter isotherms $Q_m$ and $K_L$.

## Author contributions

The manuscript was written with contributions from all authors. All authors have given approval to the final version of the manuscript. A. K. conceptualization, data curation, validation, writing original draft. S. K. and D. J. literature research, review, editing. M. M. writing and founding acquisition. V. P., M. Z., M. L. N. contributed during discussion and manuscript writing.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The research leading these results has received funding from the European Union Horizon 2020 research and innovation programme under GrapheneCore3 No 881603 – Graphene Flagship; SH1 Graphil project, and from the FLAG-ERA III project GOFOR-WATER, No 825207.

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